Thermodynamics

Chemistry 171 course guidelines

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Office Hours:	MW 1:00pm - 2:00pm
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Lectures:	MW 11:00-12:15
Problem Section:	F 11:00-11:50 (Optional)
Textbooks:	E. Brian Smith *Basic Chemical Thermodynamics*, and Levine *Physical Chemistry* (both required)

Assignments:

Readings from Smith, handouts, and problems. The problem sets are to be handed in for grading at the beginning of the lecture on the due date. The teaching assistants will go over the problems (as well as answer questions about course material) during the Friday problem session.

Examinations and grading:

There will be two in-class examinations during the quarter and a final examination during the regular final exam period. The class will be graded as follows:

Two in-class exams (15% each)	30%
Final Exam	40%
Problem Sets	30%
TOTAL	100%

The course will be graded on this basis. Homework is very important since it is a way to make sure that you understand the material as we go along. Homework is due at the begining of class on the due date (typically Monday, unless noted otherwise). Late homework will not be accepted without prior approval of the instructor. The lowest homework grade will be automatically dropped.

The two in-class examinations will be given on Monday, October 24 and Monday, November 14. The final exam will be given on Wednesday, December 14, from 8:30-11:30am. Students who wish to have an exam re-graded must have written their exam in permanent ink, and give notification within one week after the papers have been returned to the class, along with a note detailing the reason for the re-grading request. All exams handed in for re-grading will be entirely re-graded. No examinations will be accepted for re-grading after this one week period.

Course Outline

1. **Introduction**

   Equilibrium, reversibility, ideal gas, van der Waals gas

   (Smith §1; Levine §2, §2.1; A&S §1)

2. **Energy**

   Work, heat, temperature, zeroth and first laws of thermodynamics, conservation of energy, enthalpy, heat capacity, state functions

   (Smith §2; Levine §2; A&S §2)

3. **Entropy I: Entropy in terms of heat**

   Reversibility and equilibrium (again), entropy, entropy interpreted in terms of heat flow

   (Smith §3.1-3.9; Levine §3.1-3.5 ; A&S §3.1-3.5)

4. **Entropy II: The molecular basis of entropy**

   Molecular basis of entropy, statistical basis for the second law, third law, heat engines, entropy of a gas expanding

   (Smith §3.10-3.13; Levine §3 ; A&S §3.6-3.14)

5. **Equilibrium I: The concept of free energy**

   Free energy, Helmholtz free energy, Gibbs free energy, phase equilibria

   (Smith §4.1-4.5; Levine §4; A & S §4.1-4.7)

6. **Equilibrium II: Applications of free energy concepts**

   Clapeyron equation, Clausius-Clapeyron equation, chemical potential, equilibrium between reactants, basic results of chemical thermodynamics

   (Smith §4.6-4.15; Levine §4)

7. **Ideal systems**

   what is an ideal solution, properties, mixtures of liquids, change in freezing/boiling points, osmotic pressure, solubility of solids

   (Smith §6; Levine §7.3, §8, §9)

8. **Non-ideal systems I: Chemical equilibrium**

   Chemical equilibria in solution, electrochemical cells

   (Smith §7, A & S §5, parts of §7 and §8; Levine §8, §9)

9. **Non-ideal systems II: Phase transitions**

   what is a phase transition, first and second order phase transitions, phase transitions in chemistry and biology

   (lecture notes)

10. **Molecular basis of thermodynamics** (time permitting)

    microstates, macrostates, Boltzmann factor, partition function, free energy, energy, entropy

    (Smith §9)

Contents

1 Introduction

1.1 What is thermodynamics?

1.1.1 Historical perspective

There was a time, not so long ago, when a new technology was in the process of changing the world: the way business and human interactions were being fundamentally changed. Vast national networks were being constructed at great expense to take advantage of this new technology. Fortunes were won and lost and a new wealthy elite was formed due to the success of this new technology and scientists and engineers at the worlds most prestigious institutions were scrambling to study this new technology in order to harness, understand, and improve this new technology. The world would never the same.

What am I talking about? The internet perhaps? Well, no, I'm talking about the steam engine in the late 1800's. With steam engines came railroads, the ability to go from New York to San Francisco without passing Antartica, and the onset of the industrial revolution. Clearly life was never the same.

Clearly steam engines were the heart of this revolution, and it took a principle place in this advance. Thus, understanding steam engines was the biotechnology or nanotechnology of its day. And like these fields, there were numerous surprises in our study of this new field. While steam engines may seem to be common place, there were fundamental physical insights missing at that time. These fundamental insights arose from understanding how heat moves and this field in general is thus called thermodynamics.

However, if thermodynamics was only relevant for steam engines, none of us would be studying it today. As we will see, thermodynamics is at the heart of many important areas of modern science, including biotechnology and nanotechnology and the mysteries first seen with steam engines are as important, relevant, and as counter intuitive now as they were then.

1.1.2 What can thermodynamics tell us?

Thermodynamics is a theory which gives us a set of relations between *macroscopic* properties we can measure (temperature, volume, pressure, length). What's really remarkable about it is that it requires no assumptions about the nature of the underlying molecules (or even that molecules exist!). Thus, it is really very powerful, especially in cases where one does not know the molecular nature of the system of interest or if this nature is very complicated.

Traditional (boring?) examples:

- air conditioners, refrigerators
- gases, liquids
- pressure cookers

Modern examples:

- drug design
- protein folding
- viral infection

Many of these questions revolve around understanding the nature of a reaction, i.e.

$$A + B \rightleftharpoons C$$

which could be

$$\text{drug bound} \rightleftharpoons \text{drug free in solution}$$

or

$$\text{protein unfolded} \rightleftharpoons \text{protein folded}$$

etc.

What is the final result of the reaction (do we get products or reactants – and in what concentrations)? How can we drive the reaction in the direction we want? How do these reactions depend on external conditions, such as temperature, pressure, pH, ionic concentrations, etc? How can we *quantitatively* understand these systems and potentially improve upon them?

These are some of the questions that thermodynamics answers. However, thermodynamics does not say anything about time. Thermodynamics will tell us what the eventual result will be, but cannot say how long the reaction will take. However, for the question above, we care more about the final state than how we get there. In this case, thermodyanmics can yield some very powerful tools to answer these questions.

1.2 An analogy to mechanical systems

We make an analogy to mechanical systems because we have some physical intuition for these systems, and there are many concepts which carry over. Moreover, in the cases where our intuition does not carry over, that will be even more interesting and important.

1.2.1 Types of energy

For example, consider someone sledding on a hill. What he cares about is that there are some forces which bring him down (and that there is a certain amount of work he has to do to climb up the hill to go again). Thus, there are three important quantities/aspects:

1. **Force**: In this case gravity
2. **Distance**: In this case how high he has to climb up in order to go sledding again
3. **Work**: How much work he has to do to climb up again

So what's going on here? Let's consider the case of downhill and then going back up. When going down hill, potential energy is turned into kinetic energy (i.e. sledding), which is then turned into friction (heat created when the sled stops). When going up the hill, some chemical energy (breakfast) is turned into potential energy (climbing the hill).

Let's use this example to review the different types of energy. **Potential energy** energy can be turned into some other form; it is in a sense "stored" energy. For the case of the sleding example, $U = mgh$, where U is the potential energy, m is the mass, g is the gravitational acceleration, and h is the height of the hill. **Kinetic energy** is energy associated with motion, for example ($(1/2)mv^2$ per degree of freedom). **Heat** is a third type of energy. We'll talk about this in much more detail. Actually, in sense a course on *thermo*dynamics is all about heat. In this example, we see that heat is the final form of energy.

As in mechanics, **equilibrium** is an important concept in thermodynamics as well. There are several, equivalent ways of understanding it.

1. point where the forces are balanced

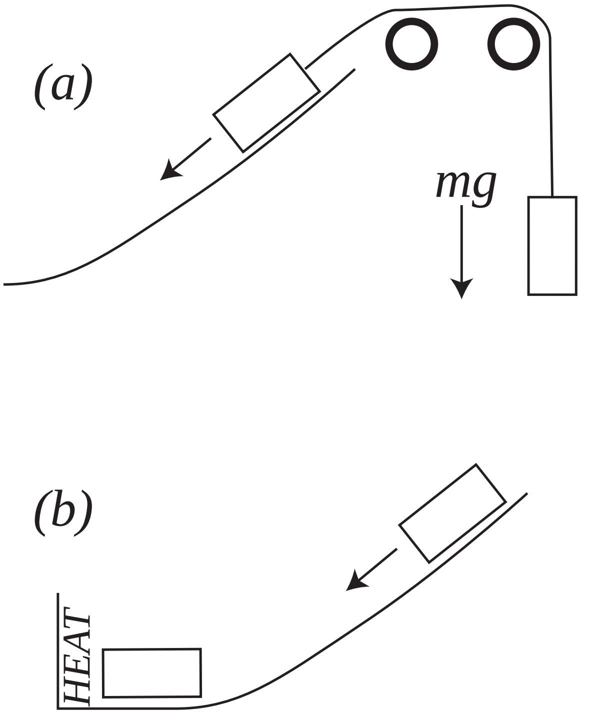

Figure 1.1: Different paths for lowering a block.

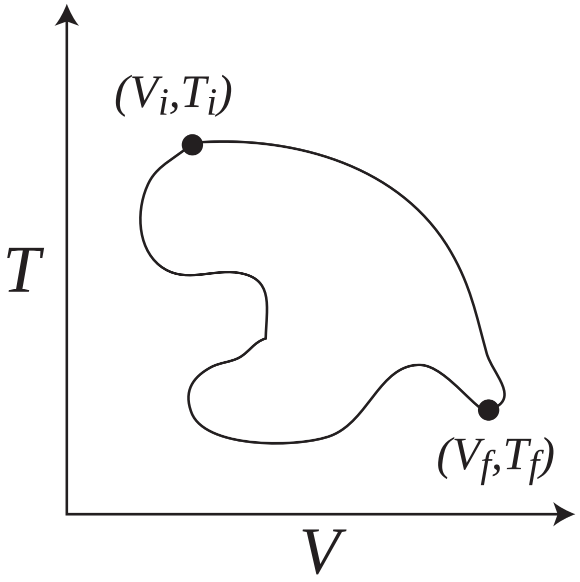

Figure 1.2: Different paths in (V, T) space. In both cases, the energy is the same, i.e. independent of path. Path independence is a hallmark property of state functions.

2. state at which the system has minimized it's potential energy
3. small changes require the maximum amount of work
4. state at which the system will remain if we wait for a long time

To illustrate this, consider a pendulum which has some friction at the pivot point. It will swing for a while, but eventually it will stop swinging and simply rest at the bottom. This is the equilibrium state, since it agrees with the definition above.

1.2.2 Reversibility

Reversibility is a very important another concept in thermodynamics which has analogies in mechanical systems.

Most processes in life are irreversible, i.e. once changed, the system does not return back to the initial condition. For example

- When a drop of dye is placed in a bucket of water, it spreads throughout the bucket: it rarely spontaneously comes together to form the initial droplet
- If you start out with a deck of cards which is ordered (say by suite and card value) and then shuffle the deck, it never (on time scales we live in) comes back to the original order

An example of a reversible system is a pendulum with *no friction.* In this case, the pendulum will swing back and forth forever. At the top of its swing, the pendulum has the maximum potential energy and no kinetic energy. At the bottom, it has the reverse: all of its potential energy has been turned into kinetic energy. The reason why this process is reversible is that there is no wasted energy: all the potential energy is turned into kinetic energy and that's precisely the amount of energy needed to bring it back to the top level.

A more mathematical way to think about it is the following. One can imagine an irreversible process as follows. Let's say we have two masses M_1 and M_2 on a pulley. If the masses are equal $M_1 = M_2$, then the system is in equilibrium. If one mass is larger by some significant amount, eg $M_1 = M_2 + \Delta M$, then the system would quickly change (mass 1 would fall). As the mass falls a distance h, this work will be ΔMgh (note that while mass 1 is going down, mass 2 is being pulled up!). However, we could make only a small change in M_1, i.e. $M_1 = M_2 + dM$, where $dM/M_1 \ll 1$, then only an infinitesimal quantity of work $dmgh$ would be required to restore the system. Also, at every point during the reversible process, $M_1 = M_2 + dM$ which is virtually indistinguishable from the equilibrium $M_1 = M_2$ (since dM is so small).

Thus, to summarize, reversible systems occur in situations when the system is essentially in equilibrium during the transition and at each step, only an infinitesimal amount of work would be necessary to truly restore equilibrium.

1.2.3 A mystery unfolds: watching energy isn't enough!

Our analogy of a sled sliding down a hill is a good one in many ways, but does seem to break down in certain situations. It is an example of an **exothermic reaction**, i.e. heat is given off. This occurs in the sled case since the potential energy of the sled is turned into heat by friction. This heat raises the temperature of the surroundings.

However, there are **endothermic** reactions too. In these cases, heat is absorbed (and the temperature goes down) and the total energy goes up. In the sled example, this would be like the sled spontaneously going up hill! Clearly there is something fishy here.

In mechanical systems, looking for the energy minimum is enough to tell the equilibrium state of the system. That's not the case in thermodynamic systems. There's clearly something missing here – some concept we need to add in order to explain thermodynamic systems.

Thermodynamics has new ways to look at energies which clear up this seeming contradiction. However, the intuition of mechanical systems will still be with us in many ways. In particular, our first goal is to find some quantity analogous to the energy whose minimum, in thermodynamic systems, will be the equilibrium state.

2 Energy

2.1 Ideal gases: A simple system to play with

Ideal gases are a natural place to start learning about thermodynamics. We have some intuition about how gases work and an "ideal" gas is a simple model of how gases work. In particular, an ideal gas is a great model system to learn and test our understanding of thermodynamics since all of the fundamental thermodynamic properties we will talk about can be found in them and they allow us to study thermodynamics without getting lost in too much math. Later on, we will study more realistic gases and see the nature of the differences.

2.1.1 Basic properties

Like many types of matter, we characterize an ideal gas by certain properties: volume (V), pressure (P), temperature (T), and how many moles of atoms are in the gas (n). There is a simple expression relating these quantities:

$$PV = nRT$$

This equation is called the **equation of state** for this system, since it relates the **state variables** (P, n, V, and T) in this case. Actually, many gases behave like ideal gases in certain conditions (yea, you guessed it, in so-called "ideal" conditions).

There are two types of properties here:

1. **Extensive properties** are properties which are related to "how much stuff" there is. For example, n and V are extensive properties. If the system is duplicated, these variables get doubled.
2. **Intensive properties** are independent of the size of the system. For example, P, T, are intensive properties. So is the density $\rho = N/V$, where N is the total number of atoms.

2.1.2 A brief glimpse of phase transitions

When gases cool, they condense to liquids. When liquids cool, they freeze into solids. These are two examples of phase transitions. However, ideal gases cannot have phase transitions. This is what is meant by "ideal." Thus, far from the phase transition, they are good models, but do not work well near the transition.

What makes a phase transition? Interaction. Gas particles start to stick together at lower temperatures and form a liquid. How can we model this interaction? We can modify the ideal gas equation to include interactions. We'll do so in two steps:

1. What's the probability that a gas particle will bump into another one? The density $\rho = N/V$ is a lot like a probability that we'll find a given particle at a given spot. If the density is high, then there is a high probability that the particle is there. The probability of finding two particles at the same spot goes like the ρ^2. It's like what's the probability of flipping two coins and having them both come up heads: it's the probability of one coming up heads squared.

   When two particles get close, they attract each other and lead to a force which brings them together. We can include this force as a modified pressure. This makes the equation of state

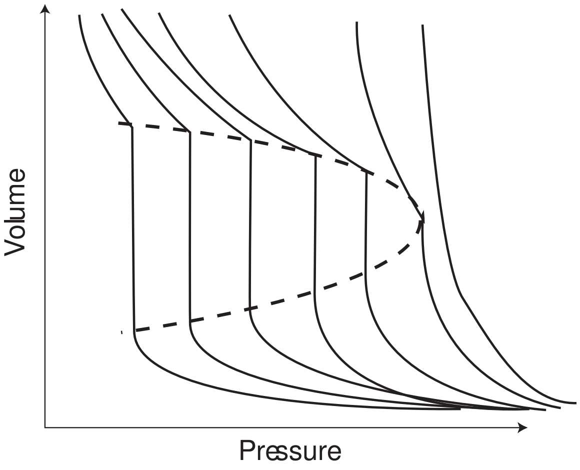

Figure 1.3. Isothermal transformations of a van der Waals gas: volume dependence on the temperature. Plotted here are curves at a fixed temperature (curves on the right are at the highest temperature). For transformations at low temperature (curves on the left), we see that there is a discontinuity in the transition: as the pressure is increased, there is a jump in the volume (V) from high volume (gas) to low volume (liquid). An ideal gas will not have this transition and will always be a gas. The dotted line marks the boundary of the unstable region (where the jump occurs).

become

$$(P + a\rho^2)V = nRT$$

which can be rewritten

$$(P + an^2/V^2)V = nRT$$

The constant a has to do with how strong is the attraction between atoms.

2. Next, we have to also include the fact that two atoms can't be in exactly the same place. What this means is that if a gas of n moles of particles are in a box of volume V, each particle cannot be anywhere in that volume V, as part of the volume is filled with the gas. If we say that the volume of an individual gas molecule is b, then the total volume of the gas particles themselves is nb. Thus, the amount of space available is now only $V - nb$. This leads to another change in the equation of state:

$$(P + an^2/V^2)(V - nb) = nRT$$

The equation above is the **Van der Waals' equation** and is the first step to describe a non-ideal gas and actually goes a long way. What's different about a van der Waals (VdW) gas vs an ideal gas? VdW gases can change their phase and go from a gaseous to a liquid phase. This is called a **phase transition**. If we look at pressure vs volume (or temperature vs volume), we see that there is a discontinuity in the volume as it jumps from one size to another. This discontinuity reflects the fact that liquids take up much less volume than gases.

2.2 Work

Work is the transfer of energy from one *mechanical* system to another. It is always completely convertible to the lifting of a weight.

For example, when we put a book on a high shelf, we are doing work against the force of gravity. We can write the work in terms of this force and displacement (how high we placed the book):

$$w = \int_{h_i}^{h_f} \vec{F} \cdot d\vec{h}$$

where $\vec{F}$ is the force, $d\vec{h}$ is the displacement vector (distance and direction of the displacement), h_i is the initial height the book and h_f is the final height.

In chemistry, we usually don't talk about force and distance, but instead a different pair: pressure and volume. Pressure acts like the force and volume acts like the distance. For example, consider a gas inside a piston. The external air pressure P_{ex} is pushing against the piston. Since pressure is force per unit area, $P_{\text{ex}}\ F/A$ or $F\ P_{\text{ex}}A$. We can put this into the equation above to get

$$w = \int_{h_i}^{h_f} (-P_{\text{ex}}A)dh$$

Note that we put in $-P_{\text{ex}}A$ instead of $P_{\text{ex}}A$. This minus sign says that the direction of the force is opposite to the pressure and comes from the dot product in the original equation. In other words, when we compact the gas, we are doing work on it (imagine compressing a balloon). The change in volume is written in terms of the change in height dh and the area of the piston A, i.e. $Adh = dV$.

Thus, we can write

$$w = -\int_{V_i}^{V_f} P_{\text{ex}}dV$$

If the external pressure is continually adjusted so that it is kept equal to the pressure of the gas inside the cylinder (P), then the system is always at equilibrium. Why? Well, think about the case when $P_{\text{ex}} > P$. In this case, then there would be an imbalance (since there was more force pushing in, than pushing out). This imbalance would be corrected (and would remain stable) only when there was an equal force pushing in and out (and therefore an equal pressure $P_{\text{ex}} = P$). Thus, under these conditions

$$w_{\text{rev}} = -\int_{V_1}^{V_2} PdV$$

We'll cover this in more detail in §2.4, after we work through a few more concepts.

Keep in mind that we can talk about work be a positive or negative value. A positive value for work means we need to do work to make the process occur. A negative value means that the process can do work (rather than needing us to put work into the system). For example, compressing a gas (eg compressing a balloon) requires work (and thus work value is positive). If we let the balloon re-expand, this does not require any additional work, but rather has the ability to do some work (eg push a weight) and thus has a negative work value. Mathematically, we see this since compression has $dV < 0$ (and thus $w > 0$) and expansion has $dV > 0$ (and thus $w < 0$).

There are lots of other types of work. Remember that work means creating potential energy. So, for example, we could do this by

1. stretching a spring ($dW = \gamma dR$), where γ is the tension of the spring and dR is the amount we've stretched it
2. compressing a gas ($dW = -PdV$)
3. putting an atom in an electric field ($dW = -EdQ$)

You probably notice a trend here. The change in work is often written as $dW = IdN$, where I is some **intensive** state variable (like tension, pressure, or electric field strength) and N is some **extensive** quantity (such as the amount stretched, volume, or charge). These are called **conjugate pairs**.

2.3 Heat

2.3.1 Heat and disorder

Heat is often related to disorder. There is a link, but it is somewhat subtle and often over simplified. We'll get a more sophisticated understanding of heat as we go through the course, but for now consider the following discussion. Without work, the universe tends to disorder. If you need proof, come by and see the desk in my office. Why? "Non-random" scenarios are rare compared to random-ones. For example, consider a deck of cards. There are only a few possibilities of what we would call an ordered sequence (eg sorted by suite, or value), but there are exponentially "random" ways to order the deck. We see this since it is extremely rare that shuffling will lead to an ordered arrangement.

Thus, in terms of concepts of equilibrium, the random orderings ("states") are the equilibrium states. If we continue shuffling, we will always end up with another random state. If we want to get an ordered state, we have to do work.

So, if systems tend toward random configurations, then what is the relationship between randomness and heat and temperature? Heat is an example of random motion of molecules. This random motion (i.e. heat) is a by product which often reflects not doing as much work as possible. For example, if we could pull a weight up a hill without friction, then all of our energy would be converted directly to work (against gravity to bring the weight up the hill). However, this is rarely the case and often some of our energy is lost in friction (which leads to heat) and is therefore not converted to work. We will see this explicitly in an example in the next section.

2.3.2 Heat and temperature

We've mentioned that heat and temperature are related. Certainly, it makes sense that as you add more heat, the temperature should go up, but how are they more precisely related? They are related by the heat capacity C:

$$C = \frac{dq}{dT}$$

Or in other words, if we increase the temperature by dT, then we add $dq = CdT$ more heat to the system.

The heat capacity depends on several aspects of the material we are addressing. First, since T is intensive, but the heat Q is extensive[1], so the heat capacity must also be extensive. This means that if we double the size of our material (keeping the material's properties constant), the heat capacity will double.

What else does the heat capacity depend on? It also depends on particular molecular aspects of the material. For example, imagine having one mole of uni-atomic gas (eg O atoms). If we double the amount of gas (keeping the pressure constant, and therefore doubling the original volume), then the heat capacity doubles. What do you expect to happen to the heat capacity if the O atoms combine to create O_2 molecules? We originally had 2 moles of O atoms and now we only have one mole of O_2 molecules. It turns out that the heat capacity will go down, but not to the original level. A mole of O_2 molecules has a greater heat capacity than a mole of O atoms because the O_2 molecules have more

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[1] Why is heat extensive? Think about it this way, if we have a hot piece of coal at 100 C and then add another one, the temperature is the same but the amount of heat given off has doubled.

degrees of freedom to move around. As you'll see later in statistical mechanics, the heat capacity is directly related to the number of degrees of freedom in the system.

2.3.3 Temperature and equilibrium: the zeroth law of thermodynamics

What happens when we put a warm body next to a cold one? The hot one cools down and the cold one warms up. This continues until both bodies are at the same temperature. Another way to say this is, if there is a temperature gradient (differential in temperature), then heat will flow. The equilibrium state is the state where the temperatures are equal. Thus, "thermal equilibrium" between two bodies means that their temperatures are equal.

This has deep implications for the meaning (and usefulness) of the concept of temperature. Consider the case where we have *three* bodies: A, B, and C. If A and C are in thermal equilibrium and B and C are in thermal equilibrium, then by the definition of thermal equilibrium above, then A and C have the same temperatures ($T_A = T_C$) and B and C have the same temperatures ($T_B = T_C$). This further means that $T_A = T_C = T_B$ and thus $T_A = T_B$. Again, using the definition of thermal equilibrium if $T_A = T_B$, then A and B are in thermal equilibrium.

This leads us to the statement that "if two bodies are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other." This statement is called the "zeroth" law of thermodynamics. If it weren't true, then temperature would not be a useful concept.

2.3.4 What does "constant temperature" really mean?

It is important to consider what we mean when we say "constant temperature." How does one keep a system at constant temperature? To do so, one puts it in contact with a heat bath. What that means is that heat will be transfered back and forth from the system (eg the ideal gas in the examples above) to the heat bath in order to maintain the temperature constant.

How does this maintain a constant temperature? Since the heat bath is so much larger than the system, any fluctuation in the system will be small for the bath and at thermal equilibrium, the temperature of the bath will always dominate. For example, the system might have 1 mol of particles, but the bath might have 100 moles. Even a large change in heat in the system is a minimal change for the bath, and thus the temperature of the bath won't change and thus the temperature of the system (which is in thermal equilibrium with the bath) won't change either.

2.4 First law of Thermodynamics: Conservation of energy

In an **isolated system** (i.e. not in contact or able to exchange matter or energy with another body), the total amount of energy is always constant, although it may be converted into another form of energy. Conservation of energy means that the total energy of the whole system does not change. It is important to consider what we mean by "whole system." By that we mean the body we are interested in and its surroundings. For example, when a skier slams into a tree, the kinetic energy is converted into heat, which is dissipated to the environment. If we consider just a skier, then energy was "lost" to the environment, but the total energy of the whole system (environment + skier) is constant.

Let's generalize the idea of the skier hitting the tree. In general, we can imagine some thermodynamic transformation from state A to state B. The change in energy can be written

$$\Delta U = U_B - U_A = q + w$$

Recall that there are two types of energy, work (w) and heat (q).

It is important to notice that ΔU depends only on the initial and final states and not the path taken. However, different paths may lead to different values of q and w. We can illustrate this by considering two ways we can lower a block on a ramp (see Smith Fig. 2.4 on page 15).

1. **Connect the block to a body of equal mass and let the block down slowly**. In this case, the system is in equilibrium, since the masses of the two bodies are equal (and the gravitational and tension forces are therefore balanced). If we give the block a small push downward, the block will slowly move down the ramp. Since the block moves down infinitesimally slowly, it will generate no heat. Thus, The block will be able to raise the body (do work) without generating any heat, and
$$\Delta U = -Mgh = w$$
   So, by letting the block down in this way, we've converted all of the original potential energy in the block into new potential energy of the second body. All of the energy is in the form of work.

   This is also a good example of a reversible transformation. Reversible systems are (1) typically done slowly, consisting of many small steps; (2) the system is at equilibrium during each step of the transformation (we see this since the forces are balanced at each step); and (3) the maximal amount of work is done, i.e. no heat is generated.

2. **Just let it go.** If we didn't attach any additional mass and just let the original block go down the ramp, all of the potential energy would be converted into heat (via friction). Thus,
$$\Delta U = -Mgh = q$$

In both cases, we have lower the block (and thus used its potential energy), but for different uses. The key point is that the change in energy is the same (it's equal to the original potential energy in the block). All paths you can imagine would lead to the same ΔU, although they could have different combinations of heat and work done.

Finally, we see that the generation of heat accompanies irreversible transitions, where as reversible transitions do the maximal amount of work ($\Delta U = w$ and thus generate no heat $q = 0$).

2.5 Reversible and irreversible isothermal transformations of a gas

2.5.1 Mathematical approach

In §2.1, we showed that for a reversible transformation,

$$w_{\mathrm{rev}} = -\int_{V_1}^{V_2} P dV$$

In the light of the reversible transformation example from the previous section, let's think about what the above equation means. Recall that the integral $\int f(V)dV$ can be thought as a sum

$$\int_{V_i}^{V_f} f(V)dV = \lim_{\delta v \to 0} \sum_{v=V_i}^{V_f} f(v)\delta v$$

In other words, doing an integral is like doing a larger series of summations, each infinitesimally small. What does each summation mean in this case? Each summation here is the work $P\delta v$ of making a small δv change in volume. Thus, the integral is the mathematical manifestation of a reversible process. Just as reversible processes combine a large number of small steps, an integral is the sum of an infinite number of infinitesimal steps.

What would the work be for an one step reaction? If we just let the system go, then we would have just one step, and the work will be (for an isothermal, i.e. constant temperature, transition)

$$w_{1-\text{step}} = -P_f \Delta V = P_f(V_f - V_i) = \frac{nRT}{V_f}(V_i - V_f) = nRT\left(\frac{V_i}{V_f} - 1\right)$$

We don't integrate since we made one big, fast change.

How does this differ for an ideal gas? The reversible reaction would do

$$\begin{aligned} w_{\text{rev}} &= -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -\, nRTV|_{V_i}^{V_f} = -nRT(\ln V_f - \ln V_i) \\ &= -nRT\ln\left(\frac{V_f}{V_i}\right) = nRT\ln\left(\frac{V_i}{V_f}\right) \end{aligned}$$

If you stick in numbers for the ratio V_i/V_f, you'll see that the reversible work case always does more work. In the one step case, where does the extra energy go? Heat!

Finally, in the limit when the ratio of the old and new volumes $x \equiv V_i/V_f$ is close to 1 (i.e. the change is small), then we expect that the two equations should be equal. Physically, this occurs since a small change in volume should be reversible (as it's only a minor change in the system from equilibrium).

If $x \equiv V_i/V_f$ is close to 1, then we can write the Taylor series approximation for $\ln x \approx (x - 1)$ to first order. Thus, for a small change, we get

$$w_{\text{rev}} = nRT\left(\frac{V_i}{V_f} - 1\right) = w_{1-\text{step}}$$

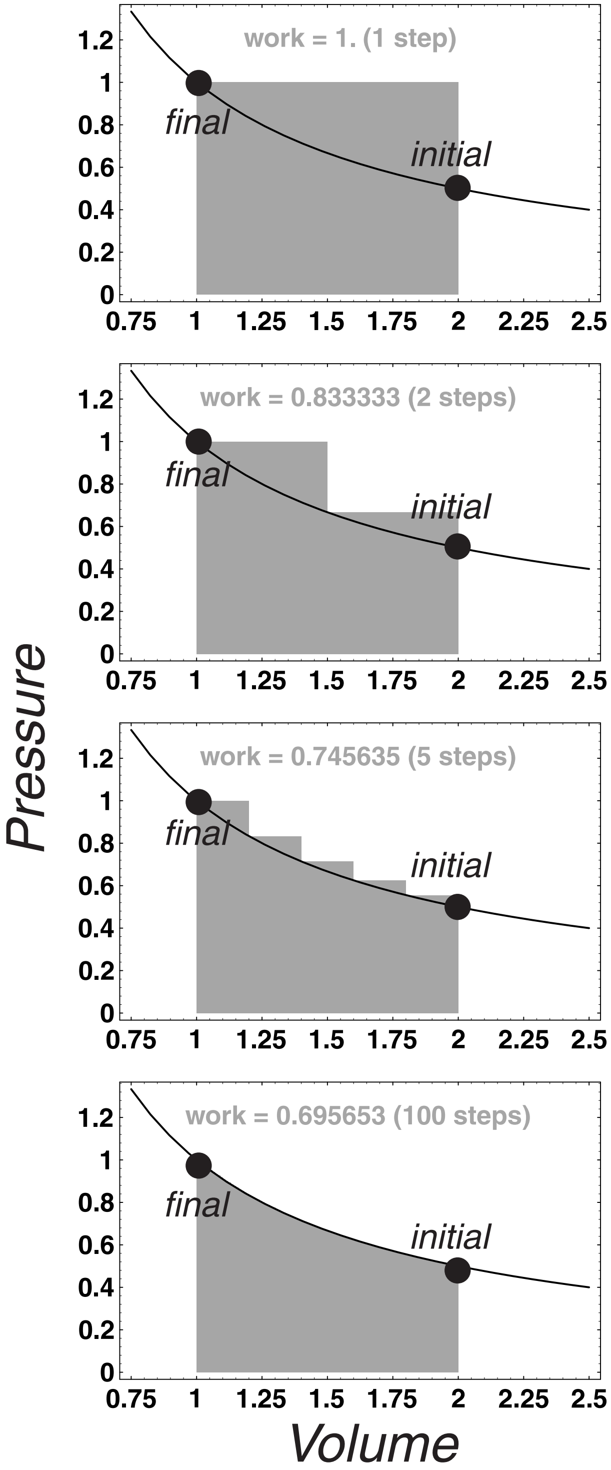
Just as we suspected, for a small change in volume (which is a small perturbation and thus a reversible transformation), the two equations are the same. However, for larger changes in volume, the reversible transformation will always yield more work.

2.5.2 Mathematical vs graphical approach

This approach above is a very mathematical approach. There is another way to look at transformations. Instead, let's consider a graphical approach. We can graph the pressure vs the volume at a fixed temperature (recall, we are doing an *isothermal* transformation of an ideal gas).

In this type of plot, we can graphically view the work from each step of the transformation as a rectangle. This is possible since the one step work value is $w_{1-\text{step}} = -P_f \Delta V$: the graphical representation of the magnitude of this work value is a rectangle with width ΔV and height P_f. Multistep transformations can be considered as a series of steps and thus viewed as a series of rectangles.

2.5.3 Compression



We can compress a gas using just one step or using multiple steps. In both paths, the initial and final states (eg as determined by volume and pressure) are identical. What's different about these paths? As we've seen in previous examples, the amount of heat and work differ.

Let's first tackle the amount of work done. In a one-step process, the work done is given by

$$\begin{aligned} w_{1-\text{step}} &= -P\Delta V = -P_f(V_f - V_i) \\ &= -1 \times (1-2) = 1 \end{aligned}$$

Note that ΔV here is negative (as we are compressing). If we compress in a multi-step process, then we can minimize the amount of work it will take to compress the gas. We use less work because we apply less pressure. In the two-step case, we first apply a pressure of 0.667 and then apply a pressure of 1.0. Thus, the work we do in this case is less

$$\begin{aligned} w_{2-\text{step}} &= -P_s(V_s - V_i) - P_f(V_f - V_s) \\ &= -0.667 \times (1.5-2) - 1 \times (1-1.5) \\ &= 0.833 \end{aligned}$$

where $\cdots_s$ are denotes the middle step.

What is the least amount of work we will have to do? In the limit of ∞ steps, we say the step size is very small: $\Delta V \rightarrow dV$ and our sum of steps becomes an integral. The work in this case is

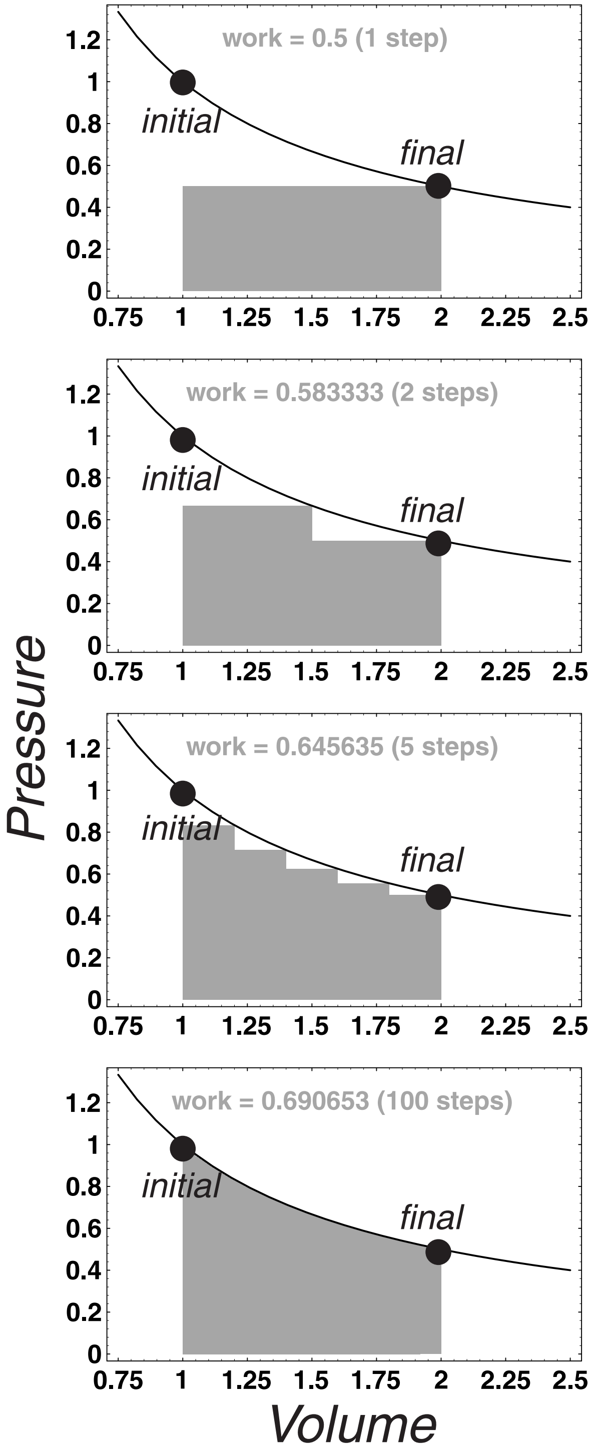
$$w_{\infty-\text{step}} = -\int_{V_i}^{V_f} P(V)dV = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

For the specific case on the left, we know that $P_f V_f = nRT = 1$, so $w_{\infty-\text{step}} = \ln 2 \approx 0.693$. As we add steps, the work we need to do to compress the gas becomes less and less. This work is minimized for the case of a reversible path.

It is important to keep track of minus signs. For the reversible case, we say that 0.693 units of work are done on the gas, but that -0.693 units of work are done by the gas. Thus, in this sense, the gas does the most amount of work in the reversible reaction since

$$(w_{\infty-\text{step}} = -0.693) > (w_{2-\text{step}} = -0.833) > (w_{1-\text{step}} = -1)$$

2.5.4 Expansion



Now we will expand the gas. Again, we can do so in one-step or with many steps. In the case of a one-step expansion, the work done on the gas is

$$\begin{aligned} w_{1-\text{step}} &= -P\Delta V = -P_f(V_f - V_i) \\ &= -0.5 \times (2-1) = -0.5. \end{aligned}$$

This work is negative, since the gas is expanding and thus releasing potential energy. This means that the gas can do 0.5 units of work on some other system.

In a fashion similar to the previous section, we calculate the reversible work

$$w_{\infty-\text{step}} = -\int_{V_i}^{V_f} P(V)dV = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

which in this case is $w_{\infty-\text{step}} = -\ln 2 \approx -0.693$ in terms of work done on the gas or 0.693 in terms of work the gas can do.

Thus, we see that the reversible path can do the most work. Moreover, we see that the reversible reaction releases the same amount of work that we have put in. This is why we consider it to be reversible: if we put 0.693 units of work into the system to compress the gas, a reversible expansion will give exactly the same 0.693 units of work. Thus, a reversible reaction wastes no energy and can go on compressing and expanding (reversibly!) forever.

Of course, real systems are never perfectly reversible. For the one-step case, we see that we have to put in twice as much work as we get out (1.0 vs 0.5 units). Thus, the work provided in expansion will never be sufficient to fully recompress the gas.

2.5.5 A careful accounting of heat and work

I have not mentioned heat yet to avoid complication and confusion. The tricky part about thinking about heat in this case comes from (1) keeping track of minus signs (like we had to do in the case of work) and (2) remembering that our gas is in thermal contact with a heat bath.

The energy of ideal gases are only related to their temperature. Thus, along an isotherm, the energy is also constant and thus $\Delta U = 0$. Since $\Delta U = \not{d}q + \not{d}w$, along an isotherm we get $\not{d}w = -\not{d}q$. Here's where the signs become important, especially to understand whether heat is entering or leaving (and entering or leaving what: the gas or the heat bath).

For example, consider the case of the one-step compression. In this case, we do work on the gas $\not{d}w_{1-\text{step}} = 1$ and so $\not{d}q_{1-\text{step}} = -1$. This means that one unit of heat is transfered to the heat bath. In the case of reversible compression, we require less work $\not{d}w_{\text{infty}-\text{step}} = \ln 2 \approx 0.693$ and so we put less heat into the heat bath $\not{d}q_{\infty-\text{step}} = -\ln 2$ (0.693 units of heat are transfered to the heat bath).

Now let's consider expansion. In one-step expansion, the gas does work on the system (aka negative work is done on the gas) and we found that $\not{d}w_{1-\text{step}} = -0.5$. Thus, $\not{d}q_{1-\text{step}} = 0.5$. This means that 0.5 units of heat were absorbed by the system (i.e. taken from the heat bath). For the reversible case, we found $\not{d}w_{\text{infty}-\text{step}} = -\ln 2$ and $\not{d}q_{\text{infty}-\text{step}} = \ln 2$. This means that $\ln 2 \approx 0.693$ units of heat were absorbed. We see that the reversible expansion absorbed more heat or in other words, the one-step (irreversible) reaction left more heat in the heat bath.

What pattern do we see here? Let's make a table of the work and heat:

direction	$w_{1-\text{step}}$	$w_{\infty-\text{step}}$	$q_{1-\text{step}}$	$q_{\infty-\text{step}}$
compression	1.0	0.693	-1.0	-0.693
expansion	-0.5	-0.693	0.5	0.693

We see that $\not{d}w_{\text{rev}} < \not{d}w_{\text{irrev}}$ and $\not{d}q_{\text{rev}} > \not{d}q_{\text{irrev}}$ (note that this is the **w**ork done on the gas and the heat absorbed by the gas respectively).

If we talk about how much **w**ork can be done by the gas (i.e. the negative of how much work is done **on** the gas) and the amount of heat transfered to the heat bath (the negative of the amount of heat absorbed):

direction	$w_{1-\text{step}}$	$w_{\infty-\text{step}}$	$q_{1-\text{step}}$	$q_{\infty-\text{step}}$
compression	-1.0	-0.693	1.0	0.693
expansion	0.5	0.693	-0.5	-0.693

We find that the reversible reaction can always do the maximal work and transfers the least amount of heat. **Getting the minus signs straight here is extremely important!**

2.6 State functions

2.6.1 Mathematical properties

In §2.3, we saw that the value for the internal energy ΔU after a transformation was indepdent of the path taken. A thermodynamic variable with this property is called a state function. During a transformation, state functions depend only on the initial and final states, and do not depend on the path taken. Accordingly, q and w **are not** state functions, since they do depend on the path taken.

The path independent aspect of state functions is very powerful: you don't need to know the path taken to know how the state function has changed, only the beginning and end of the path. Other examples of state functions are pressure P, volume V, and temperature T.

State functions have important mathematical properties which are related to their path independent nature:

1. If we integrate a state function

   $$\Delta U = \int_A^B dU \; ,$$

   then ΔU depends only on the beginning and end points, A and B. For this reason, dU is said to be an **exact differential**. Since q and w are not state functions, their differentials are called **inexact differentials** and are written with a bar in the d: $\not{d}w$ and $\not{d}q$.

2. We can write an exact differential in terms of some other coordinates. For example, let's say that the energy of some system depends on its volume V and temperature T. Then we can write,

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

   Here, we have used **partial derivatives** ($\partial U/\partial dV$) instead of **total derivatives** (dU/dT). $(\partial U/\partial dV)_T$ is the rate of change of the energy with respect to changes in volume, holding temperature constant.

   The equation above may give you a better idea of what we mean by different paths: since U is a function of T and V, you could go from the initial (U_i, T_i, V_i) to final (U_f, T_f, V_f) states by different ways of varying T and V along the way. However, no matter which path you take, we know that U, T, and V are state functions, and thus

   $$\begin{aligned} \Delta U &= U_f - U_i \\ \Delta T &= T_f - T_i \\ \Delta V &= V_f - V_i \end{aligned}$$

   Also, we can write the equation for dU above as $dU = A(T,V)dT + B(T,V)dV$. Another test that dU is an exact differential is that

   $$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial B}{\partial T}\right)_V$$

   This is called Euler's criterion for exactness.

3. The order of differentiation of a state function does not matter, i.e.

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

How do we tell if a function is a state function? Any function $f(x,y)$ is a state function if it obeys *any* of the properties above.

2.6.2 Relevant statefunction to determine transformations

As we will see throughout the course, different state functions will be relevant for predicting which transformations will occur spontaneously. For mechanical systems, we know that a mechanical process will occur spontaneously if the energy is decreased (i.e. if $\Delta U < 0$).

However, $\Delta U < 0$ does not universally describe when a process will happen spontaneously. For example, consider an endothermic reaction. This may have $\Delta U > 0$, but still occurs spontaneously. Thus, the first goal for us in thermodynamics is to discover *which* state functions are relevant for describing when a given process will be spontaneously. We will find that the relevant state function will depend on the nature of the transformation.

2.6.3 At constant volume: look to the energy

For most chemical systems, the only relevant work is the PV work of a gas. Imagine a transformation in which the volume is held fixed, i.e. $dV = 0$. In this case, the change in work is $\not{d}w = -PdV = 0$. Since the energy is given by $dU = \not{d}q + \not{d}w$, then in the case of fixed volume, $dU = \not{d}q$, or in other words, all the energy change comes in terms of heat.

Remember that q is still not a state function, but U is. The reason why $dU = \not{d}q$ is that we are talking about a particular path, i.e. constant volume. If we choose a different path (eg constant pressure instead of constant volume), then $dU \neq \not{d}q$ and will instead have some other meaning.

In thermodynamics, we will build up several different state functions to correspond to different scenarios. These different scenarios correspond to which state variables (eg, P, V, T, U, N, etc) are held constant and which can vary. For systems in which the number of particles N and volume V is fixed and there is no temperature coupling to the outside world (i.e. an isolated system), energy is a very useful state function. It is useful because in this case no work is done and the change in heat is simply related to the change in energy.

2.6.4 Constant pressure? We need a new state function: enthalpy

At times it is useful to examine systems at constant pressure instead of constant volume. In this case,

$$dU = \not{d}q + \not{d}w = \not{d}q - PdV$$

and thus, the change in heat is not directly related to the energy in this case. Can we construct a new state function which is related to the change in the heat for systems at constant pressure?

We start with what we know, i.e. the first law of thermodynamics $\Delta U = q + w$ and add in the fact that now there is work done (since volume is not constant, $w = P\Delta V$. Thus, we get

$$\Delta U = U_f - U_i = q - P(V_f - V_i)$$

We can solve for the heat to get

$$q = U_f - U_i + P(V_f - V_i) = (U_f + PV_f) - (U_i + PV_i)$$

From the above, we see that we can write q in terms of a function $H = U + PV$. Since

$$\Delta H = \Delta U + P\Delta V = (U_f - U_i) + P(V_f - V_i) = q$$

Since U, P, and V are state functions, they only depend on the initial and final states. Since H is a sum of state functions, it too must only depend on initial and final states and thus must be a state function itself. We call this function the **enthalpy**.

The increase of enthalpy of a system is equal to the heat absorbed at constant pressure (assuming that the system only does PV work, as in the case of ideal gases). Enthalpy is the constant pressure analogy of energy. They are both related to the heat absorbed, but under different conditions (energy in constant volume conditions and enthalpy at constant pressure).

Since ΔU and ΔH differ only by $P\Delta V$, ΔU and ΔH are similar for processes involving solids or liquids (since the volume changes in these systems is typically small). However, in gases, the volume change is often significant and there is a big difference between ΔU and ΔH.

3 Entropy I: Entropy in terms of heat

3.1 Reversibility and equilibrium: a recapitulation

Let's briefly recap some important concepts we've learned in the previous chapter:

1. Conservation of energy: If the internal energy U changes, this change in energy will take the form of work w and/or heat q ($\Delta U = q + w$)
2. Reversible reactions: we can perform a transformation reversibly if we make the transformation in many small steps and let the system reach equilibrium at each step
3. $\dbar w_{\mathrm{rev}} < \dbar w_{\mathrm{irr}}$: work done by the system is a maximum, work done on the system is a minimum
4. $\dbar q_{\mathrm{rev}} > \dbar q_{\mathrm{irr}}$: heat absorbed is maximized, heat transfered to the heat bath is minimized

These observations will be important in our understanding of entropy and the second law of thermodynamics.

3.2 The second law of thermodynamics

The second law relates to equilibrium and reversibility:

> *Spontaneous changes are those which can be made to do work. If carried out* reversibly*, they yield a maximum amount of work. In natural processes, the maximum work is never obtained (since complete reversibility is an idealization).*

This essentially is just a summary of what we have been talking about: reversible systems can do a maximum amount of work, but this is never truly realizable.

Another way to think about this is in terms of two bodies which have different temperatures. This temperature imbalance is like a state with potential energy (although we will see that U itself is not the important concept here). The system will relax back to equilibrium when the heat goes from the hotter body to the colder one. Heat will never spontaneously go the other direction. This reformulation of the second law in terms of heat flow is the more common way in which it is stated, although it has the same fundamental roots as the previous formulation.

In the end, the important concept to understand here is that this law of thermodynamics relates to the fact that some events can occur without doing any (additional) work to cause them (the so-called "spontaneous events"), i.e. we can just let them go and they will occur. Some examples are gas fleeing a balloon or a drop of dye spreading in a bucket. There are some events which we would call "non-spontaneous" since they do not happen without doing work. Once spread out, the dye never spontaneously comes to its initial drop.

It's also intriguing to ask where in physics does it say that this shouldn't happen? Certainly Newton's equations doesn't talk about this. In fact, Newton's equations work perfectly well, either forward or backward in time. There must be something else that we're missing.

3.3 Entropy

3.3.1 Motivation for a new state function

In simple mechanical systems, the capacity to do work is simply the potential energy and the equilibrium is defined by the minimum of this potential energy. In many thermodynamic systems, looking how the total energy changes is often not very useful. In particular, in the ideal gas examples we did in the previous lectures, the total energy did not change[2], but yet work was done. Is there some state function analogous to the total energy in mechanical systems which we can use to define equilibrium states and the capacity to do work in thermodynamic systems, such as ideal gases? As you probably guessed, the answer is YES – the missing idea is the concept of entropy.

3.3.2 Building a new state function

Let's build this new state function. When we wrote the function for enthalpy, we started with the heat[3]. In this case, we will also look to the change in heat, but in a different way.

For the moment, let's only think about the case in which our system remains at equilibrium. In this case, all of the transformations we will talk about will be reversible. From the first law, we can write

$$dU = \text{đ}q_{\text{rev}} - PdV$$

if the system only does PV work. Next, we can write dU in terms of temperature and volume by the exact differential

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

For simplicity and to make this discussion more concrete, let's consider the case of an ideal gas. For an ideal gas, this simplifies to

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT$$

since at constant temperature the internal energy of an ideal gas does not depend on volume (and thus $[\partial U/\partial V]_T = 0$). We can use the definition of the heat capacity to further simplify this to

$$dU = C_V dT$$

Now, we substitute for dU from the first law above to get

$$C_V dT = \text{đ}q_{\text{rev}} - PdV$$

We can rearrange these terms and make the substitution $P = nRT/V$ to get

$$\text{đ}q_{\text{rev}} = C_V dT + \frac{nRT}{V} dV$$

Finally, we divide everything by T and define our new state function S to be

$$dS = \frac{\text{đ}q_{\text{rev}}}{T} = C_V \frac{dT}{T} + nR\frac{dV}{V}$$

Thus, we define our new state function S to be $dS \equiv \text{đ}q_{\text{rev}}/T$.

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[2] We looked at isothermal processes and the energy of an ideal gas is independent of temperature.

[3] Indeed, the change in enthalpy is equal to the change in heat at constant pressure.

3.3.3 Properties of this new state function

How do we know that S is a state function? We can integrate the right hand side to get

$$S_f - S_i = C_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Thus, S is a state function since it only depends on the initial and final states and not on the path. Thus, even for irreversible paths, ΔS will be the same.[4]

However, this does **not** mean that $dS = \not{d}q/T$ for all paths. In particular, while entropy is always equal to $dS = \not{d}q_{\rm rev}/T$, irreversible paths have $\not{d}q \neq \not{d}q_{\rm rev}$. In this case, we get $dS \neq \not{d}q_{\rm rev}$. For spontaneous changes (i.e. irreversible) $\not{d}q < \not{d}q_{\rm rev}$. Thus,

$$dS > \frac{\not{d}q}{T}$$

Since all observable processes are never completely reversible, the above inequality holds for most processes we could do in an experiment and in every day life. The equality

$$dS = \frac{\not{d}q}{T}$$

holds only for transformations that are reversible.

In an isolated system (i.e. one which cannot exchange energy with its surroundings), the system can neither do work nor absorb heat. Thus, $\not{d}q = 0$ and thus $dS = 0$, or (integrating this differential) $S =$ constant. However, for any spontaneous change $dS > 0$ since $dS > \not{d}q/T$. Thus, spontaneous changes will continue to increase entropy until it reaches the maximal value possible. At this point, the system will be in equilibrium and entropy will remain constant at its maximal value. As we will see below, for non-isolated systems (eg. systems in contact with a heat bath), we will have to consider the entropy change in both the system and its surroundings (eg heat bath). This will be demonstrated below.

3.4 Examples of transformations and their entropy changes

3.4.1 Entropy of the expansion of an ideal gas

Let's go back to the case of the expansion of an ideal gas.[5] How do we calculate the change in entropy? We know that from the first law $\Delta U = q + w$ and that $\Delta U = 0$ for isothermal transformations. Thus, $q = -w$, i.e. the heat gained by the surroundings (heat bath) is equal to work done by the system. If we continuously adjust the pressure during this transformations, we can imagine a reversible transformation. As we've discussed, this does the maximum work, and we get

$$q_{\rm rev} = -w_{\rm rev} = \int_{V_i}^{V_f} P dV$$

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[4] This demonstrates that S is a state function for ideal gases. It can be shown that it is a state function in general, but we will not cover this derivation.

[5] While it might seem that I have some pathological love for this example, it's good to return to it since it will help us build greater and greater intuition about thermodynamics (by using a now very familiar example).

For an ideal gas, we have $P = nRT/V$ and thus

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln \frac{V_f}{V_i}$$

Since $\Delta S = q_{\text{rev}}/T$, we get

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_f}{V_i}$$

This ΔS is the change in entropy of the gas. We see that expanding a gas ($V_f/V_i > 1$) increases its entropy and compressing a gas ($V_f/V_i < 1$) decreases its entropy. This explains why a gas will always flow from a smaller container into a larger one. From the above discussion, we showed that spontaneous transformations will occur if the entropy increases. If a gas moves into a larger volume, then its entropy will increase. This also explains why the gas doesn't spontaneously compress itself into a smaller volume: that would decrease the entropy and so that cannot occur spontaneously. We can make it happen, but we have to do work to decrease this entropy.

The idea of doing work to decrease entropy is common throughout all of thermodynamics. In fact, if we were happy with what a state of maximum entropy gives us, then we wouldn't have to do any work and would let thermodynamics just do its thing. However, we like order in our life and thus we do work to fight the disorder that entropy typically leads to. We'll talk more about the relationship between entropy and disorder in the coming sections.

If we talk about entropy being related to disorder and work that cannot be used, then why is the entropy change the same for irreversible and reversible reactions (recall that S is a state function)? Well, we have to look at not just the entropy for the gas but the entropy of everything. Let's take these two cases one by one:

1. **For the reversible case**, if we expand a gas, then it's entropy increases:

   $$\Delta S_{\text{gas}} = nR \ln \frac{V_f}{V_i}$$

   However, when we expand a gas reversibly, we are doing some work. In fact, the amount of work we do on the system is equal to the amount of heat that we transfer to the heat bath (since $\Delta U = 0$). In this case, since there is a change in reversible heat of the heat bath, the heat bath's entropy changes. How much? We know that the work done on the heat bath is the negative of the work done by the gas, so we get $q_{\text{bath}} = -w_{\text{bath}} = w_{\text{gas}} = -q_{\text{gas}}$. This leads to

   $$\Delta S_{\text{gas}} = -\Delta S_{\text{bath}}$$

   and thus the total entropy is unchanged

   $$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{bath}} = 0$$

   This balances out because during compression (expansion), work done on (by) the gas is exactly balanced by the work done by (on) the system. As $\Delta U = 0$ for ideal gases, $q = -w$, and thus there is a balance of heat as well. Thus balance of heat, leads to a balance of entropy, thus leading to the total change in entropy to be zero.

   Thus, in reversible transformations, entropy is exactly exchanged between the system and its heat bath.

2. **In general**, consider the fact that the gas is connected to the bath. Thus, $q_{\text{gas}} = -q_{\text{bath}}$. This connect is not necessarily reversible. From our previous discussion, we have

$$\Delta S_{\text{gas}} \geq \frac{q_{\text{gas}}}{T}$$

Similarly, for the bath, we have

$$\Delta S_{\text{bath}} \geq \frac{q_{\text{bath}}}{T}$$

The temperature T is the same in both cases, since the bath acts to maintain temperature.

Since $q_{\text{gas}} = -q_{\text{bath}}$, we can say

$$\Delta S_{\text{gas}} \geq -\frac{q_{\text{bath}}}{T}$$

Flipping the previous relationship for ΔS_{bath} and q_{bath} and multiplying by -1, we get

$$-\frac{q_{\text{bath}}}{T} \geq -\Delta S_{\text{bath}}$$

Putting this all together, we get

$$\Delta S_{\text{gas}} \geq -\frac{q_{\text{bath}}}{T} \geq -\Delta S_{\text{bath}}$$

If we add ΔS_{bath} to all sides, we get

$$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{bath}} \geq \Delta S_{\text{bath}} - \frac{q_{\text{bath}}}{T} \geq 0$$

Thus, we see that ΔS_{total} will either be zero (for the reversible case) or positive (for the irreversible case). This is a very general result.

To conclude, we see that if we want to test spontaneity of events by $\Delta S > 0$, the ΔS we're talking about must include *everything*: in order to keep track of entropy changes, we must consider both the system and its surroundings (heat bath). This will make life tricky, but it makes sense: the entropy of a substance can decrease (we know that gases can be compressed), but this reduction in entropy must be compensated by an increase in entropy somewhere else (eg in the heat bath). In fact, if we compress the gas irreversibly, then the added entropy of the bath will be greater than the entropy lost in the gas. Finally, it is impossible for the total entropy to decrease. In a way, entropy is like thermodynamic pollution/garbage: we can't get rid of it but only move it around (and in moving it around, we create more of it!).

Clearly, there must be a better way, since considering the surroundings can get quite cumbersome. Indeed, there is, as we will see later.

3.4.2 Entropy changes accompanying heat flow

We have talked about heat will flow spontaneously from a hotter to a colder body. We are now at the point where we can be more mathematical about what we mean here. Also, we know have a better idea of what we mean by "spontaneously."

Consider a process with a **reversible** transfer of heat at each temperature. If we reversibly transfer heat *from* body A *to* body B, the overall entropy change is given by

$$dS = dS_A + dS_B = \frac{\not{d}q^A_{\text{rev}}}{T_A} + \frac{\not{d}q^B_{\text{rev}}}{T_B}$$

where T_A and T_B are the temperatures of bodies A and B respectively and q^A and q^B are the heat absorbed by A and B. Since all the heat absorbed by B came from A, we have $q^B_{\text{rev}} = -q^A_{\text{rev}}$. This leads to

$$dS = dS_A + dS_B = -\frac{\not{d}q^B_{\text{rev}}}{T_A} + \frac{\not{d}q^B_{\text{rev}}}{T_B}$$

Note the $-$ sign in front of the term A body entropy term: heat (and therefore entropy) are leaving A to go to B.

Doing some algebra, we get

$$dS = \not{d}q^B_{\text{rev}} \left(\frac{T_A - T_B}{T_A T_B} \right)$$

We see that when A is hotter than B (i.e. $T_A > T_B$), then $dS > 0$. As $dS > 0$ in all observable transformations, we see that heat will from from the hot body to the cold body. This flow will continue until $T_A = T_B$. At this point, $dS = 0$ and we have reached equilibrium and heat will no longer flow.

3.5 Some comments regarding entropy

3.5.1 Energy, entropy, and equilibrium

We've now seen two ways in which systems reach equilibrium.

1. **In our mechanical examples**, the system reached equilibrium when the internal energy was a minimum (and thus the forces were balanced) or $dU = 0$. These mechanical systems operated at constant entropy and thus all that mattered was lowering the energy.
2. **In our thermodynamic examples**, we often considered the case where the energy was constant (eg for ideal gases, isothermal transformations mean isoenergetic transformations). In these cases, equilibrium is reached when entropy no longer changes and is a maximum ($dS = 0$).

But what do we do if a system which can change both its energy and entropy? In this case, we will need a new state function to describe equilibrium. We will see this in the upcoming weeks.

3.5.2 A cosmological aside

As we've seen, when we consider entropy, we must consider both the system we're interested in and its surroundings. In many cases, the system will be something in the lab, and the surroundings will be the lab itself. However, we can think about larger systems, such as the thermodynamics of the earth. In this case, the earth's surroundings are the solar system (heat is exchanged between the earth and the solar system constantly!). Of course, we could continue to go further out and consider the system to be our solar system vs other solar systems, or perhaps our galaxy.

In the end, if we consider the entropy of the whole universe, we know that $\Delta S_{\text{total universe}}$ is increasing. It will continue to increase until it reaches its maximal value and then it will be at equilibrium. This equilibrium will not be very interesting as it will be a state devoid of any order (we certainly won't be around to see it). While it's a bleak fate, it's probably 10-100 billion years away, so we have some time to make our peace with it.

3.5.3 The second law of thermodynamics: a new perspective

With our new knowledge of entropy and spontaneous properties, we can look back at our two definitions of the second law:

1. Spontaneous changes are those which can be made to do work. If carried out *reversibly*, they yield a maximum amount of work.
2. Heat will always flow from a hotter body to a colder one.

These ideas can be unified into a single equation, which is perhaps the best formulation of the second law:

$$dS \geq \frac{\not{d}q}{T}$$

and in particular

$dS > \not{d}q/T$ for spontaneous and irreversible processes
$dS = \not{d}q/T$ for reversible processes
$dS < \not{d}q/T$ is impossible

4 Entropy II: The molecular basis of entropy

4.1 The molecular basis of entropy

We have discussed some mathematical aspects of entropy, but without a microscopic interpretation, entropy is often a vague and abstract concept. We will now give a microscopic understanding of entropy. This will also (hopefully) help to shed light on the nature of heat as well.

Let's start by defining a new quantity σ. We define σ as the $\ln$ of how many different arrangement a system could have. For example, consider flipping a coin. When it lands, it can be either heads or tails. Thus, there are 2 different arrangements and

$$\sigma_{1-\mathrm{coin}} = \ln 2$$

What if we had 2 coins? How many arrangements would be possible then? Each coin would have 2 possibilities, so there would be 2^2 ways (both heads; 1st head, 2nd tails; 1st tails, 2nd heads; both tails). In general, if we have N coins, then there are 2^N different rearrangements. This means that

$$\sigma_{\mathrm{N-coins}} = \ln\left(2^N\right) = N \ln 2$$

On thing we immediately notice is that

$$\sigma_{\mathrm{N-coins}} = N\sigma_{1-\mathrm{coin}}$$

Thus, σ is extensive!

Next, let's consider something closer to the thermodynamic systems we have been discussing. How many ways are there to rearrange the N particles of an ideal gas in a volume V? Let's say that each particle has a volume b. For simplicity, let's imagine that the box is cubical and that are gas particles are little cubes as well. Then, we ask, how many ways can we arrange a cube of volume b in a cubical box of volume V? One way to answer this question is to fill the large box with particles. The box of volume V can hold V/b particles. What this means is that there are V/b different places we can put a single particle. Thus, the σ for a single gas particle is

$$\sigma_{1-\mathrm{particle}} = \ln\left(\frac{V}{b}\right)$$

Now, what if we had N ideal gas particles? Each particle could be in any of the V/b locations (note that since these particles are ideal, they can be in the same place possibly). Thus, there are $(V/B)^N$ different ways to arrange these particles. This leads to

$$\sigma_{\mathrm{N-particles}} = \ln\left(\frac{V}{b}\right)^N = N\ln\left(\frac{V}{b}\right) = N\sigma_{1-\mathrm{particle}}$$

Again, we see that σ is extensive.

Finally, how does σ change when we expand a gas of volume V_i to a volume V_f? Since $\sigma(V) = N\ln(V/b)$, we get

$$\begin{aligned}\Delta\sigma &= \sigma(V_f) - \sigma(V_i) = \left[N\ln\left(\frac{V_f}{b}\right)\right] - \left[N\ln\left(\frac{V_i}{b}\right)\right] = N\left(\ln V_f - \ln b - \ln V_i + \ln b\right)\\ &= N\ln\left(\frac{V_f}{V_i}\right)\end{aligned}$$

Now, this looks familiar! The entropy of expanding a gas is given by

$$\Delta S = Nk \ln \left(\frac{V_f}{V_i} \right)$$

where we have used $Nk = nR$, i.e. the Boltzmann constant k and the number of atoms N instead of the gas constant R and the number of moles n. Thus, for an ideal gas, we can write

$$\Delta S = k \Delta \sigma$$

Or in other words

$$\text{entropy} = k \ln (\# \text{ of configurations})$$

and

$$\text{change in entropy} = k \, (\text{change in } \ln \# \text{ of configurations})$$

While I won't prove this, **these relationships between S and σ hold not just for an ideal gas, but for all systems.**

4.2 The statistical basis of the Second Law

With a microscopic interpretation of entropy, we can better understand the second law. Why do we expect entropy to always increase? It has to simply do with probability. Let's say 100 people flipped a coin. What do we expect? We certainly don't expect that all will come up heads. That's unlikely. It's much less unlikely that 50 people will have heads and 50 people will have tails. The reason why is that there are many ways in which one can have a 50/50 split, but only one way in which everyone has heads. Thus, simply probabilistically, it's more likely to have the 50/50 split, which is a more "random" arrangement.

Similarly, imagine that we had a sealed jar of gas in a box. If we open the jar, we expect that the gas will spread out throughout the box. Why? We have given reasons due to maximizing entropy and the second law, but let's think about what this means. First, how many ways are there of arranging the particles in the jar? For a jar of volume V_j, we have W arrangements

$$W_j = \exp(\sigma(V_j)) = \left(\frac{V_j}{b} \right)^N$$

Similarly, for the whole box (which has volume V_b), we have

$$W_b = \exp(\sigma(V_b)) = \left(\frac{V_b}{b} \right)^N$$

What are the odds that randomly the gas will be in one of the arrangements in which all of the particles are in the jar? This is the number of jar arrangements divided by the number of box arrangements, or

$$\text{odds} = \frac{W_j}{W_b} = \left(\frac{V_j}{V_b} \right)^N$$

To make this more concrete, let's say that the box is 10L and the jar is 1L and there is a mole of gas. Then, we get

$$\text{odds} = \frac{W_j}{W_b} = \left(\frac{1}{10}\right)^N \approx 10^{-10^{23}}$$

or a 1 out of $10^{10^{23}}$ chance of occuring! Thus, while it is *in principle* possible, it will essentially never happen. Why is this probability so low? Well, there is only a 1 in 10 chance that a single particle will be in the jar (since the box volume is 10 times as big). However, a mole of particles is a lot of particles and that's what makes an unlikely scenario for one particle into an impossibility for the whole gas all at once. It's like flipping a mole of coins and expecting all land heads up!

Finally, what are typical entropies for various substances? We expect solids to have the least entropy and gases to have the most. In the table below, we see this to be the case.

Molar entropies of substances at 298K and 1 atm pressure

Substance	S (J/K mol)
Diamond (solid)	2.4
Silver (solid)	42.7
Water (liquid)	69.9
Argon (gas)	154.7
Carbon dioxide (gas)	213.6

4.3 The third law of thermodynamics

You might be wondering what happens when a liquid becomes a gas. Why isn't that as unlikely to happen? All of the configurations we have been speaking about are assumed to be equally likely. The reason why we can say that is that all the configurations we have been talking about have the same energy U. This is true for an ideal gas, but not for a real gas. A real gas can have attraction between particles. Is is this attraction which counteracts the huge loss in entropy. We will talk about how this is possible in later lectures.

For the moment, we can simply consider the fact that we know that as we cool a gas down, it turns into a liquid. The liquid takes up much less volume and accordingly has much less entropy (there are fewer ways to arrange the liquid molecules). As we continue to cool the liquid, it turns into a solid. Solids typically have crystalline arrangements of its atoms. While the atoms in a liquid can move around, atoms in a solid are fixed in place. This leads to another drastic reduction in entropy. The only entropy left in a solid is the vibrations of atoms – small deviations from their crystal locations.

What happens to the magnitude of these vibrations as we lower temperature? The vibrations diminish and the crystal has less and less entropy (as the atoms become more and more locked into a specific place). At zero temperature, it is believed that the entropy of most substances completely vanishes, i.e. there is only one arrangement of the atoms and no kinetic energy available to lead to even small vibrations. The statement that the **entropy vanishes as $T \to 0$ is the third law of thermodynamics.**

4.4 What really is heat and how should we think about it?

I have tried to give some insight into heat, but the descriptions have been somewhat vague. The reasons for this is that while heat has to do with molecular motions, there is no simple equation to use to truly describe it and it is a somewhat abstract quantity. In many ways, it is perhaps simpler to think of it mathematically, but to get some better feeling about it, let's summarized what we have learned.

We can write this summary in terms of the important equations we have written relating to heat:

1. **Heat is a form of energy.** It is the "unused" energy, reflecting the difference between the change in internal energy ΔU and the work done on the system w

   $$\not{d}q = dU - \not{d}w$$

   For certain situations, we can more directly relate heat to other state functions. In particular:

   (a) Constant volume: we relate the heat directly to the energy

   $$\not{d}q|_V = dU$$

   (b) Constant pressure: we relate the heat directly to the enthalpy

   $$\not{d}q|_P = dH$$

2. **Heat is related to temperature.** Certainly hot things have high temperature. To make something hot, you need to transfer heat. How much? Well, that depends on the substance, via the heat capacity

   $$\not{d}q = C_V dT$$

   (at constant volume, we would use C_P for processes at constant pressure).

3. **Heat is related to entropy.** Indeed, we saw that transformations which changed entropy involved the transfer of heat. In particular,

   $$\not{d}q_{\text{rev}} = TdS$$

4.5 Examples

4.5.1 Quickies

It is important to understand and to be familiar with these different aspects of heat. In particular, one can use these different aspects to answer thermodynamic questions. For example:

1. What is the change in entropy when we raise the temperature a substance reversibly at constant pressure? (Assume that the heat capacity is independent of T).

   We know that the entropy is related to the heat by $\not{d}q_{\text{rev}} = TdS$ and the heat is related to temperature by $\not{d}q = C_P dT$. Thus, we get

   $$dS = \frac{\not{d}q_{\text{rev}}}{T} = C_P \frac{dT}{T}$$

and we integrate to get

$$\Delta S = \int dS = \int_{T_i}^{T_f} C_P \frac{dT}{T} = C_P \ \ln\left(\frac{T_f}{T_i}\right)$$

2. What is the entropy change from a liquid to a gas (under constant pressure)?

   It takes some energy to turn a liquid into a gas. We know this since it takes heat to boil water, for example. This energy needed is called the enthalpy of vaporization $\Delta H_{\rm vap}$ (enthalpy since we're talking about constant pressure).

   We can relate the enthalpy to the entropy by $\Delta H_{\rm vap} = q_{\rm rev}$ under constant pressure, and thus

   $$\Delta S_{\rm vap} = \frac{q_{\rm rev}}{T} = \frac{\Delta H_{\rm vap}}{T}$$

   where the temperature is the temperature at which the liquid becomes a gas. For example, for benzene, $\Delta H_{\rm vap} = 30.7$ kJ/mol and the normal boiling point is 353.3K. Thus, $\Delta S_{\rm vap} = 87.0$ J/K mol. This value is common for non-polar solvents.

3. Imagine two gases at the same T and P are partitioned off in a box of volume V: one in a volume of V_1 and the other in V_2 (note $V = V_1 + V_2$). Next, we remove the partition and thus left the gases mix. How does the entropy change?

   Let's take the entropy change for each gas separately. For gas 1, we say

   $$\Delta S_1 = n_1 R \ln\left(\frac{V_f}{V_i}\right) = -n_1 R \ln\left(\frac{V_1}{V}\right) = -n_1 R \ln\left(\frac{n_1}{n}\right)$$

   where $n = n_1 + n_2$. Similarly, we can write an analogous equation for gas 2:

   $$\Delta S_2 = n_2 R \ln\left(\frac{V_f}{V_i}\right) = -n_2 R \ln\left(\frac{V_2}{V}\right) = -n_2 R \ln\left(\frac{n_2}{n}\right)$$

   We find the total change in entropy to be

   $$\Delta S = n\left[-y_1 R \ln y_1 - y_2 R \ln y_2\right]$$

   where $y_i = n_i/n$ is the molar fraction of gas i.

   We see that the gases will mix completely. This mixing has the most entropy. Another way to think about it is that if we try to de-mix (eg separate out) the gases, we will have to do work against entropy.

4.5.2 Heat engines

It is possible to turn heat into work. Any device, such as a steam engine or a car, which burns fuel to do work is an example. A simple model of an internal combustion engine is a machine which takes heat (q_h) from a high-temperature reservoir (eg by burning fuel to create heat), uses some of that heat to do work (w), such as by the expansion of a gas against a piston, and then puts the unused heat (q_c) to a colder reservoir (eg radiator).

What is the maximum amount of work that we can obtain from this process? If all of these processes were reversible, then the total entropy of the system would remain constant, ie.

$$\Delta S_{\text{total}} = \Delta S_h + \Delta S_c = 0$$

Since $\Delta S_h = -q_h/T_h$ (minus sign comes since we are taking heat from the hot bath) and $\Delta S_c = q_c/T_c$, for reversible transformations we get

$$0 = \Delta S_{\text{total}} = -\frac{q_h}{T_h} + \frac{q_c}{T_c} \quad \Rightarrow \quad \frac{q_h}{q_c} = \frac{T_h}{T_c}$$

We can relate work to heat via the conservation of energy. Since the internal energy of our engine does not change with time, we can simply relate work to heat:

$$\begin{aligned} w &= q_h - q_c \\ \frac{w}{q_h} &= \frac{q_h - q_c}{q_h} = 1 - \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \\ &= \frac{T_h - T_c}{T_h} \end{aligned}$$

This ratio of work we get out of the machine over the heat we put in w/q_h is called the thermodynamic efficiency of the engine. For example, for a steam engine using steam at 400K and using a radiator at room temperature of 300K, the thermodynamic efficiency would be

$$\frac{400K - 300K}{400K} = 25\%$$

i.e. only one-quarter of the heat is converted into work. If the radiator over-heats ($T_c = T_h$), then we get no work. How do we get maximum efficiency? If we have a really, really cold radiator (i.e. $T_c = 0$), then we would get 100% efficiency. Why do we get 100% efficiency when $T_c = 0$? In this case, we have extracted all of the possible heat we can (it's not possible to get to any lower temperature) and moreover there is no more heat energy left (since at $T = 0$ there are no molecular motions), thus all of the heat energy must be transformed into work.

4.5.3 Protein folding

To end this section on entropy and as a lead-in for our next section on free energy, I'll lay out what is the so-called "Protein Folding problem" and how it relates to entropy.

Proteins are polymers of amino acids: long chain molecules. They are "manufactured" by the cell and come off the assembly line in a completely disordered form. Why do we expect them to be disordered? Let's think about the entropy of a polymer chain. Let's simplify this by imagining walking on a chess board. At each step, you can go forward, backward, left, or right (4 directions). If you take N steps, there are 4^N possible ways to choose a path. For polymers in three dimensional space (the chess board is a two dimensional example), one could approximate the number of possible walks as 6^N. Even for relatively short chains, this is a lot of possible configurations. The corresponding entropy

$$S = k \ln 6^N = kN \ln 6$$

is pretty large.

What's exciting about proteins is that they will *fold* from one of the 6^N conformations into a single, particular conformation. In other words, the conformational entropy essentially vanishes, i.e.

$$S = k \ln 1 = 0$$

Why do proteins actually fold into a single conformation? Probabilistically, one would say that there are so many unfolded conformations, why does the protein stay in a single fold? The reason why proteins fold (and why gases become liquids and then solids, etc) is that one can fight the entropy by making certain configurations have low energy. The folded state of proteins are believed to have lower energy and that's why they stay in these states.

When both energy and entropy change, how can we tell which one wins and which one is relevant? This important question has a pretty simple answer, which we will see in the next section, when we define (yet another) state function, to answer this particular question.

5 Equilibrium I: The concept of free energy

5.1 Helmholtz free energy

5.1.1 Derivation

In the previous section, I alluded to a new state function which will help us sort out when entropy is important and when energy dominates. This new state function is called the free energy.

When we created the enthalpy state function, we said that we wanted something to reflect the change in heat at constant pressure. In this case, we have a very different goal. In the previous section, we saw that using just entropy alone required us to consider the entropy changes of both the system and its surroundings. This is often difficult to do and best to avoid if possible. But how can we avoid doing this?

One way around this is to saw that we want to build a state function which reflects the nature of equilibrium. To find such a state function, we return to the idea of maximum work. In the last unit, we defined equilibrium as the case when a system can do maximum work. For example, a reversible reaction can do the maximum amount of work. We will now introduce thermodynamic functions which are indicate whether one can do the maximum amount of work and thus tell us whether we are at equilibrium. Also, we will in this section always consider systems at constant temperature.[6]

For a reversible reaction, we have

$$dU = \not{d}w_{\rm rev} + \not{d}q_{\rm rev}$$

Since we can relate the change in reversible heat to entropy by

$$dS = \frac{\not{d}q_{\rm rev}}{T}$$

We can write

$$dU = \not{d}w_{\rm rev} + TdS$$

rearranging, we get

$$\not{d}w_{\rm rev} = dU - TdS$$

Thus, it is natural to define a new state function, called the **Helmholtz free energy** F[7]

$$F = U - TS$$

since (at constant temperature)

$$dF = dU - TdS = \not{d}w_{\rm rev}$$

One way to think of the free energy is that *it is a measure of the maximum work the system can do on its surroundings*. Just as mechanical systems work to decrease U, molecular systems (at constant T and V) try to reduce F to reach equilibrium. What does this mean? In mechanical systems, we expect spontaneous processes to occur only if $dU < 0$. Apples spontaneously fall from trees, but they never spontaneously leap from the ground into the sky. Similarly, spontaneous processes in molecular

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[6] For systems at constant energy, it is more natural to just look at how the entropy changes.

[7] The Helmholtz free energy F is often called just the free energy and written as A.

systems occur only if $dF < 0$. If there is a state with lower free energy, then the system will eventually get there.[8]

What happens at equilibrium? At equilibrium, we expect that the system will do no work and thus $dF = 0$. This naturally parallels $dU = 0$ in mechanical systems.

5.2 Another way to look at free energy and equilibria

In section 3, we talked about

$$dS \geq \frac{\not{d}q}{T}$$

and said that $dS > \not{d}q/T$ for spontaneous processes and $dS = \not{d}q/T$ for reversible processes.

Now, we'll see what the interpretations of this are for other statefunctions. Let's take dU for example. From the first law, we have $dU = \not{d}q + \not{d}w$ and thus $\not{d}q = dU - \not{d}w$. For a gas, we have $\not{d}w = -PdV$ and thus $\not{d}q = dU + PdV$. Putting this into the inequalityabove, we get $TdS \geq dU + PdV$. Rearranging terms, we get

$$dU \leq TdS - PdV$$

Thus, we see at constant S and V we have $dS = 0$ and $dV = 0$, thus leading to the inequality

$$dU \leq 0$$

Thus, under constant S and V, spontaneous processes must have $dU < 0$.

We can do the same thing with other statefunctions. For example, for the Helmholtz free energy $F = U - TS$, we calculate the total derivative $dF = dU - TdS - SdT$. Solving for dU, we get $dU = dF + TdS + SdT$. Inserting into $dU \leq TdS - PdV$, we get

$$dF + TdS + SdT \leq TdS - PdV$$

Simplifying, we get

$$dF \leq -SdT - PdV$$

Thus, we see at constant T ($dT = 0$) and V ($dV = 0$), we get

$$dF \leq 0$$

and more specifically that spontaneous events must have $dF < 0$ under constant T and V.

This is a general scheme in order for us to see how statefunctions describe equilibrium and spontaneity.

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[8] I say "eventually" here since thermodynamics can only describe properties at equilibrium (i.e. what they will be like if we wait a long time). Thermodynamics does not talk about how long it may take to reach equilibrium (you'll have to wait for kinetics in Chem 175 to learn about this).

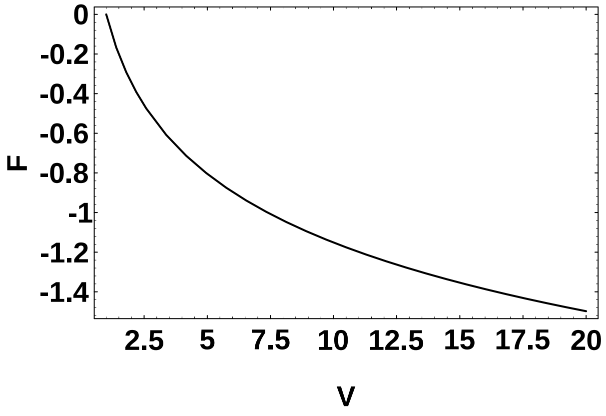

Figure: Free energy of an ideal gas vs volume. We see that the free energy deceases as we increase volume. If we add in the interactions of the box, then there will be some free energy minima at the volume corresponding to the volume of the box. Without a box, the free energy would push the gas to expand forever!

5.2.1 Free energy of an ideal gas: a derivation of $PV = nRT$

Let's write the free energy for an ideal gas. First, we need to know the energy at constant temperature. The energy of an ideal gas does not depend on volume and only depends on temperature.[9] Thus, at constant temperature, we can write U as a constant. Moreover, we are free to set the zero of energy wherever we like, so we can just say that $U = 0$. This makes sense for an ideal gas since there are no interactions between particles (and this is what typically we would put in U anyway).

As for the entropy at constant temperature, we can relate it to the number of possible particle rearrangements. We said that for an ideal particle, each particle can be in V/b places and thus all n moles of particles can be in $(V/b)^n$ places, and thus

$$S = nR \ln \frac{V}{b}$$

where b is the volume of a gas particle. Thus, we get

$$F = U - TS = -TnR \ln \frac{V}{b}$$

Since $dF = \not{d}w_{\text{rev}} = -PdV$, we can write

$$P = -\frac{dF}{dV} = -T \left[-\frac{dS}{dV} \right] = \frac{nRT}{V}$$

and thus we get

$$PV = nRT$$

Thus, we see we naturally get the equation of state from the free energy. Moreover, let's consider the case of a gas given room to expand: in that case, the expanded version of the gas has a much lower free energy and thus we expect the system to expand such that it lowers its free energy.

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[9] This is true for an ideal gas since the only energy is kinetic energy (the particles do not interact by definition). If the particles interacted, then we would add a term to incorporate this interaction and this term would depend on the density of particles.

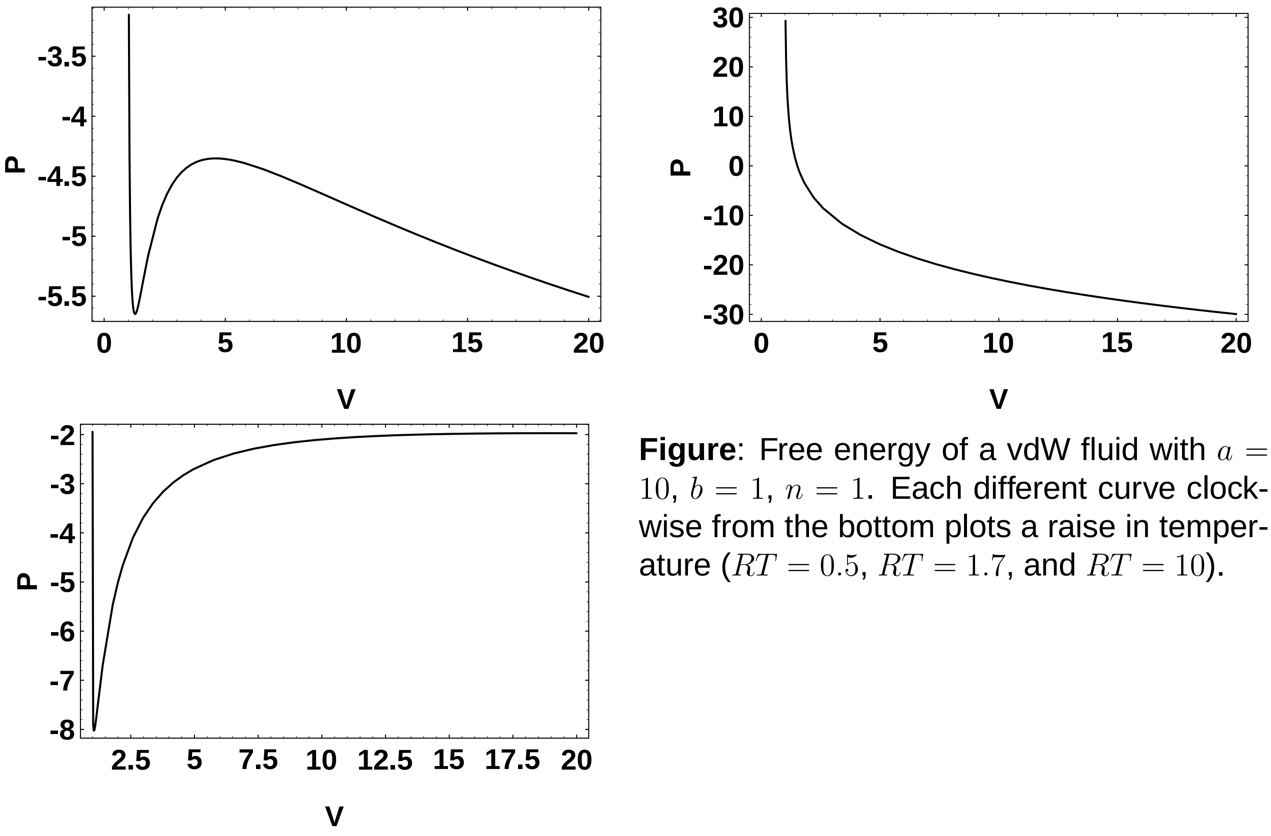

Figure: Free energy of a vdW fluid with $a = 10$, $b = 1$, $n = 1$. Each different curve clockwise from the bottom plots a raise in temperature ($RT = 0.5$, $RT = 1.7$, and $RT = 10$).

5.2.2 Free energy of a van der Waals fluid

What do we need to do to calculate the free energy of a vdW fluid? We need to add some sort of interactions between particles and decrease the entropy to account for the fact that two particles cannot be at the same place at the same time.

For the interaction between particles, we would say that

$$U = -an\rho = -a\frac{n^2}{V}$$

This is along the lines of the argument I made in the first lecture: the interaction energy per unit volume goes like the density (ρ) squared since the density is like the probability of finding a single particle. Thus, the total energy is this energy per unit volume times the volume. Here a is the strength of the interaction: for attraction between particles, $a > 0$.

Next, we need to modify the entropy. Before, we said that each particle can be in V/b places. Now, we will say that each particle can only be in $(V - nb)/b$ places. Thus, the entropy is

$$S = nR\ln\left(\frac{V - nb}{b}\right)$$

and thus the free energy is

$$F = -a\frac{n^2}{V} - TnR\ln\left(\frac{V - nb}{b}\right)$$

We can again use this to calculate the pressure:

$$P = -\frac{dF}{dV} = -a\frac{n^2}{V^2} + \frac{nRT}{V - nb}$$

and thus we get

$$\left(P + an^2/V^2\right)(V - nb) = nRT$$

i.e. the equation of state for a van der Waals fluid, as we expected.

Let's look at the free energy in a bit more detail to understand how this works. How do we expect the free energy to behave vs temperature? At low T, the energy is more important than the energy and at high T, entropy is more important. In the figure, we have plotted the vdW free energy vs temperature. There are three important temperature regimes:

1. At low temperatures, the free energy is dominated by the energy as we expected and we get a liquid due to the attractive interaction between particles. We know that it is a liquid since the minima in free energy is at the volume bn which is the volume of the particles themselves (there is no space between particles as in a gas).
2. At high temperatures, we find just the reverse. The free energy constantly decreases as we increase V, reflecting the fact that a gas wants to fill up as large a volume as possible.
3. At an intermediate temperature, we see that there are two minima of sorts: one at the volume of a liquid and one at the volumes of a gas. The existence of two free energy minima reflects the **co-existence** of both a liquid and gas states.[10]

It is important to consider **how to interpret free energy minima**. Mathematically, free energy minima are locations where $dF/dX = 0$ and $d^2F/dX^2 > 0$, where X is some state function of interest, such as volume. This mathematical definition is important, but is not very insightful. How does one interpret energy minima in mechanical systems? Energy minima are equilibrium locations. In particular, since the force $f = -dU/dx$, then $dU/dx = 0$ means that $f = 0$ and at such locations, all the forces are balanced. In the case of a vdW fluid, $P = -dF/dV$ and thus free energy minima correspond to locations where $P = 0$. This can result from the fact that the substance is a liquid, or that the pressure from the box matches the pressure of the fluid.

The van der Waals fluid is a nice system to look at the relevance of the free energy. Calculating the free energy and looking for minima is pretty common practice for understanding the phase behavior of substances.

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[10] There is a lot of interesting science to talk about here, especially relating to the coexistence and the nature of how this system goes from being a liquid to a gas. For now, I will only state that since there are two free energy minima (at the liquid and gas volumes), the volume of the system "jumps" as we raise temperature from $V \approx 1$ to the volume of the container. This jump is a signal of a **phase transition**. Free energy calculations are a natural way to examine phase transitions in all sorts of systems, from physical examples, such as gases and liquids to biophysical examples such as proteins and lipid membranes.

5.3 Gibbs free energy

5.3.1 Derivation

Many experiments are performed at constant pressure rather than constant volume. Indeed, that was the motivation of deriving (and using) the enthalpy rather than the energy. Is there some constant pressure version of the free energy F? As you probably suspected, there is.

Under constant pressure conditions, we can write

$$đw_{\mathrm{rev}} = -PdV + đw_{\mathrm{additional}}$$

where $đw_{\mathrm{additional}}$ is the work other than PV work done on the system. From here, we continue the derivation as we did for F, i.e. we say

$$đw_{\mathrm{rev}} = dU - đq_{\mathrm{rev}}$$

and

$$đq_{\mathrm{rev}} = TdS$$

thus

$$đw_{\mathrm{additional}} - pdV = dU - TdS$$

and it is natural to define a new state function G called the **Gibbs Free Energy** such that

$$G = U + PV - TS = H - TS$$

At constant P and T, we find

$$dG = dU + pdV - TdS = đw_{\mathrm{additional}}$$

Thus, G acts like F but under constant pressure situations. It is related to the maximum (non-PV) work done by the system, and like F, minimizing G is the constant P and T analog of minimizing U for mechanical systems. Also, of note is that we see that to turn F into G, one trades U for H. Thus, all of the intuition we have built can be naturally applied to the constant pressure case by simply exchanging energy for enthalpy.

5.3.2 Example: Dimerization

Consider the reaction

$$\mathrm{N_2O_4} \rightleftharpoons \mathrm{2NO_2}$$

When dimerized, the enthalpy is lower $H_{\mathrm{N_2O_4}} < H_{\mathrm{2NO_2}}$ since there are extra bonds formed. However, the dimerized state has lower entropy $S_{\mathrm{N_2O_4}} < S_{\mathrm{2NO_2}}$ since there are fewer degrees of freedom and thus fewer ways to arrange the particles. Thus, we see that at high temperatures, the dimer will disassociate and at low temperatures it will associate.

5.4 Phase Equilibria

In the previous section, we showed how a vdW fluid can be either a gas or a liquid. We also saw that there were cases where both gas and liquid phases had similar free energies and thus both phases coexisted. In this section, we will follow up on these concepts and flesh out the details.

Before we get started, we'll have to go over some basics of how the Gibbs free energy depends on pressure and temperature. In particular, we will write the differential dG in a new way. Starting from the definition of the Gibbs free energy

$$G = U + PV - TS$$

we can write the complete differential (i.e. nothing held constant):

$$dG = dU + PdV + VdP - SdT - TdS$$

We can also write dU in terms of heat and work:

$$dU = đq_{\mathrm{rev}} + đw_{\mathrm{rev}}$$

We can write the entropy in terms of the reversible heat $đq_{\mathrm{rev}} = TdS$ and for a system which only does PV work, then $đw_{\mathrm{rev}} = -PdV$. Thus,

$$dU = TdS - PdV$$

We can stick this into the formula for dG above to get

$$\begin{aligned} dG &= (TdS - PdV) + PdV + VdP - SdT - TdS \\ &= VdP - SdT \end{aligned}$$

This form of dG will be useful in studying the variation of G with pressure and temperature.

5.4.1 Warm-up I: Pressure-dependence of the free energy

At a constant temperature, $dT = 0$. Thus,

$$dG = VdP, \text{ or } \left(\frac{\partial G}{\partial P}\right)_T = V$$

For an ideal gas, $V = nRT/P$ and thus

$$dG = VdP = nRT\frac{dP}{P}$$

For a change in pressure from P_i to P_f, we get

$$\Delta G = G_f - G_i = nRT\int_{P_i}^{P_f}\frac{dP}{P} = nRT\ln\frac{P_f}{P_i}$$

We can use this to study the pressure dependence of the enthalpy of an ideal gas.[11]

In chemistry, it is common to relate the free energy of a gas to the **standard free energy** G^0. G^0 is defined as the free energy of one mole of the gas at 1 atm, i.e.

$$G = G^0 + RT \ln \frac{P}{P^0}$$

where $P^0 = 1$ atm. It is also written as

$$G = G^0 + RT \ln(P/\mathrm{atm})$$

or simply

$$G = G^0 + RT \ln P$$

This is notation and convention and certainly nothing deep, although it can be confusing if you haven't seen this before.

5.4.2 Warm-up II: Temperature variation of the free energy

Again, we use $dG = VdP - SdT$, but now we say that pressure is constant, or $dP = 0$. This leads to

$$dG = -SdT, \text{ or } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

We can use this to rewrite G. Starting from

$$G = H - TS$$

we insert the above formula for S to get

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

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[11] Since we can also write

$$G = H - TS$$

then at constant temperature, we get

$$dG = dH - TdS$$

and

$$\frac{dG}{dP} = \frac{dH}{dP} - T\frac{dS}{dP}$$

Since the entropy is $S = -nR\ln(P_f/P_i)$ and thus

$$dS = -nR\frac{dP}{P} \Rightarrow \frac{dS}{dP} = \frac{-nR}{P} = -\frac{V}{T}$$

also, from above we have $dG/dP = V$. Thus leads to

$$\begin{aligned} \frac{dH}{dP} &= \frac{dG}{dP} + T\frac{dS}{dP} \\ &= V - V = 0 \end{aligned}$$

Thus, H does not depend on P (since $dH/dP = 0$).

and divide everything by T^2 to get

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

Now notice the following mathematical simplification:

$$\left[\frac{\partial\left(G/T\right)}{\partial T}\right]_P=-\frac{G}{T^2}+\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

This allows us to write

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

in differential form, or

$$\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P=-\frac{\Delta H}{T^2}$$

in terms of the change in G and H in a reaction. These are the **Gibbs-Helmholtz equations**. They are important since they relate the temperature dependence of the free energy (and hence the position of equilibrium) to the enthalpy change. We'll use this in the next section.

5.4.3 Phase diagrams

We can use $G = H - TS$ to understand why there are different phases of matter stable under different conditions. The phase with the lowest free energy is the most stable. For example:

phase	enthalpy (H)	entropy (S)
solids	very negative H ($\lvert H\rvert$ is large and $H < 0$) strong attraction between atoms	small entropy ($S \approx 0$) few re-arrangements of atoms
liquids	intermediate H ($H_{\text{solid}} < H_{\text{liq}} < H_{\text{gas}}$) some attraction between atoms	intermediate entropy ($S_{\text{solid}} < S_{\text{liq}} < S_{\text{gas}}$) some re-arrangements of atoms
gases	small H ($H \approx 0$) little attraction between atoms	huge entropy (S is large) many re-arrangements of atoms

How can we see this in terms of the Gibbs free energy? If we plot $G(T)$, then the slope of this curve is related to the entropy (since $(\partial G/\partial T)_P = -S$). The gas phase has the largest negative slope since it has the most entropy. When the curves for $G(T)$ of different phase intersect, we know that their free energies are equal, or if we transform from one phase to another under these conditions, $\Delta G = 0$. Recall that we've talked about $dG = 0$ as an indicator of equilibrium. Now, we are talking about two phases being in equilibrium: both phases are present and one can spontaneously reversible transform from one to the other.

What is the temperature at which this occurs? For example, if we are given the enthalpy and entropy of fusion, then we know that the fusion temperature is given by

$$\Delta G = \Delta H - T\Delta S = 0 \quad \Rightarrow \quad T = \frac{\Delta H}{\Delta S}$$

One can draw diagrams which describe the phase boundaries in the P, T plane. These diagrams are called phase diagrams. They give us insight into which properties lead to the existence of which phases.

5.5 A review of our state functions S, U, H, F, G

5.5.1 When is a processes spontaneous and when is it reversible?

We have now seen all of the major state functions in thermodynamics and are (finally) at the point where we can actually do some interesting things. Before moving on, let's just summarized what we've learned.

First and foremost, these state functions are useful for determining equilibrium and whether a process will spontaneously occur. These functions differ in how these processes occur. In particular, what aspects are held fixed (V, P, T?) and which can vary. We summarize the state functions below.

variable(s) held constant	**Irreversible processes (spontaneous)**	**Reversible processes (equilibrium)**
q	$dS > 0$	$dS = 0$
V,S	$dU < 0$	$dU = 0$
P,S	$dH < 0$	$dH = 0$
V,T	$dF < 0$	$dF = 0$
P,T	$dG < 0$	$dG = 0$

There's a clear pattern here: equilibrium means $dX = 0$, where X is the appropriate state function and for spontaneous processes $dX < 0$ (except for entropy for which $-dS < 0$). Understanding the thermodynamics of what happens spontaneously and what does equilibrium look like is now just a matter of deciding which conditions are relevant for the system desired (i.e. is the experiment done at constant pressure or constant volume?) and then calculating or measuring the appropriate state function.

5.5.2 Natural variables

There are important relationships between these state functions. We can begin to see these relationships by writing the state functions in terms of T and P for closed systems (i..e in which matter cannot be transfered) involving only PV work:

$$\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dF &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}$$

We have already derived some of the equations above. The derivations of the others are similar and will be on a future problem set. Another important trend to notice is that the differentials on the right hand side match which state variables are held constant for the respective state function (eg P and T are constant in Gibbs free energy calculations and $dG = -SdT + VdP$, i.e. dT and dP appear in dG. Similarly, dS and dP appear in dH). The variables that are held constant for a particular state function (which are differentials in the equations above) are called **the natural variables** of the system; they play an important role (see below).

The equations above are useful because they allow us to come up with some nifty relationships between state variables. For example:

- From $dF = -SdT - PdV$ we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

- From $dG = -SdT + VdP$ we get

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

There are similar relationships obtained from the equations for dU and dH above.

Finally, knowing the natural variables of a system is very important. If a thermodynamic potential is known in terms of its natural variables, then all thermodynamic potentials can be calculated! For example, let's say that we know the function $G(T,P)$. T and P are the natural variables for G. From $G(T,P)$ we can calculate:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{and} \;\; V = \left(\frac{\partial G}{\partial P}\right)_T$$

and then plug in these values to calculate the other state functions starting from $G = U + PV - TS$:

$$\begin{aligned} U &= G - PV + TS = G - P\left(\frac{\partial G}{\partial P}\right)_T - T\left(\frac{\partial G}{\partial T}\right)_P \\ H &= G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P \\ F &= G - PV = G - P\left(\frac{\partial G}{\partial P}\right)_T \end{aligned}$$

This would not be possible if G is known as a function of V and T or P and V.

It is important to remember that U, H, F, and G are state functions. They have the same Δ value, irrespective of the path taken in the transformation. For example, while H is typically defined in terms of constant pressure, we can calculate H for constant volume situations. It doesn't have the same significance under constant volume ($dH = \not{d}q_P$, ie for constant pressure only), but we can still calculate it.

5.5.3 Maxwell relations

Finally, we can use the relationships above to go one step further and relate the state changes in the state variables to each other. Since dU, dH, dF, and dG are exact differentials in the equations in §5.4.2, the mixed second derivatives of the coefficients of the two terms on the right hand sides are equal (as we discussed in §2.7):

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

Now that we know that these derivatives are related to P, V, T, etc, this allows us to calculate even more relationships. For example, from $dG = -SdT + VdP$ we get

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

If we take one more mixed derivative, we get

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left(\frac{\partial V}{\partial T}\right)_P$$

Using the other thermodynamics potentials, one gets other relations:

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\
\left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V
\end{aligned}$$

There relations are called **Maxwell relations**, named for James Maxwell, who first derived them. The Maxwell relations are important because they are of considerable help in reaching our objective of expressing any thermodynamic property of a system in terms of easily measured physical quantities.

5.6 Chemical potential

So far, we have talked only about systems which contain only one type of chemical component. We have also only talked about systems in which the number of molecules is constant. In order to treat systems with different chemical constituents or where the number of molecules must vary, we need to add another important concept: that of a chemical potential.

For a pure substance or a system of constant chemical composition, we can write

$$dG = VdP - SdT$$

If the number so moles of various components of the system, $n_1, n_2, \ldots, n_i$, vary, we may add further terms to this equation:

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 \; + \; \cdots \; + \; \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_j$$

where the subscript n_j denotes that the quantities of all components, except the on in the derivative, are held constant. We define the **chemical potential** μ_i of the ith component

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

and thus we can write the Gibbs free energy as

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

This equation is sometimes called the fundamental equation of chemical thermodynamics.

What's a good way to think about μ? From its definition, μ is the change in free energy when we change the number of components, so it is the extra free energy gained (or lost) when extra components are added. "Components" often refers to particles, so then in that case μ would be the change in free energy when we change the number of particles. In the previous cases, we have held n fixed, although this is not universally the case and often the number of particles can change.

μ is also useful for thinking about the balance of particles achieved at equilibrium. At constant T and P, if we transfer dn_i moles of i from A to B, we get

$$dG = [\mu_i(B) - \mu_i(A)]dn_i$$

At chemical equilibrium $dG = 0$ and thus this is achieved when

$$\mu_i(B) = \mu_i(A)$$

This is a useful definition of the position of chemical equilibrium.

Since the free energy is extensive, for a pure substance we get

$$\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{T,P,n_j} = \frac{G}{n}$$

Thus, since

$$G = G^0 + nRT\ln(P/\mathrm{atm})$$

we get

$$\mu = \mu^0 + RT\ln(P/\mathrm{atm})$$

Thus, μ has a similar pressure dependence as G. Moreover, we can use this to talk about the case in which there is more than one component. For example, ideal gases in a container do not interact and act as if they were alone in the container. Thus, we get for each component i

$$\mu_i = \mu_i^0 + RT\ln(P_i/\mathrm{atm})$$

6 Equilibrium II: Applications of free energy concepts

6.1 Equilibrium between gaseous reactants

6.1.1 Simple example

Consider the equilibrium

$$A(g) \rightleftharpoons B(G)$$

This is the simplest type of chemical equilibrium. One example of this is the transformation between two isomers, such as n-butane and isobutane. If dn_A moles of A are converted into dn_B moles of B at constant T and P, we have $dG = \mu_A dn_A + \mu_B dn_B$ where $dn_A < 0$ and $dn_B > 0$. We can define an **extent of reaction** ξ which is 0 when the reaction position is entirely to the left (all at A) and 1 when everything is at B. More explicitly, we can write

$$\xi = \frac{n_B}{n_{\text{tot}}} = \frac{n_{\text{tot}} - n_A}{n_{\text{tot}}}$$

where $n_{\text{tot}} = n_A + n_B$ is a constant (there are isomerations going on, but no particles are leaving or coming); for simplicity, we set $n_{\text{tot}} = 1$.

This allows us to write

$$d\xi = dn_B = -dn_A$$

and

$$dG = (\mu_B - \mu_A)d\xi$$

at constant T and P. The reaction will proceed until equilibrium, i.e. when

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$$

Since

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A$$

this occurs at the balance of the chemical potentials $\mu_A = \mu_B$ as we discussed previously. Since

$$\mu_i = \mu_i^0 + RT\ln(P_i/\text{atm})$$

we can write

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A = \mu_B^0 - \mu_A^0 + RT\ln\frac{P_B}{P_A}$$

We can further simplify this since we know that $\mu_B^0 - \mu_A^0 = \Delta G^0$, i.e. the free energy difference at one mole is the free energy difference between the two chemical potentials. Thus

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^0 + RT\ln\frac{P_B}{P_A}$$

Thus, at equilibrium we get

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0 \qquad \Rightarrow \qquad \Delta G^0 = -RT \ln \frac{P_B}{P_A}$$

We call the value of $K_P \equiv P_B/P_A$ at equilibrium the **equilibrium constant** of the reaction, ie..

$$\Delta G^0 = -RT \ln K_P$$

or equivalently

$$K_P = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

Finally, for an ideal gas it is easy to rewrite the definition of the equilibrium constant in terms of concentrations $c_i = n_i/V_i$ instead of pressures P_i. Since at constant T we can write $P_i = RT(n_i/V_i) = RTc_i$, we get

$$K_P = \frac{P_B}{P_A} = \frac{c_B RT}{c_A RT} = \frac{c_B}{c_A} = K_C = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

From this we see that the direction of the reaction will depend on the free energy. If $\Delta G < 0$, then more products will be formed and $c_B > c_A$.

Note that in order to derive the result $K_P = \exp(-\Delta G^0/RT)$, we used an ideal gas approximation and then to get $K_P = K_C$, we used the ideal gas approximation again. One should be careful in that in general $K_P = \exp(-\Delta G^0/RT)$ does not hold for non-ideal gases. However, the relationship with K_C *does* hold:

$$K_C = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

holds in general, independent of whether we are talking about ideal gases or not. This result is usually most easily derived from statistical mechanics and I will not derive it here.

6.1.2 Generalization to all reactions

We can generalize these results to more complicated reactions. For the reaction

$$a_1 A_1 + a_2 A_2 + \cdots + a_i A_i \rightleftharpoons b_1 B_1 + b_2 B_2 + \cdots + b_j B_j$$

we would have

$$dG = \sum_i \mu_{A_i} dn_{A_i} + \sum_j \mu_{B_i} dn_{B_i} \equiv \sum_i \mu_i dn_i$$

We can still define ξ, although it is a bit more complicated. It is easier to write its derivative

$$d\xi = -\frac{dn_{A_1}}{a_1} = -\frac{dn_{A_i}}{a_i} = \frac{dn_{B_1}}{b_1} = \frac{dn_{B_j}}{b_j} \equiv \frac{dn_i}{\nu_i}$$

where ν_i represents the stoichiometric coefficients a_i, b_i, etc. The get the signs straight, the ν_i for the products are defined as positive and for the reactants are defined as negative. Thus

$$dG = \sum_i \mu_i dn_i = \sum_i \mu_i \nu_i d\xi \quad \text{and thus} \quad \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \mu_i \nu_i$$

Since $\mu_i = \mu_i^0 + RT\ln(P_i/\text{atm})$, we obtain

$$\begin{aligned}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= \Delta G^0 + RT\ln\left[\frac{\prod_i (P_{A_i}^{a_i}/\text{atm})}{\prod_j (P_{B_j}^{b_j}/\text{atm})}\right] = \Delta G^0 + RT\ln\left[\prod_i (P_i^{\nu_i}/\text{atm})\right] \\ &= \Delta G^0 + \sum_i \nu_i RT\ln(P_i/\text{atm})) = \Delta G^0 + RT\ln K_P\end{aligned}$$

With this, we can write the equilibrium constants

$$K_P = \prod_i (P_i^{\nu_i}/\text{atm})^{\nu_i}$$

and thus at equilibrium

$$\Delta G^0 = -RT\ln K_P$$

Again, we can write K_P in terms of concentrations to calculate K_C: If we define

$$K_c = \prod_i \left(\frac{c_i}{c^0}\right)^{\nu_i}$$

then we can try to express K_c in terms of K_P. To do so, we first write K_P and use the ideal gas equation of state to substitute $P_i = RTn_i/V_i = RTc_i$:

$$K_P = \prod_i \left(\frac{P_i^{\nu_i}}{P^0}\right)^{\nu_i} = \prod_i \left(\frac{RTc_i}{P^0}\right)^{\nu_i} = \left(\frac{c^0RT}{P^0}\right)^{\sum_i \nu_i} K_c$$

6.2 Clapeyron equation

We've talked about phase equilibria now in a couple of different ways (i.e. in terms of free energy and in terms of chemical potentials). The Clapeyron equation connects up P, V, T, and H in a new way, which is often useful for thinking about phase transitions.

Consider two phases, a liquid and its vapor in equilibrium at temperature T and pressure P. If we slightly change T and P, we get the new values $T + dT$ and $P + dP$. Since

$$dG = VdP - SdT$$

we can write the change in free energies for both the liquid and gas phases:

$$\begin{aligned} dG_l &= V_l dP - S_l dT \\ dG_g &= V_g dP - S_g dT \end{aligned}$$

Under the new conditions (i.e. temperature $T+dT$ and pressure $P+dP$), we can calculate equilibrium by $dG_l = dG_g$. Equating these two we get

$$V_l dP - S_l dT = V_g dP - S_g dT$$

and by rearranging, we can put this in the form

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}}$$

Since at $dG_l = dG_g$ the two phases are in equilibrium, we can write

$$\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T_{\text{trans}}\Delta S_{\text{vap}} = 0 \qquad \Rightarrow \qquad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{trans}}}$$

Taking this and putting it into our previous formula, we get

$$\frac{dP}{dT} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} = \frac{\Delta H_{\text{vap}}}{T_{\text{trans}}\Delta V_{\text{vap}}}$$

It is important that T_{trans} is the transition temperature (boiling point in this case). More generally, we can write

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta H}{T_{\text{eq}}\Delta V}$$

We write this equation in this form to stress that this doesn't just have to refer to a liquid boiling and becoming a gas, but rather the equilibrium between two phases in general.

It is important to stress that this equation, called the **Clapeyron equation**, is very general and its derivation has not used any approximations, but simply applied the concepts of equilibrium and the Gibbs free energy.

6.3 The vaporization of liquids

6.3.1 From the point of the Clausius-Clapeyron equation

We can now take the Clapeyron equation and extend it to describe the vapor pressure of gases. To do so, we will make three approximations. We start with the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}}$$

Recall that $\Delta V_{\text{vap}} = V_g - V_l$. The volume of gases are much larger than that of liquids. For example, at 300K and 1 atm pressure, $V_g \approx 24,000\text{cm}^3$ while $V_l \approx 100\text{cm}^3$ for one mole. Thus, since $V_g \gg V_l$, we make our first approximation and say that

$$\Delta V_{\text{vap}} = V_g - V_l \approx V_g$$

Also, if we assume that the gas is ideal, then

$$V_g = \frac{nRT}{P}$$

Thus, putting these together, we get

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}} = \frac{\Delta H_{\text{vap}}}{T(nRT/P)} = \frac{\Delta H_{\text{vap}}}{nRT^2}P$$

we can rearrange this to get

$$\frac{\Delta H_{\rm vap}}{nRT^2} = \frac{dP}{PdT} = \frac{d\ln P}{dT}$$

Finally, if we make the approximation that ΔH is independent of temperature, then we get

$$\ln P = -\frac{\Delta H_{\rm vap}}{nRT} + \text{const}$$

The equation above is called the **Clausius-Clapeyron** equation. As you see, it relates the vapor pressure of a liquid to is enthalpy change per mole on vaporization. It is important to stress that unlike the Clapeyron equation, we did use three approximations here which might limit its applicability.

6.3.2 From the point of view of free energy and vapor pressure

Let's think about vaporization from the point of view of the free energy gain upon vaporization. The free energy of one mole of an ideal gas is given by

$$G_g = G_g^0 + RT\ln(P/\text{atm})$$

where P is the vapor pressure of the liquid. G_g^0 is the free energy of one mole of vapor at 1 atm pressure (i.e. standard conditions). We will assume that the free energy of the liquid G_l is independent of pressure . Thus, the free energy change of vaporization is

$$\Delta G = G_g - G_l = G_g^0 - G_l^0 + RT\ln(P/\text{atm})$$

where we have assumed that $G_l \approx G_l^0$ (which is a good approximation since the liquid free energy is not strongly dependent on temperature). Since the liquid and vapor are in equilibrium, we have $\Delta G = G_g - G_l = 0$, i.e. $G_g = G_l$ and thus

$$\Delta G^0_{\rm vap} = G_g^0 - G_l^0 = -RT\ln(P/\text{atm})$$

This equation tells us that the vapor pressure of a liquid is determined by the free energy change when one mole of liquid is vaporized to produce one mole of vapor **at 1 atm pressure**. At the normal boiling point where the liquid is in equilibrium with its vapor at 1 atm pressure, $P = 1$ and thus in that case $\Delta G^0_{\rm vap} = 0$.

To explore the temperature dependence of the vapor pressure, we first take the derivative of both sides of the above equation with respect to T:

$$\begin{aligned} \ln(P/\text{atm}) &= -\frac{\Delta G^0_{\rm vap}}{RT} \\ \frac{d\ln P}{dT} &= -\frac{1}{R}\frac{\partial(\Delta G^0_{\rm vap}/T)}{\partial T} \end{aligned}$$

where we have used the fact that $d\ln(P/P^0)/dT = d\ln P/dT - d\ln P^0/dT = d\ln P/dT - 0$. Notice the form of the right hand side above. It is very similar to the Gibbs-Helmholtz equations derived earlier:

$$\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

Using this, we get

$$\frac{d\ln P}{dT} = \frac{\Delta H^0_{\rm vap}}{RT^2}$$

which is the Clausius-Clapeyron equation we derived in another way in the previous section.

The usefulness of this relation is the ability to relate quantities such as enthalpy to others which can be easily measured, like P vs T.

6.3.3 Example: Change of vapor pressure with temperature

A liquid boils when its partial pressure equals the atomospheric pressure. One way to think of this is that since $\Delta G = -RT\ln(P/{\rm atm})$, when $P = 1$ atm, then $\Delta G = 0$ and the free energy of liquid and gas are the same, hence the liquid will boil.

Hence, the boiling point is the temperature at which the liquid's vapor pressure equals the applied pressure P on the liquid. We can use the Clausius-Claperon equation to find the pressure at which a liquid will boil at a different pressure.

For example, ethanol boils at 78°Cunder normal atmospheric pressure (1 atm = 760 torr). To what value must P be reduced if we want to boil ethanol at 25°Cin vacuum distillation? To answer this, consider the variation of the vapor pressure given by the Clausius-Claperon equation :

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2}$$

If we assume that the enthalpy of the reaction is not temperature dependent, we can integrate the above to get

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

So, in this example, we'll set state 2 to the normal boiling point (ie., $T_2 = (78+273) = 351$K and $P_2 = 760{\rm torr} = 1{\rm atm}$) and we'll set state 1 to the new temperature ($T_1 = 25+273 = 298$K). Solving for P_1, we find $P_1 = 70$ torr, which is relatively close to the experimental value of 60 torr. Error results from the assumptions of ideal gas and temperature independence of the enthalpy of reaction.

6.4 Le Chatelier's Principle

Le Chatelier's principle is a good mnemonic to remind us how the system will change to restore equilibrium:

> *Perturbations of a system at equilibrium will cause the equilibrium position to change in such a way as to tend to remove the perturbation.*

For example, if heat is released in a reaction $(\Delta H < 0)$, lowering the temperature will lead to more products (and thus more heat). With the results of this section, we can put this statement on a more mathematical foundation. In particular, to derive this result, we want to relate the equilibrium constant K_P (which tells us which direction the reaction will go: $K_P > 1$ means more product, $K_P < 1$ means more reactants) and the temperature. Using the Gibbs-Helmholtz equation

$$\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

and the definition of K_P

$$\ln K_P = -\frac{\Delta G^0}{RT}$$

we get

$$\frac{\partial \ln K_P}{\partial T} \;=\; -\frac{1}{R}\frac{\partial(\Delta G^0/T)}{\partial T} = \frac{\Delta H^0}{RT^2}$$

How should we think about the above equation? If $\Delta H^0 < 0$, then lowering T means increasing K_P, which means that there will be more products.

We can put other forms of Le Chatelier's principle into more quantitative form. However, it is easier to do this on a case by case basis, rather than in some general formulæ. Thus, it is best to use this principle as a check of one's results and as a general guide for physical intuition.

6.5 Basic Results of Thermodynamics

There are a few key relationships which arise from the results of the recent sections. They have the following forms:

1. Relationship between the equilibrium position and the free energy:

   $$\Delta G^{\ominus} = -RT\ln K$$

   Here we write $\Delta G^{\ominus}$ to denote that it is a standard free energy change for one mole of reaction for the equation which describes equilibrium (note that ΔG^0 is more specific – it enforces that $P = 1$ atm, whereas $\Delta G^{\ominus}$ does not).

   K is some quantity which characterizes the equilibrium position in terms of the amounts of materials present. Thus, K could be an equilibrium constant or a vapor pressure, for example.

2. Relationship between the equilibrium position and the enthalpy:

   $$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^{\ominus}}{RT^2}$$

   Again K denotes the position of the reaction and $\Delta H^{\ominus}$ is the standard enthalpy change for one mole (not necessarily at 1 atm).

3. Relationship between the equilibrium position and the volume:

   $$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^{\ominus}}{RT}$$

   $\Delta V^{\ominus}$ is the standard volume change for one mole (not necessarily at 1 atm).

4. Relationship between the concentration and the free energy:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^{\ominus} + RT \ln \prod_i \left(\frac{c_i}{c^{\ominus}}\right)^{\nu_i}$$

Where $c_i/c^{\ominus}$ is the concentration increase over the standard concentration $c^{\ominus}$. These equations depend on the fact that

$$\mu_i = \mu_i^{\ominus} + RT \ln \left(\frac{c_i}{c^{\ominus}}\right)$$

7 Ideal solutions

In this section, we will talk about mixtures of components in terms of solutions. In solutions, we have some solute mixed into the solvent. There is a lot that thermodynamics can say about such systems. Here, we will lay the ground work for thinking about solutions. In the next section on chemical equilibrium, we will start to apply these ideas to interesting chemical (eg electrochemistry) and biochemical (eg ATP hydrolysis) reactions.

For now, let's consider an **ideal solution**. Just as "ideal" gases were a useful concept since the math was simple but yet the results were important (and relevant for many gases), ideal solutions are a starting point for thinking about all solutions, whether they are ideal or not.

What is all of this good for? Common applications are the so-called **colligative properties**. For example, why does adding salt to water lower its freezing point (thus melting ice near 30F) or raise its boiling point? Of course there are more sophisticated applications, but we will not go into them here.

7.1 Ideal and "truly ideal" solutions

7.1.1 Warmup: a mixture of ideal gases

Before talking about ideal solutions, let's first tackle something much easier and more familiar: a mixture of ideal gases. Consider that we have m different types of gases in a box. What's the total pressure on the box? Since the gases are ideal, they do not interact with each other and only induce pressure on the box. Thus, the total pressure will be the sum of the partial pressures P_i of the m gases:

$$P = \sum_{i=1}^{m} P_i$$

Similarly, the change in free energy (at constant pressure and temperature) can be obtained by saying that

$$dG = \sum_{i=1}^{m} \mu_i dn_i$$

We can integrate this to get

$$G = \sum_{i=1}^{m} \mu_i n_i$$

i.e. the total free energy is the sum of the chemical potentials weighted by the respective numbers of moles of each gas n_i. Since each gas is ideal, we can write the pressure dependence of each μ_i as

$$\mu_i = \mu_i^0 + RT\ln(P_i/\mathrm{atm})$$

where μ_i^0 is the standard state (1 atm) chemical potential and P_i is the partial pressure of the gas. So, what we've written is the chemical potential (and therefore the free energy) in terms of a standard state chemical potential and the partial pressure of the gas. In the next section, we will derive something very similar for ideal solutions.

7.1.2 Definition and basic relationships of an ideal solution

To think about ideal solutions, consider a solution with two components: 1 and 2. A typical place to begin is with the simple fact that the total pressure will be the sum of the pressures

$$P = P_1 + P_2$$

We can make this more interesting and useful by making an approximation. In this approximation, we say that the pressures P_i are related to the respective vapor pressures of a mole of the pure substances P_i^* by

$$P_i = x_i P_i^*$$

where x_1 is the mole fraction of component 1 **in solution** ($x_1 \equiv n_1/n$) and P_1^* is the vapor pressure of pure component 1. From the above equations, we get

$$P = x_1 P_1^* + x_2 P_2^*$$

This is **Raoult's Law** and it applies to all ideal solutions.

Why do we call these ideal solutions? Partly because they are simple and we can write the pressure in terms of a simple sum of the pressures of the individual components. This means in a sense that there is no interaction (terms like $P_1 \times P_2$ might signify some sort of interaction). Also, we can make a connection to ideal gases. To do so, we make the following argument. If the vapor follows the ideal gas law, the chemical potential of component i in this phase may be expressed as

$$\mu_i(g) = \mu_i^0(g) + RT \ln(P_i/\mathrm{atm})$$

This is just the pressure dependence of the chemical potential of an ideal gas that we talked about earlier. At equilibrium between the liquid and gas, we must have $\mu_i(g) = \mu_i(\mathrm{soln})$. Thus, we can write the chemical potential of component i in the solution phase

$$\mu_i(\mathrm{soln}) = \mu_i^0(g) + RT \ln(P_i/\mathrm{atm})$$

but since $P_i = x_i P_i^*$, we get

$$\begin{aligned} \mu_i(\mathrm{soln}) &= \mu_i^0(g) + RT \ln[(x_i P_i^*)/\mathrm{atm}] \\ &= [\mu_i^0(g) + RT \ln(P_i^*/\mathrm{atm})] + RT \ln x_i \end{aligned}$$

Since for the pure case, we have $\mu_i^*(l) = \mu_i(g)$ in equilibrium, and that $\mu_i(g) = \mu_i^0(g) + RT \ln(P_i^*/\mathrm{atm})$, we get

$$\mu_i^0(g) + RT \ln(P_i^*/\mathrm{atm}) = \mu_i^*(l)$$

is simply the chemical potential of the pure liquid (at its natural vapor pressure P^*), we give it the designation $\mu_i^*(l)$. This let's us write the chemical potential of component i in the solution phase in a simple manner

$$\mu_i(\mathrm{soln}) = \mu_i^*(l) + RT \ln x_i$$

This equation holds for all components of an ideal solution and provides a more useful definition of ideal behavior than Raoult's Law. We should also compare the equation above to that derived in the previous section for a mixture of ideal gases. The forms are very similar. It is for this reason also that one can consider a solution of this form to be "ideal."

7.1.3 “Truly ideal” solutions

How much more ideal can solutions get? In many cases, it would be much easier to write $\mu_i(\mathrm{soln})$ above (i.e. in terms of $\mu_i^0(g)$) rather than in the ideal solution definition (which uses $\mu_i^*(l)$). Solutions for which the above holds at all pressures are called **truly ideal solutions**. In this case, the equation above simplifies to

$$\mu_i(\mathrm{soln}) = \mu_i^0(l) + RT\ln x_i$$

at 1 atm pressure.

How good is this approximation? Well, the heart of this approximation is the assumption that $\mu_i(l)$ does not strongly depend on pressure. Let's see how true this is. We can include the pressure dependence and write

$$\mu_i(l) = \mu_i^0(l) + \left(\frac{\partial \mu_i}{\partial P}\right)_T \Delta P$$

Since

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)\right]_T = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)\right]_T = \left[\frac{\partial}{\partial n_i} V\right]_T = \frac{V}{n_i} = V_i$$

where V_i is the molar volume of i, we get

$$\mu_i(l) = \mu_i^0(l) + V_i(l)\Delta P$$

and thus

$$\mu_i(\mathrm{soln}) = \mu_i^0(l) + V_i(l)\Delta P + RT\ln x_i$$

Note that ΔP is the *excess* pressure on the system (i.e. the total pressure minus the standard pressure (1 atm)). In many cases (eg when pressure is not that far from 1 atm, say 1-10 atm), $V\Delta P$ is small and this term can be ignored. This leaves

$$\mu_i(\mathrm{soln}) = \mu_i^0(l) + RT\ln x_i$$

which can be considered as the definition of a truly ideal solution.

Finally, how should one think about ideal solutions in terms of some molecular foundation? We said that an ideal gas gas no interactions between particles. An ideal solution requires that all interactions (between like and unlike molecules) should be the same. Both ideal gases and solutions and simple models and idealizations of real systems. However, there are limiting cases of real systems which do obey these relationships. Finally, these equations are a natural starting point to write a theory for non-ideal systems.

7.1.4 Example: ideal solutions of solids in liquids

Consider a solid dissolving in a liquid to form an ideal solution. In the solid state, the solute has lower energy, but in the solution state, the solute has greater entropy (since it can be dispersed over a greater volume). Thus, equilibrium will be a balance between these forces mediated by the temperature. At equilibrium, we must have $\mu_2(s) = \mu_2(\mathrm{soln})$, where the subscript 2 denotes the solute and a subscript of 1 denotes the solvent. For a truly ideal solution, we can write the standard state chemical potential of the solute as

$$\mu_2(s) = \mu_2(\mathrm{soln}) = \mu_2^0(l) + RT\ln x_2$$

Since the pressure dependence of the solid chemical potential is not significant, we can write $\mu_2(s) = \mu_2^0(s)$, and thus we get

$$RT \ln x_2 = \mu_2^0(s) - \mu_2^0(l) = -\Delta G_{2fus}^0$$

where ΔG_{2fus}^0 is the free energy change in melting (fusion). From the Gibbs-Helmholtz equation

$$\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

we get

$$\left(\frac{\partial \ln x_2}{\partial T}\right)_P = \frac{\Delta H_{fus}^0}{RT^2}$$

where ΔH_{fus}^0 is the heat of fusion of the solid (for simplicity, we will drop the 2 subscript). At the melting point of the solid (T_{fus}) the solubility x_2 will be 100% since all of the solid would be a liquid and the two liquids would form an ideal solution. We can integrate the equation above to get

$$\ln x_2 - \ln(1) = \int_{T_{fus}}^{T} \frac{\Delta H_{fus}^0}{RT^2} dT = -\left[\frac{\Delta H_{fus}^0}{RT}\right]_{T_{fus}}^{T} = \frac{\Delta H_{fus}^0}{R}\left(\frac{1}{T_{fus}} - \frac{1}{T}\right)$$

If we look at experimental data (eg see Smith, p. 89), we find excellent (quantitative) agreement between the prediction above and experiment for the solubility of naphthalene in benzene. This means that naphthalene in benzene is an ideal solution. However, there are some solvents (eg cyclohexane) for which this equations does not work. We will explore such non ideal solutions in more detail in the next section.

7.2 Another way to view ideal solutions

In this section, I'll present another way to derive the results we just examined. In a sense, we'll go "backwards," starting from the mixing entropy.

7.2.1 Thermodynamic properties

What is the Gibbs Free Energy, enthalpy, and entropy for an ideal gas? Let's start with the Gibbs free energy, from which we can calculate everything else.

We define $\Delta G = G(\mathrm{soln}) - G^*(\mathrm{l})$. Inserting chemical potentials, we get

$$\Delta G = n \sum_i x_i \mu_i(\mathrm{soln}) - n \sum_i x_i \mu_i^*(\mathrm{l})$$

Using our formulae for ideal solutions, we get

$$\Delta G = n \sum_i x_i \left[\mu_i^*(\mathrm{l}) + RT \ln x_i\right] - n \sum_i x_i \mu_i^*(\mathrm{l})$$

We see that the $\sum_i x_i \mu_i^*(\mathrm{l})$ terms cancel, leaving

$$\Delta G = nRT \sum_i x_i \ln x_i$$

This is a remarkably simple equation. The entropy can be found by

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = -nR\sum_i x_i \ln x_i$$

This should look familiar – it's the mixing entropy.[12] The enthalpy can also be found easily:

$$\Delta H = \left(\frac{\partial \Delta G/T}{\partial T}\right)_P = 0$$

Thus, we see that the only entropy is mixing entropy and the enthaply is zero: there is no enthalpy difference upon mixing ($H_{\text{soln}} = H_{\text{l}}$) and all the free energy difference comes from the mixing entropy. This makes ideal solutions a lot like ideal gases.

7.2.2 Mixing entropy

What is the mixing entropy and where does it come from? Consider a mixture of two components: 1 and 2. We have N_1 and N_2 molecules of 1 and 2 respectively and $N = N_1 + N_2$ total molecules.

How many ways are there of rearranging these molecules? To make this more concrete, consider a lattice where we'll place these molecules (just as we did with the ideal gas entropy derivation). In this case, assume that there are N sites on the lattice, so all sites are occupied. However, how many ways of occupying the sites are there?

One way to think of this is that there are N sites total and we need to choose N_1 sites to place component 1. How many ways are there of choosing N_1 sites out of N total? This is a common combinatorial problem, and the answer is

$$W_{\text{mix}} = \binom{N}{N_1} = \frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1!N_2!}$$

To get the entropy, we take the log: $S = k \ln W$. To simplfy the expression, it's natural to use Stirling's approximation, which says that $\ln N! = N \ln N$. With this approximation (which is remarkably accurate for N¿10 and since we considering quantities on the molar scale), we get

$$S_{\text{mix}}/k = N\ln N - N_1 \ln N_1 - N_2 \ln N_2$$

We can simplify this to get

$$S_{\text{mix}}/k = (N_1+N_2)\ln N - N_1 \ln N_1 - N_2 \ln N_2 = -N_1 \ln\left(\frac{N_1}{N}\right) - N_2 \ln\left(\frac{N_2}{N}\right)$$

Finally, since the molar ratios are the same as the molecular ratios (i.e. $N_1/N = n_1/n$), we get

$$S_{\text{mix}} = -nR\left[\left(\frac{n_1}{n}\right)\ln\left(\frac{n_1}{n}\right) + \left(\frac{n_2}{n}\right)\ln\left(\frac{n_2}{n}\right)\right] = -nR\left[x_1 \ln x_1 + x_2 \ln x_2\right]$$

---

[12] For the derivations of ΔS and ΔH, it is important to consider the possibility that $dx_i/dT \neq 0$. In general, $d(\ln x_i)/dT = \Delta H/RT^2$ and since $d(\ln x_i) = dx_i/x_i$, thus $dx_i/dT = x_i \Delta H/RT^2$. Thus, in the cases where there is not a phase transition (i.e. $\Delta H = 0$), $dx_i/dT = 0$. Cases with a phase transition are like the melting example above. Cases without one would be where we want to examine the entropy difference between solution and liquid phases. In this case, the entropy is just the mixing entropy. This can be seen more directly in the next section.

where x_i are the mole fractions. Finally, this result can be generalized to get the more familiar result

$$S_{\text{mix}} = -nR \sum_i x_i \ln x_i$$

This is a very general result and comes just from the combinatorics of mixing.

7.2.3 From the mixing entropy to Raoult's law

Another way to think about ideal solutions is to build the chemical potentials from a simple model. Here's our model:

1. The entropy of mixing is just $\Delta S_{\text{mix}} = -nR \sum_i x_i \ln x_i$
2. The solution components have no change in enthaply upon mixing: $\Delta H = 0$. This approximation for the enthaply probably the weaker approximation and something we will address with Henry's law.

In general, we have

$$\Delta G_{\text{mix}} = G(\text{soln}) - G^*(l) = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

With the two assumptions above, we get

$$G(\text{soln}) - G^*(l) = nRT \sum_i x_i \ln x_i$$

We can put in the consitutents with

$$G(\text{soln}) - G^*(l) = \sum_i n_i \mu_i(\text{soln}) - \sum_i n_i \mu_i^*(l) = RT \sum_i n_i \ln x_i$$

Taking the derivative with respect to n_i, we get

$$\mu_i(\text{soln}) = \mu_i^*(l) + RT \ln x_i$$

Here, we can use the result from the chemical equilibrium of the pure liquid with the pure gas:

$$\mu_i^*(l) = \mu_i^*(g) = \mu_i^0(g) + RT \ln P_i^*/P^0$$

and solve for solution state chemical potential of i:

$$\mu_i(\text{soln}) = \mu_i^0(g) + RT \ln P_i^*/P^0 + RT \ln x_i$$

Finally, we can combine the log terms to get

$$\mu_i(\text{soln}) = \mu_i^0(g) + RT \ln x_i P_i^*/P^0 = \mu_i^0(g) + RT \ln P_i/P_0$$

if we set $P_i = x_i P_i^*$, which is what Raoult's law says.

7.3 Henry's Law: the simplest form of break down from ideality

Consider a dilute solution, i.e. not much solute in the solvent. In this case, the solvent molecules will be surrounded typically by other solvent molecules and thus the solvent behaves very much like it would in its pure form. This allows us to write the partial pressure

$$P_{\text{solvent}} = x_{\text{solvent}} P^*_{\text{solvent}}$$

This is inline with what would be suggested by Raoult's law for ideal solutions.

However, now consider the solute in this case. Since the solution is dilute, it is not like the solute in its pure form. The solute molecules will be typically surrounded by solvent molecules instead of by other solute molecules as one would have in the pure form. Thus, the relationship we wrote above for the solvent often does not hold for the solute:

$$P_{\text{solute}} \neq x_{\text{solute}} P^*_{\text{solute}}$$

However, often one can write a similar equation to describe the solute:

$$P_{\text{solute}} = x_{\text{solute}} P^{\ominus}_{\text{solute}}$$

The ability to write P_{solute} in this form is called **Henry's law**. It helps to keep life simple (since there still is a simple relationship between P_{solute} and x_{solute}, but this relationship is different from the ideal case since $P^{\ominus}_{\text{solute}} \neq P^*_{\text{solute}}$. What's a good way to think about $P^{\ominus}_{\text{solute}}$? Perhaps the simplest way is to just consider that Henry's law dictates that $P_{\text{solute}}/x_{\text{solute}} = \text{constant}$ and that constant is $P^{\ominus}_{\text{solute}}$. In a sense, Raoult's law can be considered as a special case of Henry's law (i.e. special since Raoult's law says that $P^{\ominus}_{\text{solute}} = P^*_{\text{solute}}$ which is not always true.

From here, we can write, as we did before, the pressure dependence of the chemical potential

$$\mu_i = \mu_i^0 + RT \ln P$$

Inserting Henry's law, we get

$$\mu_i = \mu_i^0 + RT \ln(x_{\text{solute}} P_i^{\ominus}) = [\mu_i^0 + RT \ln P_i^{\ominus}] + RT \ln x_i$$

We can define $\mu_i^{\ominus} \equiv \mu_i^0 + RT \ln P_i^{\ominus}$ to get

$$\mu_i = \mu_i^{\ominus} + RT \ln x_i$$

Which is the same form as we had before, except that the pure state chemical potential μ_i^* is substituted for a new value $\mu_i^{\ominus}$. Physically, $\mu_i^{\ominus}$ is the chemical potential of a hypothetical liquid whose vapor pressure is $P_i^{\ominus}$. However, its sometimes simplest to ignore any physical interpretation for $\mu_i^{\ominus}$ and just consider it to be a constant that is fitted to experimental data.

The relationship above can be used to derive a useful result. Consider a solute distributed between two immiscible (i.e. not capable of being mixed) liquid phases α and β. Following the above, we can write

$$\begin{aligned} \mu(\alpha) &= \mu^{\ominus}(\alpha) + RT \ln x(\alpha) \\ \mu(\beta) &= \mu^{\ominus}(\beta) + RT \ln x(\beta) \end{aligned}$$

At equilibrium between the two phases α and β, we have $\mu(\alpha) = \mu(\beta)$. This yields

$$\mu^{\ominus}(\alpha) + RT\ln x(\alpha) = \mu^{\ominus}(\beta) + RT\ln x(\beta)$$

which can be simplified to

$$\frac{x(\alpha)}{x(\beta)} = \exp\left(-\frac{\mu(\alpha)^{\ominus} - \mu(\beta)^{\ominus}}{RT}\right)$$

Since $\mu(\alpha)^{\ominus}$ and $\mu(\beta)^{\ominus}$ can be considered to be constants (and are constant at any temperature), we get

$$\frac{x(\alpha)}{x(\beta)} = \text{constant}$$

Thus, if the solute follows Henry's law in both phases, the ratio of its concentrations will be constant. This result is often called the **Nernst Distribution Law**.

8 Non-ideal solutions

8.1 The concept of activity

8.1.1 Basic definitions and relations

In the previous section, we showed how in dilute solutions, one can model the solvent using Raoult's law

$$\mu_i = \mu_i^0 + RT\ln x_i$$

but we needed to modify our equation for the solute by using Henry's law

$$\mu_i = \mu_i^{\ominus} + RT\ln x_i$$

However, in many real-life situations (such as in electrochemistry as well will see in the next section), even the Henry's law modifications break down and we need to do something more realistic. This is where the concept of **activity** comes in. In particular, we now write

$$\mu_i = \mu_i^0 + RT\ln a_i$$

where a_i is defined to be the activity of component i. The activity can be thought as the *effective* mole fraction of component i relative to its standard state. This effective mole fraction may differ greatly from the real mole fraction. This is due to the interactions between molecules which ideal solutions ignore. We can define an **activity coefficient** to describe these deviations:

$$\gamma_i = \frac{a_i}{x_i} = \frac{\text{effective mole fraction}}{\text{real mole fraction}}$$

To get a better idea of what a_i is, let's consider a liquid mixture. We will say that in the solution, we can write for component i

$$\mu_i(\text{soln}) = \mu_i^*(l) + RT\ln a_i$$

and in the gas phase we can write

$$\mu_i(g) = \mu_i^0(g) + RT\ln(P_i/\text{atm})$$

We have shown that for the liquid case, we can write

$$\mu_i^*(l) = \mu_i^0(g) + RT\ln(P_i^*/\text{atm})$$

Since the liquid phase is a pure substance. At equilibrium, we have $\mu_i(g) = \mu_i(\text{soln})$. Putting these together, we get

$$\mu_i^0(g) + RT\ln(P_i^*/\text{atm}) + RT\ln a_i = \mu_i^0(g) + RT\ln(P_i/\text{atm})$$

which reduces to

$$a_i = \frac{P_i}{P_i^*}$$

This also makes sense in the light of the interpretation of the activity as an effective mole fraction. We can go one step further and say that if the gas phase behaves like an ideal gas, we can write $P_i = y_i P$, where y_i is the mole fraction of the gas. With this, we find

$$\gamma_i = \frac{a_i}{x_i} = \frac{(P_i/P_i^*)}{x_i} = \frac{y_i P}{x_i P_i^*}$$

8.1.2 Activity of solids in liquids

When we looked at the solubility of naphthalene in various solvents, we found that in benzene, the solution was close to ideal, but was not ideal for a hexane solvent. How do we model these differences? Using the concept of activity. At equilibrium, we have

$$\mu(s) = \mu(\mathrm{soln}) = \mu^0(l) + RT\ln\gamma x$$

We would say that for benzene $\gamma = 1$ and for hexane $\gamma \neq 1$. The precise value of γ would be fit from experimental data.

We could have also thought of this in terms of Henry's law. In this case, we would have defined the acidity of the solute in terms of Henry's law standard state $\mu^\ominus$. This would give us

$$\mu(\mathrm{soln}) = \mu^\ominus + RT\ln\gamma x$$

Here we also have the define γ values for the solvents. However, the γ values used in this prescription (i.e. with Henry's Law standard states $\mu^\ominus$ will not have the same numerical values as when we used regular standard states μ^0). Why bother doing this? Well, it turns out that while naphthalene in hexane is not an ideal solution (and thus does not follow Raoult's law), it does follow Henry's law and thus in this case $\gamma = 1$ (for μ defined in terms of $\mu^\ominus$).

8.1.3 Activity in aqueous solutions

Many chemical experiments are carried out in aqueous solutions and it is important to define activities in these cases, since these solutions are often not ideal.

If the solute follows Henry's Law, then

$$\mu_i = \mu_i^\ominus + RT\ln a_i = \mu_i^\ominus + RT\ln\gamma_i x_i$$

This is often the case when the solution is very dilute.

For an electrolyte solution, we need to make a small modification. We need to write properties in terms of the molality (moles per kg). In this case, we can write for an ideal solution

$$\mu_i = \mu_i^\ominus + RT\ln\left(\frac{m_i}{\mathrm{mol\ kg^{-1}}}\right)$$

and for a non-ideal solution

$$\mu_i = \mu_i^\ominus + RT\ln a_i = \mu_i^\ominus + RT\ln\left(\frac{\gamma_i m_i}{\mathrm{mol\ kg^{-1}}}\right)$$

In this case, $\mu_i^\ominus$ is the chemical potential of an ion in a solution of unit molality. For notational simplicity, we will now drop the units $\mathrm{mol\ kg^{-1}}$ and have m values implicitly include them.

Let's consider a simple electrolyte reaction:

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-}$$

Sodium chloride is essentially fully dissociated $\mathrm{NaCl} \rightarrow \mathrm{Na}^+ + \mathrm{Cl}^-$ in aqueous solution. We can only deal with the overall activity a_{NaCl} as we have no way of determining a_{Na^+} and a_{Cl^-} independently. We can calculate a_{NaCl} as follows. As each of the ions would be expected to follow Henry's Law independently, the total chemical potential can be written

$$\begin{aligned}\mu_{\mathrm{tot}} &= \mu_{\mathrm{Na}^+} + \mu_{\mathrm{Cl}^-} = \left(\mu^{\ominus}_{\mathrm{Na}^+} + RT\ln a_{\mathrm{Na}^+}\right) + \left(\mu^{\ominus}_{\mathrm{Cl}^-} + RT\ln a_{\mathrm{Cl}^-}\right)\\ &= \left(\mu^{\ominus}_{\mathrm{Na}^+} + \mu^{\ominus}_{\mathrm{Cl}^-}\right) + \left(RT\ln a_{\mathrm{Na}^+} + RT\ln a_{\mathrm{Cl}^-}\right)\\ &= \mu^{\ominus}_{\mathrm{tot}} + RT\ln a_{\mathrm{NaCl}}\end{aligned}$$

Thus, we see that

$$a_{\mathrm{NaCl}} = a_{\mathrm{Na}^+} \times a_{\mathrm{Cl}^-}$$

and since $a_i = \gamma_i m_i$, we get

$$a_{\mathrm{NaCl}} = \gamma_{\mathrm{Na}^+} m_{\mathrm{Na}^+} \times \gamma_{\mathrm{Cl}^-} m_{\mathrm{Cl}^-}$$

Since we have equal mole components of both ions, we get $m_{\mathrm{Na}^+} = m_{\mathrm{Cl}^-} \equiv m$ is the molality of the solution. We can define a new activity coefficient $\gamma_\pm$ by the geometrical mean of the γ values of the ions

$$\gamma_\pm = \left(\gamma_{\mathrm{Na}^+}\gamma_{\mathrm{Cl}^-}\right)^{1/2}$$

This is natural as we are taking the means of logs:

$$\ln\gamma_\pm = \frac{1}{2}\left(\ln\gamma_{\mathrm{Na}^+} + \ln\gamma_{\mathrm{Cl}^-}\right)$$

so we are in the end taking the mean of the contributions to the free energy. With $\gamma_\pm$, we can write

$$a_{\mathrm{NaCl}} = \left(\gamma_\pm m\right)^2$$

When the electrolyte solution is more complex, i.e.

$$\mathrm{M}_p\mathrm{A}_q \rightleftharpoons p\mathrm{M}^+ + q\mathrm{A}^-$$

we get

$$a_{\mathrm{M}_p\mathrm{A}_q} = (a_{\mathrm{M}^+})^p (a_{\mathrm{A}^-})^q$$

and

$$\gamma_\pm^{p+q} = (\gamma_{\mathrm{M}^+})^p (\gamma_{\mathrm{A}^-})^q$$

8.2 Chemical equilibria in solution

In the previous sections, we have mostly talked about the equilibria of gas phases. Indeed, when we derived the equation

$$\mu_i(g) = \mu_i(g)^0 + RT\ln(P_i/\mathrm{atm})$$

we explicitly used the ideal gas equation. In solution, life is a bit different. It is for this reason that we introduced the activity and wrote instead

$$\mu_i = \mu_i^{\ominus} + RT\ln(a_i)$$

Now we will consider the simplified equilibrium

$$A \rightleftharpoons B$$

We can write the following equations to describe this system:

$$\begin{aligned}\mu_A &= \mu_A^\ominus + RT\ln a_A = \mu_A^\ominus + RT\ln \gamma_A m_A\\ \mu_B &= \mu_B^\ominus + RT\ln a_B = \mu_B^\ominus + RT\ln \gamma_B m_B\end{aligned}$$

At equilibrium, $\mu_A = \mu_B$ and

$$\Delta G^\ominus = \mu_B^\ominus - \mu_A^\ominus = -RT\ln a_B/a_A = -RT\ln K_a$$

where $\Delta G^\ominus$ is the change in free energy when a mole of A at unit molality is transformed into a mole of B at the same concentration (with both solutions behaving as if they are extremely dilute).

8.3 Electrochemistry

8.3.1 Equilibrium and free energy I: Legendre transforms

There is another way to introduce new state functions such as H and G which is more mathematical and perhaps a little less intuitive than the methods we used earlier. However, it can help clear up some aspects of how we defined F, G, etc and is in general useful – especially when we want to include new effects, such as electrostatic potentials in electrochemistry into our thermodynamic potentials.

Here's a mathematical run down of a Legendre transform. Consider a function $f(x)$. Now suppose that we want to write $f(x)$ in terms of its slope p, instead of x. To make this concrete, consider the Helmholtz free energy $f(V, T)$. Imagine that we want to write $F(V, T)$ in terms of its slope $dF/dV = -P$, i.e. we want to write F in terms of pressure and thus get the Gibbs free energy.

How do we do this? At each value of x, we can write $f(x)$ in terms of its slope p by the definition of the slope (slope equals the rise over the run, so):

$$p = \frac{y - g(p)}{x - 0}$$

where $g(p)$ is the intercept of the tangent line. We can rearrange the above to get

$$g(p) = f(x) - px$$

We call $g(p)$ the Legendre transform of $f(x)$. In the case of transforming the Helmholtz free energy into Gibbs, we have the simple connection that $x = V$, $f(x) = F(V, T)$, $p = dF/dV = -P$, and $g(p) = G(P, T)$ and thus we get

$$G(P, T) = F(V, T) + PV$$

Note that the sign is flipped since $p = -P$.

We could do the same for all the other thermodynamic potentials. Starting from the entropy (which we have a microscopic understanding of), we can Legendre transform to create the other thermodynamic potentials.

As another example, we can use Legendre transformations to write the Gibbs free energy for fixed chemical potential μ_i instead of fixed number of particles n_i. In this case, we make the connection that $x = n_i$ (since the original Gibbs free energy is for fixed n_i) and $p = \partial G/\partial n_i$. Then we get

$$G(\mu_i, T, P) = G(n_i, T, P) - \left(\frac{\partial G}{\partial n_i}\right) n_i$$

In principle, there are still many things which are typically held constant for which we can perform further transformations to create new free energies. We will create another one in the following sections.

8.3.2 Equilibrium and free energy II: Electrochemical work

What is electrochemical work? We can start with Coulomb's law, which dictates the strength of interactions between charges:

$$\vec{f} = \frac{1}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r^2}\vec{r}$$

We can calculate the work as we did before

$$w_{\text{elec}} = \int \vec{f} \cdot d\vec{r} = -\frac{1}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r} = -\phi Q$$

where

$$\phi = \frac{1}{4\pi\epsilon_0}\frac{Q_1}{r}$$

is the electrostatic potential and $Q = Q_2$ is our test charge. In chemistry, we often assume that the potential ϕ is defined by the surroundings and what we are changing is the amount of charge (eg by the flow of ions). In this case, we can take the derivative of w_{elec} to get

$$dw_{\text{elec}} = -\phi dQ$$

(Note that the above is sometimes, eg. in Smith, written in terms of the electromotive force E as $w_{\text{elec}} = -EQ$).

8.3.3 Equilibrium and free energy III: A new free energy (sort of)

Now, we will use a Legendre transform to introduce a modified G (called the **transformed Gibbs energy** G') to include electrochemical work. With this new work, we can define the Legendre transform

$$G' = G - \sum_i \phi_i Q_i$$

often we write the charge in terms of the charge on the ion z_i times the number of ions n_i: $Q_i = z_i f n_i$, where $f = N_A e = (6.02 \times 10^{23}) \times (1.6 \times 10^{-19}\text{C}) = 96 \times 10^3 \text{Cmol}^{-1}$ is Faraday's constant:

$$G' = G - \sum_i \phi_i z_i f n_i$$

We can similarly do this with a new (transformed) chemical potential

$$\mu_i' = \mu_i - \phi_i Q_i = \mu_i - \phi_i z_i f$$

These new transformed quantities now act just like the old ones. In a sense, they are new potentials in the the way that F is different from G, except they now include ionic degrees of freedom.

For a multiphase system involving electric potential differences between the phase, neither the potentials of the phases ϕ_i nor the amounts of each component n_i are necessarily fixed. Thus, we must allow each to possible vary and write

$$\begin{aligned} dG' &= dG - \sum_i \phi_i dQ_i - \sum_i d\phi_i Q_i \\ &= dG - \sum_i \phi_i z_i f dn_i - \sum_i d\phi_i z_i f n_i \end{aligned}$$

Finally, it is interesting to compare the form of dG and dG' when written in their respective natural variables. We can write dG' in its natural variables by noting that

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

and substituting this into our expression for dG':

$$dG' = -SdT + VdP + \sum_i \mu_i dn_i - \sum_i \phi_i z_i f dn_i - \sum_i d\phi_i z_i f n_i$$

Noting that $\mu_i = \mu_i' + \sum_i \phi_i Q_i$, we get

$$dG' = -SdT + VdP + \sum_i \mu_i' dn_i - \sum_i d\phi_i z_i f n_i$$

From the above, we see that the transformed chemical potential is defined as

$$\left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,\phi_i} = \mu_i'$$

where n_j denotes all species with $j \neq i$. Note that the transformed chemical will depend on the electric potential ϕ_i of the component phase.

When do we use μ vs μ'? When we are talking about the equilibrium between two phases α and β (even if these two phases have different potentials) we still write

$$\mu_i(\alpha) = \mu_i(\beta)$$

8.3.4 Equilibrium and free energy IV: Physical reasoning

Recall that when we originally defined the Gibbs free energy, we said that $dG = dw_{\text{additional}}$. Thus, at constant T and P, we normally defined equilibrium by

$$dG = 0 \quad (T \text{ and } P \text{ constant})$$

In electrochemistry, we finally get to a case where we have additional work, since $dw_{\text{additional}} = dw_{\text{elec}}$.

However, if we don't define a transformed chemical potential, then we must modify our concept of equilibrium. We defined a transformed chemical potential since in the electrochemical case, either $d\phi_i$ or dn_i may be non-zero. Equilibrium in this case is given by $dG' = 0$ not $dG = 0$. If we say that $dG' = 0$, what does that tell us about dG? We have

$$dG' = dG - dw_{\text{elec}}$$

So the condition of $dG' = 0$ at electrochemical equilibrium means that equilibrium in this case written in terms of dG is

$$dG = dw_{\text{elec}}$$

This result is stated in Smith without much reason why. I introduced the idea of Legendre transforms to help clear this up and explain it (in at least a mathematical form). Physically, $dG = 0$ is *not* the equilibrium criteria since the $dG = 0$ condition for equilibrium requires that Q is constant.

The relationship between the regular and transformed Gibbs free energies parallels that of the Helmholtz and Gibbs free energies. Similarly, we could have chosen not to introduce the Gibbs free energy to describe constant P equilibrium. Using an argument similar to that above, we can write

$$dG = dF - dw_{\text{PV}}$$

and thus constant P equilibrium means that $dG = 0$ or that $dF = dw_{\text{PV}}$. We could us this equilibrium condition to study all constant pressure transformations, but it is cumbersome and not as elegant — it's certainly simpler to say that equilibrium is defined as $dX = 0$, where X is the appropriate state function. Of course, this means that we have to get the correct state function for the job!

8.4 Electrochemical cells (aka batteries)

8.4.1 Fundamental equation for an electrochemical cell

Consider a simple chemical cell, illustrated in Fig. 8.1. In such a cell, when the external circuit is open, the electrodes will have different electric potentials (which arise from the tendency of the electrode material to give up electrons and pass them into solution). When the circuit is closed, chemical reactions will take place which lead to electrons being removed from one electrode and transferred to the other. This reduces the free energy and this available free energy can be harnessed to do work. This is how batteries power devices: when they are new, they have a lot of potential chemical free energy stored. As they are used, this free energy is decreased, until they reach the equilibrium conditions of no current passing (a dead battery). Batteries spontaneously drain but never spontaneously charge!

Let's think about the specifics of how this happens. In the cell in Fig. 8.1, one electrode is made of zinc surrounded by a zinc salt solution while the other is made of copper in a copper salt solution. These two solutions are linked (by the "inert electrolyte" in the diagram) in such a way that ions can flow from one compartment to the other, but this "salt bridge" is set up such that this mixing happens slowly (i.e. nearly reversibly).

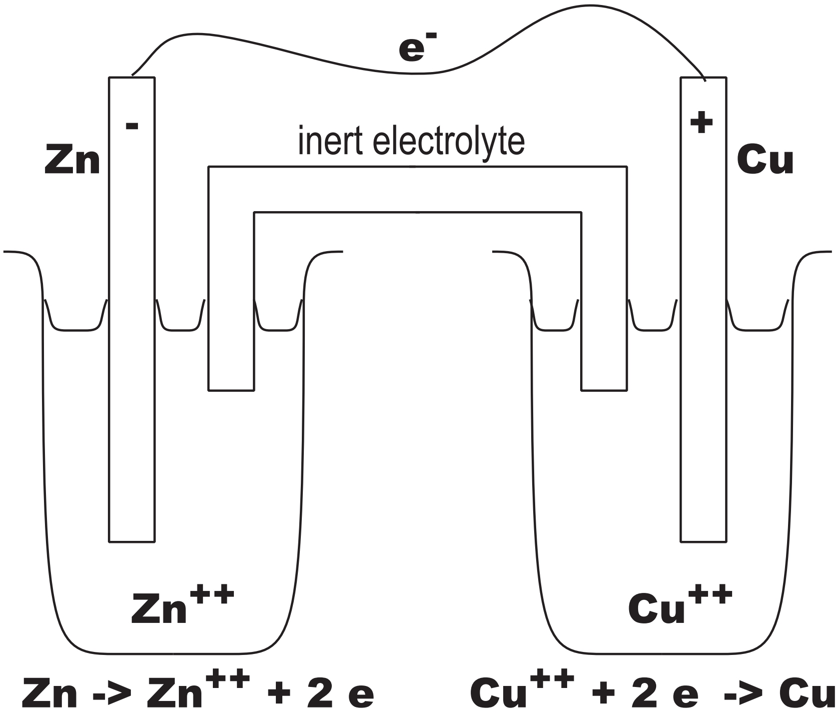

Figure 8.1: A simple electrochemical cell.

There are two different tendencies for these two electrodes. The zinc wants to form ions and give up electrons

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{++} + 2e$$

and the copper wants to pick up electrons and have copper salt deposited on the electrode as metallic copper

$$\mathrm{Cu}^{++} + 2e \rightarrow \mathrm{Cu}$$

The overall reaction is thus

$$\mathrm{Zn} + \mathrm{Cu}^{++} \rightarrow \mathrm{Zn}^{++} + \mathrm{Cu}$$

In the external circuit, electrons flow from the zinc electrode to the copper.

Let's now write the change in the transformed Gibbs free energy for this reaction. Although several phases are involved, the equilibrium condition is given by $\sum_i \nu_i \mu_i$ where ν_i are the stoichiometric coefficients as before. Thus, we get

$$\mu(\mathrm{Zn}, s) + \mu(\mathrm{Cu}^{++}, aq) = \mu(\mathrm{Zn}^{++}, aq) + \mu(\mathrm{Cu}, s)$$

If we write the μ in terms of transformed chemical potentials, we get $\mu_i = \mu_i' + z_i n_i f \phi_i$. However, for the neutral species $z_i = 0$ and thus in those cases $\mu_i = \mu_i'$. With this, we get

$$\mu'(\mathrm{Zn}, s) + \mu'(\mathrm{Cu}^{++}, aq) + 2nf\phi_R = \mu'(\mathrm{Zn}^{++}, aq) + 2nf\phi_L + \mu'(\mathrm{Cu}, s)$$

where ϕ_R and ϕ_L are the potentials of the right and left electrode respectively. Since the change in free energy can be written in terms of the difference in chemical potentials

$$\Delta_r G = \Big[\mu'(\mathrm{Zn}, s) + \mu'(\mathrm{Cu}^{++}, aq)\Big] - \Big[\mu'(\mathrm{Zn}^{++}, aq) + \mu'(\mathrm{Cu}, s)\Big]$$

we find that the reaction free energy[13] is given by

$$\Delta_r G = -2nf(\phi_R - \phi_L) = -2nfE$$

where $E \equiv \phi_R - \phi_L = \Delta\phi$ is the electromotive force (i.e. the voltage difference between the electrodes). In general, one finds that

$$\Delta_r G = -|\nu_e| nfE$$

where ν_e is the stoichiometric number of the electrons in the electrochemical reaction (in the case above $\nu_e = 2$).

To get a better sense of how these reactions work in general, consider the equation

$$A \rightleftharpoons B$$

We can write the reaction free energy as

$$\Delta_r G = \Delta G^{\ominus} + RT \ln\left(\frac{a_B}{a_A}\right)$$

Since $\Delta_r G = -nfE$, we get

$$-nfE = -nfE^{\ominus} + RT \ln\left(\frac{a_B}{a_A}\right)$$

and thus

$$E = E^{\ominus} - \left(\frac{RT}{nF}\right) \ln\left(\frac{a_B}{a_A}\right) = E^{\ominus} - \left(\frac{RT}{nF}\right) \ln K_a$$

where K_a is the equilibrium constant of the cell reaction. For a more general reaction, eg.

$$aA + bB \rightleftharpoons lL + mM$$

we would get

$$E = E^{\ominus} - \left(\frac{RT}{nF}\right) \ln\left(\frac{a_L^l a_M^m}{a_A^a a_B^b}\right) = E^{\ominus} - \left(\frac{RT}{nF}\right) \ln K_a$$

This equation (called the **Nernst equation**) relates the emf E of a cell to $E^{\ominus}$ (which is the emf of the cell when all reactants and products are in their standard states). $E^{\ominus}$ is thus called the **standard emf** of the cell.

What happens at equilibrium? In that case $\Delta_r G = 0$ and we get

$$E = -\frac{\Delta_r G}{nf} = 0 \quad \text{and} \quad E^{\ominus} = \frac{RT}{nF} \ln K_a$$

This is the mathematical description of what happens when batteries are drained dead: they reach equilibrium and then voltage (emf) no longer flows.

---

[13] By reaction free energy, we mean the free energy we have written before as

$$\Delta_r G = \frac{\partial G}{\partial \xi} = \sum_i \nu_i \mu_i$$

We can use the relationship $\Delta_r G = -nfE$ to calculate the other thermodynamic quantities. For example

$$\Delta_r S = -\left[\frac{\partial \Delta_r G}{T}\right]_P = \left(\frac{\partial E}{\partial T}\right)_P nf$$

and

$$\Delta_r H = \Delta_r G + T\Delta_r S = -nfE + \left(\frac{\partial E}{\partial T}\right)_P nfT$$

8.4.2 Standard potentials and battery emfs

Know that we have derived the basic equations for electrochemical cells, let's now apply them. Experimentalists have measured the standard emfs $E^{\ominus}$ for several different metals and ions (cf Smith p. 118). Different choices of metals lead to different properties. For example, in the cell in our previous case, we had zinc and copper. The standard emfs are

$$E^{\ominus}(\mathrm{Zn}^{++}, \mathrm{Zn}) = -0.76 \text{ volts} \quad \text{and} \quad E^{\ominus}(\mathrm{Cu}^{++}, \mathrm{Cu}) = +0.34 \text{ volts}$$

Since the total emf is given by the difference of emfs, we get for the cell in Fig. 8.1:

$$E^{\ominus} = E^{\ominus}_R - E^{\ominus}_L = 0.34 - (-0.76) = +1.10 \text{ volts}$$

The standard electrode potential is a measure of its tendency to gain electrons. If $E^{\ominus}$ is positive, then the electrode will gain electrons (as copper did in our example). The alkali metals have the most negative $E^{\ominus}$ while the halogen electrodes are very positive. These standard potentials could be called standard reduction potentials since they measure the tendency of the electrode to be reduced by the gain of electrons (high positive most likely to be reduced, most negative most likely to be oxidized).

Finally, we can use our formulæhere to describe the thermodynamics of oxidation/reduction. For example, consider the reaction

$$\mathrm{Fe}^{3+} + e^- \rightleftharpoons \mathrm{Fe}^{2+}$$

The Nernst equation may be applied to this electrode alone (relative to a standard hydrogen electrode). Thus, we get

$$E = E^{\ominus} - \left(\frac{RT}{nf}\right) \ln\left(\frac{a_{\mathrm{Fe}^{2+}}}{a_{\mathrm{Fe}^{3+}}}\right)$$

At equilibrium, there will be no emf ($E = 0$) and one finds that

$$E^{\ominus} = \left(\frac{RT}{nf}\right) \ln\left(\frac{a_{\mathrm{Fe}^{2+}}}{a_{\mathrm{Fe}^{3+}}}\right)$$

8.5 Coupled biochemical reactions

I've mentioned that biology tries hard to fight against equilibrium, since the equilibrium state for these systems is death (and we don't like death). One way in which biology keeps itself from reaching equilibrium is to have a continuous series of spontaneous reactions. But how do you make reactions which are typically not spontaneous (since they either increase enthalpy or reduce entropy or both) proceed spontaneously? By coupling of reactions: If the desired reaction increases the free energy (and thus would not be spontaneous), one can couple that with a reaction which lowers the free energy a huge amount and thus the total reaction will lower the free energy and thus will be spontaneous.

For example, cells use ATP as an energy form. ATP is created by adding a phosphate to ADP

$$\mathrm{ADP} + \mathrm{P}_i \rightarrow \mathrm{ATP} + \mathrm{H_2O}$$

This reaction requires $\Delta_r G' = 39.7$ kJ/mol of free energy. While this is a lot of free energy, keep in mind that ATP is biology's way of storing energy and this energy will be able to be used elsewhere.

The reaction would like to go in the reverse direction. However, one can create ATP from ADP by using another coupled reaction

$$\mathrm{creatine\ phosphate} + \mathrm{H_2O} \rightarrow \mathrm{creatine} + \mathrm{P}_i$$

which has a $\Delta_r G' = -43.5$ kJ/mol free energy difference.

Coupling the equations gives us the overall reaction

$$\mathrm{creatine\ phosphate} + \mathrm{ADP} \rightarrow \mathrm{creatine} + \mathrm{ATP}$$

We can calculate the reaction free energy simply as the sum of the reaction free energies of the two constituent equations: $\Delta_r G' = 39.7 + -43.5 = -3.8$ kJ/mol. Thus, since the overall reaction free energy is negative, the system will "spontaneously" create ATP.

9 Modern applications of thermodynamics

9.1 Introduction

In this chapter, we will apply the formalism and methodology developed in previous chapters on modern applications on Thermodynamics.

At its heart, these applications follow three themes for building models:

1. First start with an "ideal" model, where entropy dictates all.
2. Then add interaction in a methodical way for more complex models.
3. These models are useful in situations where the smallest details do not play a significant role – in cases where the models are "universal"

9.2 Real gases

We have talked about ideal gases and a simple extension to a van der Waals gas. Even a van der Waals gas is an approximation, which we seemed to have made somewhat arbitrarily. Is there some way to systematically make our approximations in order to handle more sophisticated models?

9.2.1 Taylor expansions

Before getting into a virial expansion and the virial equation, let's make a brief mathematical detour and talk about Taylor expansions. Consider a function $f(x)$ which might be fairly complicated. Let's say that we only need to approximate it in some region around the point x_0. A Taylor expansion tells us that we can write

$$f(x) = f(x_0) + \left.\frac{df}{dx}\right|_{x\to x_0}(x - x_0) + \ \cdots$$

and in general to all orders

$$f(x) = \sum_{i=0}^{\infty} \left.\frac{d^i f}{dx^i}\right|_{x\to x_0} \frac{(x - x_0)^i}{i!}$$

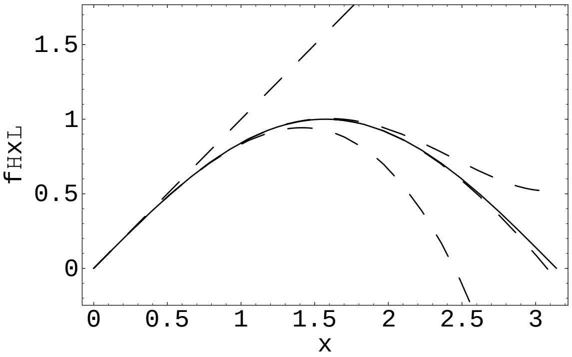

Figure: Plot of $\sin(x)$ vs x abd the first 4 non-zero terms in the Taylor expansion. We see that as we add more terms to the Taylor series, the approximation gets better and better. This is an example of a "controlled" approximation, in which there is some mathematical means to decide how we add terms.

Let's take a familiar example, the function $\sin(x)$. We can approximate this function around the point $x = 0$ to be

$$\begin{aligned} \sin(x) &= \sin(0) + \cos(0)x - \sin(0)\frac{x^2}{2} - \cos(0)\frac{x^3}{6} + \sin(0)\frac{x^4}{24} + \cos(0)\frac{x^5}{120} + \cdots \\ &= x - \frac{x^3}{6} + \frac{x^5}{120} + \cdots \end{aligned}$$

since $d\sin(x)/dx = \cos(x)$, $d\cos(x)/dx = -\sin(x)$, $\sin(0) = 0$ and $\cos(0) = 1$. The main idea here is that as we add terms to this series, the resulting approximation gets closer to the correct result.

The relevance of Taylor expansions to problems in physical chemistry in general is the concept that often we are interested in perturbations around some particular physical region of interest. We can then use Taylor expansions to test how things change as we go a little away from the original value.

9.2.2 Virial equation

We are now in a good position to understand how to systematically improve the "ideal" laws we studied. In particular, these laws were ideal in the sense that they neglected (or radically simplified) the interactions between molecules. When we introduced interactions into the ideal gas equation of state, for example, we found qualitatively different behavior. In fact, what we found was a phase transition from the gas to the liquid phase. This transition was driven by molecular interactions.

Typically, more sophisticated treatments will not have any further grand qualitative changes to the theory, but will typically make the theory more quantitative. Nevertheless, it is important to understand how this occurs and we are now in a good position to study this, considering what we have learned so far.

A natural approach would be to write the free energy for an ideal gas using a Taylor expansion as we talked about in the previous section. One way to think about this is that ideal gases are exact in the very dilute regime, where the density is essentially zero ($\rho = 0$). If we increase the density, then there is a greater chance of interaction and the gas will deviate from ideal gas properties. Typically in thermodynamics texts, one writes additional terms to correct from ideal gas behavior. At its heart, there are similarities in this approach. Here, we will take the thermodynamicist approach.

For an ideal gas, we know that

$$PV = nRT \quad \text{and thus} \quad \frac{PV}{nRT} = 1$$

In 1901, Kamerlingh-Onnes proposed an equation to describe deviations from this ideal nature. In particular, he wrote (where the density is $\rho = n/V$)

$$\frac{PV}{nRT} = 1 + B\rho + C\rho^2 + \cdots$$

As we make the gas less dilute (more dense), we start to see deviations from Ideal behavior. The character of these deviations have to do with the nature of the coefficients in our expansion. In this case, this expansion is given another name, a **virial expansion**, but the idea is the same: the first term $B\rho$ describes two body interactions, the next describes three body, etc.

Note that we can rearrange this equation into two interesting forms. First, we can solve for the pressure to get

$$P = RT\frac{n}{V}\left[1 + B\rho + C\rho^2 + \cdots\right] = RT\left[\rho + B\rho^2 + C\rho^3 + \cdots\right]$$

Thus, we are performing a Taylor expansion of the function $P(\rho)$ in small density $\rho = n/V$. We do this since we know that all gases are Ideal in the case of very low density (ideal gases assume no interactions and there are essentially no interactions if the gas is so dilute such that particles never bump into each other).

Another way to think about this is to relate the pressure P to a free energy. We can relate the pressure to the Helmholz free energy F by $P = -\partial F/\partial V$. This allows us to write

$$-\frac{\partial F}{\partial V} = RT\left[\rho + B\rho^2 + C\rho^3 + \cdots\right]$$

If we integrate both sides with respect to the volume, we get

$$\begin{aligned} F &= nRT\left[B\rho + \frac{1}{2}C\rho^2 + \cdots\right] - nRT\ln V \\ &= F_{\text{interaction}} - TS_{\text{translation}} \end{aligned}$$

where $F_{\text{interaction}} = nRT[B\rho + \frac{1}{2}C\rho^2 + \cdots]$ and $S_{\text{translation}} = nR\ln V$. We can identify the terms on the left above as the interaction free energy terms ($F_{\text{interaction}}$), since for $B = 0$, $C = 0$, etc we have a non interacting system. I say interaction free energy since in principle the coefficients B and C, etc could be temperature dependent. In that case, we could calculate an interaction entropy by

$$S_{\text{interaction}} = -\frac{\partial F_{\text{interaction}}}{\partial T} = \frac{\partial}{\partial T}nRT[B\rho + \frac{1}{2}C\rho^2 + \cdots]$$

and $S_{\text{interaction}}$ is not necessarily zero.

The second term in the free energy above $S_{\text{translation}} = nR\ln V$ is exactly the translational entropy (i.e. the entropy of choosing the positions of the molecules in the box) that we found for the ideal gas. This term does not go to zero when we turn off the interactions of course.

What do the coefficients typically look like for real gases? In most gases, the two body term becomes attractive at low enough temperatures, although the three body term is typically considered to be repulsive (liquid molecules attract each other, but only to a point – they never occupy the same space!). For example, the B coefficient is typically temperature dependent:

$$B = b_0\frac{T - T_B}{T}$$

Here, I write the characteristic temperature as T_B since this temperature has a special name – it is called the **Boyle temperature**. At this temperature T_B, the B coefficient (called the **second virial coefficient** [C is the third, and so on]) equals zero. This means that the deviation from Ideality is small and thus near its Boyle temperature, a gas behaves much like an ideal gas (although when T is far from T_B, it does not look ideal).

9.2.3 vdW fluids revisited

Finally, let's revisit our arguments for improving ideal gases. We can use the density ρ as our order parameter (gas has low density, liquid has relatively high). First, we said that we needed to improve the energy term by including interaction and wrote

$$\frac{U}{V} = -\frac{na\rho}{V} = -a\rho^2$$

Here a is the strength of the attraction between two particles. Thus, when a is positive, this energy decreases as the density increases (since the particles attract each other).

Next, we improved the entropy term by saying that particles cannot be at the same place and wrote

$$S = nR\ln(V - nb)$$

We can rewrite the entropy in terms of density $\rho = n/V$ and n and then Taylor expand for small density

$$\frac{S}{nR} = \ln(n/\rho - nb) = \ln(n/\rho) + \ln(1 - b\rho) \approx \ln(n/\rho) + b\rho - \frac{b^2\rho^2}{2} + \cdots$$

where we used the Taylor expansion $\ln(1-x) = x - x^2/2$ for small x. Thus, we get a free energy of the form

$$\frac{F(\rho)}{V} = RT\left[(b - a/RT)\rho^2 + \frac{1}{2}b^2\rho^3 + \rho\ln\rho\right] + \text{const}$$

where we have ignored terms of $\ln n$ as they are unimportant in the thermodynamic limit. There are three important terms here. We could rewrite the above as

$$\frac{F(\rho)}{VRT} = B\rho^2 + C\rho^3 - S_{\text{mix}}/RV + \text{const}$$

where

$$B = (b - a/RT) \quad \text{and} \quad C = \frac{1}{2}b^2 \quad \text{and} \quad S_{\text{mix}}/RV = -\rho\ln\rho$$

Note that there will be constants of order n that have been dropped. They are constant in the sense that they do not depend on V or ρ, just n. When we take derivatives with respect to V or ρ in order to find equilibrium behavior, these constants will disappear.

1. We interpret the first term as the second virial coefficient. We have been seeing the same behavior in many of the system we have looked at. The transition temperature is again the case where $B = 0$, i.e.

   $$B = 0 = b - a/RT_B \quad \Rightarrow \quad T_B = \frac{a}{Rb}$$

   Indeed, we could write

   $$B = b\frac{T - T_B}{T}$$

   where $T_B = a/Rb$. We write this transition temperature as T_B since this point is often called the Boyle point.

   We see that $B < 0$ for $T < T_B$ since this is where the attraction is strong enough to beat out the free energy contribution from the entropy. This competition between energy and entropy is fairly common. This is also at the heart of equations like

   $$T_B = \frac{\Delta H}{\Delta S}$$

   which we derived in previous sections for phase equilibria.

2. We interpret the second term C as the third virial coefficient. Notice that it doesn't qualitatively change with temperature: it is always repulsive. Many forces between molecules (eg Coulomb charge-charge interaction or van der Waals interactions) are **pairwise**, i.e. they involve only the interaction between two particles. Thus, often we only include two body attractive terms into the energy. There are some forces which involve many body effects (eg hydrophobicity) and thus to model these, one must typically include many body attraction as well.

   The bottom line is that this term typically balances out the attraction of the lower order term and keeps the system from collapsing to a point (infinite density).

3. Finally, the $S_{\text{mix}}/V = -R\rho \ln \rho$ is a "mixing" entropy (per unit volume). Here what we are mixing is particles with empty space (and thus there are no other terms). These terms are fairly common as well and often play an important role in the thermodynamics.

   However, don't let this formulation confuse you – this is really just something familiar. Taking

   $$S_{\text{mix}} = -RV\rho \ln \rho = -RV\frac{N}{V} \ln \frac{N}{V}$$

   we can simplify this to be

   $$S_{\text{mix}} = -RN \ln \frac{N}{V} = NR \ln V - NR \ln N$$

   We have been ignoring terms which just depend on N and $N \ln N$ was one of them. The other term is familiar to us: it's the translational entropy.

9.2.4 Understanding isotherms

Consider the Gibbs free energy $G = F + PV$ of a vdw fluid:

$$G = F + PV = -a\frac{N^2}{V} - NkT \ln(V - Nb) + PV$$

At equilibrium, the system will want to go to the absolute free energy minimum. To calculate this, we consider $\partial G/\partial V = 0$ and thus we find

$$\frac{\partial G}{\partial V} = a\frac{N^2}{V^2} - \frac{NkT}{V - Nb} + P = 0$$

solving for P, we get

$$P = -a\frac{N^2}{V^2} + \frac{NkT}{V - Nb}$$

which we can rearrange to the more familiar equation of state

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

Let's expand this to see all the terms. We get

$$PV - PNb + \frac{aN^2}{V} - \frac{abN^3}{V^2} = NkT$$

If we multiply by V^2 and arrange the terms, we get a cubic equation

$$PV^3 - (PNb + NkT)V^2 + aN^2V - abN^3 = 0$$

which has three solutions. What could these solutions be?

Recall that $\partial G/\partial V = 0$ will hold for the absolute minimum, but also metastable minima as well as maxima – anywhere that the slope is zero. Thus, we have to be careful in how we intepret this equation. It will yield solutions which are not the true free energy minima, but the maxima and meta stable minima as well.

For example, for a system with two phases, we expect that $\partial G/\partial V = 0$ will hold for three points: two free energy minima and one maxima. Finally, there is an interesting point where these roots of $\partial G/\partial V = 0$ coincide, i.e. that there is just a single free energy minima. This point is called the **critical point**. For temperatures below the critical point temperature ($T < T_c$), there will be two phases. For $T > T_c$, there will be no real difference between the two phases. At the critical point ($T = T_c$) there is some pretty unusual behavior, but such aspects are beyond the scope of this course.

9.2.5 Calculation of Liquid-vapor equilibria

If one looks at an isotherm, one will see that the isotherm goes through an inflection in the co-existence region. How does one know where to delineate this region? Ones does this with the **Maxwell construction**. Simply put, we know that the coexistence region is delineated by the point where the free energy of each phase is equal. At constant temperature, we have $dF = -PdV$. Thus, we can find the point where the free energies are equal by integrating along the equation of state

$$\Delta F = -\int PdV$$

where P is the pressure from the equation of state and the integral is done over the appropriate pressure range for each of the two phases.

While performing this integral mathematically can be difficult for complex equations of state, one can do so graphically by looking at the area under the curve in the equation of state and recognizing that this area is in fact the integral above.

9.2.6 Law of corresponding states

Let's explore the van der Waals equation of state. If we look at pressure vs volume (or temperature vs volume), we see that there is a discontinuity in the volume as it jumps from one size to another. This discontinuity reflects the fact that liquids take up much less volume than gases. However, as we raise the temperature, we find that the transition becomes less and less discontinuous, and at a particular point (called the critical point), the transition is no longer discontinuous. Finally, above the critical point, there is no transition at all: there is no simple distinction between liquid and gas.

To see this more clearly, we can do some algebra. We can find out where the critical point is in terms of the molecular parameters a, b, and n by the following means. For $T < T_c$, there are three roots to the vdW equation. At $T = T_c$, these three roots must fuse together. Thus, in the neighborhood of the critical point, the equation of state must take the form

$$(V - V_c)^3 = 0$$

We can expand the cubic to get

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0$$

and compare this to the vdW equation at the critical point ($T = T_c$, $P = P_c$), i.e.

$$(P_c + an^2/V^2)(V - nb) = nRT_c$$

which we can multiply through to get

$$P_cV - P_cnb + an^2/V - an^3b/V^2 = nRT_c$$

If we multiply by V^2/P_c, we get

$$V^3 - nbV^2 + (an^2/P_c)V - an^3b/P_c = (nRT_c/P_c)V^2$$

which we can rewrite as

$$V^3 - \left(nb + \frac{nRT_c}{P_c}\right)V^2 + \frac{an^2}{P_c}V - \frac{an^3b}{P_c} = 0$$

Comparing terms, we get $V_c^3 = an^3b/P_c$ and $3V_c^2 = an^2/P_c$. Thus, $V_c/3 = V_c^3/(3V_c^2) = nb$. From here, we get

$$RT_c = \frac{8a}{27nb} \qquad P_c = \frac{a}{27n^2b^2} \qquad V_c = 3nb$$

Thus, we see that we can rewrite the vdW equation in terms of the values of P, V, and T at the critical point ($\overline{P} = P/P_c$, $\overline{P} = V/V_c$, and $\overline{T} = T/T_c$) instead of the molecular parameters a, b, and n. We find a very simple relationship:

$$\left(\overline{P} + \frac{3}{\overline{V}^2}\right)\left(\overline{V} - \frac{1}{3}\right) = \frac{8}{3}\overline{T} \tag{1}$$

What does this mean? It means that the molecular parameters (a, b, n) are important in determining the critical point (i.e. T_c, P_c, and V_c) but otherwise are not important. In other words, we would expect that different gases would all follow the same equation (above), if we correct for differences in the values of T_c, P_c, and V_c. The idea that the vdW equation above (or any equation of state) can *universally* describe many different types of gases is called the **law of corresponding states** and is a powerful property common to many systems in statistical mechanics.

9.3 Polymers

Polymers have become an important material in chemistry, physics, chemical engineering, and biology, due to their broad applicability in materials, industrial applications, as well as many important biological biopolymers (DNA, RNA, and proteins). While there are vast differences between different polymers on a chemical level, there are many properties which are independent of these chemical details, and thus are “universal” in the sense previously described. Here, we examine some of these properties.

9.3.1 Universal aspects of polymers: persistence length

One of the more important universal properties of polymers is the persistence length. Different polymer chemistries vary in their stiffness: for example, DNA is very stiff whereas proteins are fairly flexible. To quantify this, one can define a **persistence length** as the typical length scale at which the polymer can bend.

To quantify this, let's consider more directly the correlation function $\langle \vec{u}_i \cdot \vec{u}_j \rangle$. If the chain is very flexible, then this correlation function vanishes. However, for a stiff chain, this correlation function will not vanish and instead will decay with a characteristic length ℓ:

$$\langle \vec{u}_i \cdot \vec{u}_j \rangle = \exp(-|i-j|/\ell) \tag{2}$$

This chacteristic length is called the **persistence length**, since it describes over what length scale the bond vectors $\vec{u}_i$ decorrelate.

One can imagine taking any polymer, whose normal monomer-monomer distance is a and recasting it as a polymer made of effective "quasi-monomers" separated by a distance ℓ. This new polymer will be completely flexible. In general, when we talk about the statistical mechanics of polymers, we will assume that this "quasimonomer renormalization" has been preformed and that we are working with an effective model in which the chain is flexible. Chemical differences between polymers only changes the value of ℓ (for example for proteins $\ell \approx 1$ nm and for DNA $\ell \approx 1\mu$m), but afterwards is not important.

9.3.2 The central limit theorem

A favorite question of mine is "why does taking more data points help"? The reason is that adding up random noise converges. For example, let's say that we flipped a series of coins and added up the result to be x (heads = +1, tails = -1). If we added the sum of N flips, the average would be 0, i.e. we'd expect an equal number of heads and tails. However, if we reproduced this test several times, what would the distribution of x look like? It turns out that it's a Gaussian distribution:

$$P(x) = \frac{1}{\sqrt{2\pi N}} \exp(-x^2/2N)$$

with a mean of $\langle x \rangle = 0$ and a standard deviation of $\sqrt{N}$. The standard deviation tells us the breadth of the distribution. We know that the widest this distribution could be is N (the maximal value of x is N – i.e. when all coins turned up heads – and the minimal is $-N$ when all were tails).

This result has uncountable applications and is a very important concept to remember. It's especially interesting to look at the fractional standard deviation, i.e.

$$\frac{\text{standard dev}}{N} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

We see that the fraction of the width gets smaller and smaller as we do more flips – it gets more and more likely to get the mean. This is why it's useful to take more data points in lab. The random deviations that one produces get averaged out, and moreover as one takes more points, one converges at the right answer with greater certainty.

9.3.3 Random walk

The simplest model of a polymer is a random walk. We assume that the polymer does not interact with anything, and can be modeled as the path a diffusing polymer takes. First, it is natural to calculate the probability distribution for the end to end distance of this polymer. To do this, we can assume that each link of the polymer is oriented in a random manner. To simply our thinking, let's consider a polymer constrained to a cubic lattice. Then, each link can be oriented $\pm a$ in each dimension, where a is the length of a link.

In each dimension, we can add up these random variables to get the total end to end vector. We know from the central limit theorem that the probability distribution for a sum of random variables is Gaussian

$$P(R_x) = \left(2\pi N_x a^2\right)^{-1/2} \exp(-R_x^2/2N_x a^2)$$

with zero mean and a variance $N_x a^2$, where N_x are the number of steps taken in the x direction. Since there are three dimensions, $N_x = N/3$, i.e. a third of the steps will be in the x dimension. Since we have random sums in each dimension, the end to end distance distribution takes the form (where d is the number of dimensions)

$$\begin{aligned} P(\vec{R}) &= P(R_x)P(R_y)P(R_z) \\ &= \left(2\pi N a^2/3\right)^{-3/2} \exp(-3R_x^2/2Na^2)\exp(-3R_y^2/2Na^2)\exp(-3R_z^2/2Na^2) \\ &= \left(2\pi N a^2 \middle/ 3\right)^{-d/2} \exp(-3\vec{R}^2/2Na^2) \end{aligned} \tag{3}$$

where $\vec{R}^2 = R_x^2 + R_y^2 + R_z^2 = |\vec{R}|^2$.

However, we're concerned with the magnitude of this vector only, i.e. the end to end distance $R = |\vec{R}|$. Its distribution takes the form

$$P(R) = \left(2\pi N a^2/3\right)^{-3/2} 4\pi R^2 \exp(-3R^2/2Na^2) \tag{4}$$

We got this value from the fact that there are $4\pi R^2$ vectors $\vec{R}$ of length R. Another way to think of it is that $P(\vec{R})$ is the probability of finding a particular vector $\vec{R}$, whereas $P(R)$ is the probability of finding any vector of length R. Thus, the two are related by $P(R) = 4\pi R^2 P(\vec{R})$.

We can calculate properties of the polymer from this distribution. For example, we can calculate the mean squared end to end distance $\left\langle \vec{R}^2 \right\rangle = Na^2$. We can also calculate an entropy by saying that the number of states $\Omega(R)$ with end to end distance R is $\Omega(R) = P(R)\Omega$, where Ω_{tot} is the total number of states (and thus is a constant):

$$S(R)/k = \ln \Omega_{\text{tot}} P(R) = -\frac{3}{2}\frac{R^2}{Na^2} + \ln \frac{R^2}{(2\pi N a^2/3)^{3/2}} + \ln \Omega_{\text{tot}} + c \tag{5}$$

where c is a constant.

9.3.4 Flory's theory for a self-avoiding walk

In the previous sections, we have been talking about a random walk, which does not interact with anything. For example, it can bump into itself. Of course, this is not physical and real polymers are **self-avoiding walks**, i.e. their segments have some excluded volume.

A simple, elegant, and remarkably quantitative theory for self-avoiding walks was posed by **Flory**. Flory's idea for self avoiding walks is much like van der Waals approach to fluids: start with the ideal case (for polymers, a random walk), and then add in interactions. To write the free energy of a self-avoiding walk, we combined the entropy from the random walk

$$S(R) = -\frac{d}{2}\frac{R^2}{Na^2} \tag{6}$$

(where we have ignored the $\ln R$ term as it is most relevant at small R) with a term for the energy taken from the second virial term

$$E(R) = NB\rho = NB\frac{N}{V} = B\frac{N^2}{R^d} \tag{7}$$

where we have absorbed constants (such as kT) into the definition of B. Also note that we have set the volume to scale like $V \sim R^d$; this allows us to solve the problem for arbitrary dimensionality. Since the excluded volume makes the chain repel itself, then we know that B has to be positive.

From this, Flory calculated the free energy

$$F(R) = B\frac{N^2}{R^d} + T\frac{d}{2}\frac{R^2}{Na^2} \tag{8}$$

and found the equilibrium state by finding the free energy minimum

$$\frac{\partial F}{\partial R} = -Bd\frac{N^2}{R^{d+1}} + 2T\frac{d}{2}\frac{R}{Na^2} = 0 \tag{9}$$

which leads to

$$T\,R^{d+2} \;=\; Ba^2\,N^3 \quad\Rightarrow\quad R \sim N^{\nu} \tag{10}$$

where $\nu = 3/(d+2)$ is an example of a **critial exponent** for the self-avoiding polymer walk. It describes how the typical size of the polymer scales with the number of monomers N. To see the accuracy of **Flory theory**, let's compare the Flory result for ν to the exact results. The agreement is striking — the Flory result is correct in $d = 1, 2, 4$ and within 3% of the result for $d = 3$. While these results are striking, this was in some sense a bit of luck, since one can show that this accuracy is caused by a convienent cancellation of errors. Nevertheless, Flory theories of this form (i.e. start with the random walk entropy and add in interactions via the energy term) are a very common way to describe polymers and can be very accurate.

spatial d	ν_{Flory}	ν_{exact}
1	3/3=1	1
2	3/4	3/4
3	3/5	≈ 0.586
4	3/6=1/2	1/2

Before going on, let's think about what we would expect ν to be like. Consider a d dimensional box. The number of things which can fit in that box scales like its volume, i.e. $N \sim R^d$ and thus $R \sim N^{1/d}$ and thus $\nu = 1/d$ in this case. Thus, it is natural to interpret $1/\nu$ as the **fractal dimensionality** of the system. For example, random walks scale like $R \sim N^{1/2}$ and thus have $\nu = 1/2 = 1/d_f$ and thus have a fractal dimensionality of $d_f = 2$.

What does this mean? For random walks in $d = 2$, we expect that it will completely fill the 2D plane. However, random walks in 3D will not. Finally, this means that since the trajectories of random walks have essentially a two dimensional nature, then in $d \geq 4$, we expect that they will never intersect (or very rarely, much fewer than order N times and thus in the thermodynamic limit, their interaction is irrelevant). Thus, in $d = 4$, we would expect that even self-avoiding walks would behave like random walks. To test this, let's look at the Flory result. We find that $\nu = 1/2$ for $d = 4$ and thus even in four dimensions, self-avoiding walks scale like random walks.

However, for other dimensions, we see a strong deviation from the random walk behavior. Certainly in $d = 1$, we expect that a self-avoiding chain would have to be completely stretched out, i.e $R \sim N$ and thus $\nu = 1$, which is what Flory theory derives in this case. In $d = 2$ and 3, the result is not so glaring, but we still find that the repulsion due to excluded volume makes the chain swell, and thus have a higher ν than that of a random walk.

9.3.5 Coil to globule transition

When the chain is a random walk, it is much like an ideal gas, as it doesn't interact with itself and simply tries to maximize entropy. When we put in excluded volume, the chain swells. However, if the chain attracts itself, then one would expect that the chain would condense into something equivalent of a liquid, called a polymer **globule**, where the chain is compact and the size scales like the volume $R \sim N^{1/d}$.

To predict the coil to globule transition, one can simply write a free energy in the form of a virial expansion

$$F = NB\rho + NC\rho^2 \tag{11}$$

where B and C are the second and third virial coefficients, respectively. Under the solvent conditions where the polymer is self-avoiding (called a **good solvent**), we expect $B > 0$, and thus the free energy minima occurs at $\rho = 0$, i.e. the coil state. When the polymer attracts itself (in a so-called **poor solvent**), then $B < 0$. In this case, we have a free energy minima at

$$\frac{dF}{d\rho} = NB + 2NC\rho = 0 \quad \Rightarrow \quad \rho = -\frac{B}{2C} \tag{12}$$

As the density gets greater, the approximation to keep terms only up to the third virial coefficient becomes worse and worse. However, from this simple expression, one can see that there is a gradual transition from coil to globule, i.e. as B goes negative, the density gradually decreases. This is different from the gas-liquid transition of the van der Waals equation, which predicts a jump in the density. These two styles of phase transitions (gradual vs a jump) are called **first order phase transitions** and **second order phase transitions**, respectively. We'll talk in more detail about what these terms mean later in the course.

9.3.6 Another approach: Starting from the number of states

Consider a one-dimensional random walk, moving up or down. We start by examining the number of states with $N_\uparrow$ steps up and $N_\downarrow = N - N_\uparrow$ steps down. This is simply the way of choosing $N_\uparrow$ out of

N and is given by the binomial coefficient

$$\Omega(N_\uparrow, N) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!(N-N_\uparrow)!}$$

The corresponding entropy

$$S(N_\uparrow, N) = k\ln\Omega(N_\uparrow, N) = k\ln\left[\frac{N!}{N_\uparrow!(N-N_\uparrow)!}\right]$$

can be simplified using Stirling's formula in the large N and $N_\uparrow$ limit, i.e. $\ln N! = N\ln N$, to get

$$\begin{aligned}
S(N_\uparrow, N) &= k\ln\Omega(E,N) = k\left[N\ln N - N_\uparrow\ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow)\right] \\
&= Nk\left[\ln N - (N_\uparrow/N)\ln N(N_\uparrow/N) - (1-N_\uparrow/N)\ln N(1-N_\uparrow/N)\right] \\
&= -Nk\left[\frac{N_\uparrow}{N}\ln\frac{N_\uparrow}{N} + \frac{N-N_\uparrow}{N}\ln\frac{N-N_\uparrow}{N}\right]
\end{aligned}$$

Now, consider that the number of steps up and down will likely be close to $N/2$ when taken at random: $N_\uparrow = N/2 + \delta_\uparrow$ and $N_\downarrow = N/2 + \delta_\downarrow = N/2 - \delta_\uparrow$. Then, we can rewrite $N_\uparrow/N = (1/2)(1 + 2\delta_\uparrow/N)$ and $N_\downarrow/N = (1/2)(1 + 2\delta_\downarrow/N)$ and the above as

$$S(\delta_\uparrow, N) = -Nk\left\{\left(\frac{1}{2}\right)\left(1+2\frac{\delta_\uparrow}{N}\right)\ln\left[\left(\frac{1}{2}\right)\left(1+2\frac{\delta_\uparrow}{N}\right)\right] + \left(\frac{1}{2}\right)\left(1-2\frac{\delta_\uparrow}{N}\right)\ln\left[\left(\frac{1}{2}\right)\left(1-2\frac{\delta_\uparrow}{N}\right)\right]\right\}$$

Using the Taylor expansions $\ln(1+x) \approx x - x^2/2$ and $\ln(1-x) \approx -x - x^2/2$ and keeping all of the terms up to order $\delta_\uparrow^2$, we get

$$\begin{aligned}
S(\delta_\uparrow, N) &= Nk\ln 2 - Nk\left(\frac{1}{2}\right)\left[\left(1+\frac{2\delta_\uparrow}{N}\right)\left(\frac{2\delta_\uparrow}{N} - \frac{2\delta_\uparrow^2}{N^2}\right) + \left(1-\frac{2\delta_\uparrow}{N}\right)\left(-\frac{2\delta_\uparrow}{N} - \frac{2\delta_\uparrow^2}{N^2}\right)\right] \\
&= Nk\ln 2 - 2k\frac{\delta_\uparrow^2}{N}
\end{aligned}$$

Note that $Nk\ln 2$ is the total entropy (number of walks). Since the end to end distance in one dimension is given by $R/a = N_\uparrow - N_\downarrow = 2\delta_\uparrow$, we get

$$S(R,N) = Nk\ln 2 - 2k\frac{R^2}{4Na^2} = Nk\ln 2 - k\frac{R^2}{2Na^2} \tag{13}$$

and thus

$$\Omega(R,N) = 2^N\exp(-R^2/2Na^2)$$

This is the result in one dimension. Next, we address the multidimensional case.

9.4 Ising model

The Ising model was originally formulated as a model for magnetism. However, due to its simplicity, it has been applied to many different systems, including the helix-coil transition in DNA, neural networks, etc — just about any system which is based on elements which can take on 1 of 2 states.

9.4.1 The Non-interacting Ising model: a simple but useful model

In this section, we will examine such a simple model. It was originally intended as a simple model for ferromagnetism, but as we will see, it can be used for many systems including gases, liquids, and DNA helices.

In the model, there are N sites. Each site has a spin which can be either up or down. Thus, the total entropy is

$$S_{\text{tot}} = k \ln 2^N = Nk \ln 2$$

However, what is of more interest is the entropy as a function of $N_\uparrow$. We start by examining the number of states with $N_\uparrow$ spins up and $N_\downarrow = N - N_\uparrow$ spins down. This is simply the way of choosing $N_\uparrow$ out of N and is given by the binomial coefficient

$$\Omega(N_\uparrow, N) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}$$

The corresponding entropy

$$S(N_\uparrow, N) = k \ln \Omega(N_\uparrow, N) = k \ln \left[\frac{N!}{N_\uparrow!(N - N_\uparrow)!} \right]$$

can be simplified using Stirling's formula in the large N and $N_\uparrow$ limit, i.e. $\ln N! = N \ln N$, to get

$$\begin{aligned} S(N_\uparrow, N) &= k \ln \Omega(E, N) = k \left[N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) \right] \\ &= Nk \left[\ln N - (N_\uparrow/N) \ln N(N_\uparrow/N) - (1 - N_\uparrow/N) \ln N(1 - N_\uparrow/N) \right] \\ &= kN \ln N - Nk \left[\frac{N_\uparrow}{N} \ln \frac{N_\uparrow}{N} + \frac{N - N_\uparrow}{N} \ln \frac{N - N_\uparrow}{N} \right] \end{aligned}$$

In the non-interacting Ising model, the spins only interact with the external magnetic field (not with each other). We define the energy of this interaction to be $U = -mB(N_\uparrow - N_\downarrow)$, i.e. the energy is the net number of spins point up times the field strength B and the magnetic moment per spin m. The minus sign is there since it is energetically favorable to point in the direction of the field (up). The energy simplifies to $U = -mB[N_\uparrow - (N - N_\uparrow)] = -mB[2N_\uparrow - N]$.

Now, we have all the terms we need for the free energy:

$$F(N_\uparrow) = U(N_\uparrow) - TS(N_\uparrow) = -mB[2N_\uparrow - N] - kT \left[N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) \right]$$

To find the equilibrium behavior, we find $dF/dN_\uparrow = 0$. After taking the derivative, we get

$$\frac{dF}{dN_\uparrow} = -2mB + kT[1 + \ln N_\uparrow - 1 - \ln(N - N_\uparrow)] = 0$$

We can rearrange terms to get

$$\frac{2mB}{kT} = \ln \left[\frac{N_\uparrow}{N - N_\uparrow} \right] = -\ln \left[\frac{N - N_\uparrow}{N_\uparrow} \right] = -\ln \left[N/N_\uparrow - 1 \right]$$

which simplifies to

$$N_\uparrow = N \frac{1}{\exp(-2mB/kT) + 1} = N \frac{\exp(mB/kT)}{\exp(-mB/kT) + \exp(mB/kT)}$$

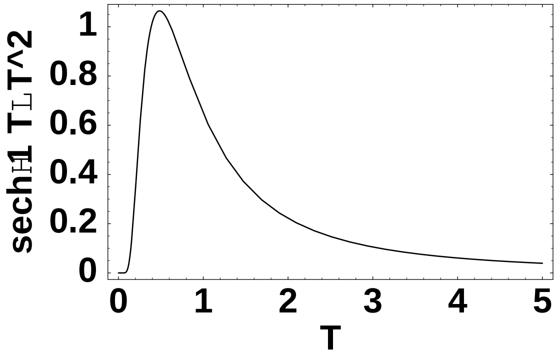

Figure: Plot of $\mathrm{sech}^2(1/T)/T^2$ vs T, corresponding to the heat capacity C_V of an Ising system. We see that the heat capacity is definitely not constant as a function of T. Moreover, there is a peak in the heat capacity at $RT = mB$.

Since $N_\downarrow = N - N_\uparrow$, we also get

$$N_\downarrow = N\frac{\exp(-mB/kT)}{\exp(-mB/kT) + \exp(mB/kT)}$$

From the equilibrium values for $N_\uparrow$ and $N_\downarrow$, we can calculate the other thermodynamic quantities by inserting the values for $N_\uparrow$ and $N_\downarrow$ above into formulae. For example, for $U = -mB(N_\uparrow - N_\downarrow)$, we get

$$\begin{aligned} U &= -mB\left[\frac{N\exp(mB/kT)}{\exp(-mB/kT) + \exp(mB/kT)} - \frac{N\exp(-mB/kT)}{\exp(-mB/kT) + \exp(mB/kT)}\right] \\ &= -NmB\tanh(mB/kT) \end{aligned}$$

Since $U = -mB(N_\uparrow - N_\downarrow) = -mBM$, we see that the magnetization M can be written as

$$M = N\tanh(mB/kT)$$

You might not be familiar with hyperbolic functions. Here are some definitions and useful derivatives:

$$\sinh(x) = \frac{1}{2}\left[\exp(x) - \exp(-x)\right] \quad \text{and} \quad \cosh(x) = \frac{1}{2}\left[\exp(x) + \exp(-x)\right]$$

$$\frac{d}{dx}\sinh(x) = \frac{1}{2}\left[\exp(x) + \exp(-x)\right] = \cosh(x) \quad \text{and} \quad \frac{d}{dx}\cosh(x) = \frac{1}{2}\left[\exp(x) - \exp(-x)\right] = \sinh(x)$$

$$\tanh(x) = \frac{\sinh(x)}{\cosh(x)} \quad \text{and} \quad \mathrm{sech}(x) = \frac{1}{\cosh(x)^2}$$

Finally, we can calculate a heat capacity:

$$C_V = \frac{\partial U}{\partial T} = -\frac{\partial}{\partial T}NmB\tanh(mB/kT) = Nkm^2B^2\mathrm{sech}^2(mB/kT)$$

We see a very interesting behavior: there is a peak in the heat capacity around $T = mB/k$. This signals that something is happening at this temperature. Indeed, this is the point where the system crosses over from the low to high temperature behavior.

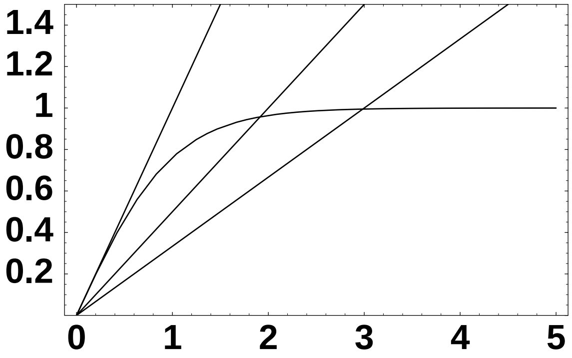

Figure: Plot of x, $x/2$, $x/3$, and $\tanh(x)$ vs x. The intersection points are the solutions to the equation $x/a = \tanh(x)$. We see that there can be 1 or 2 solutions corresponding to $m = 0$ and some non-zero m.

9.4.2 Basic forms of interaction in the Ising model

Basic ideas. Finally, the title of this chapter was "The Non-interacting Ising model." These spins do not interact. Interaction would mean that one spin would affect its neighbor: if a spin is pointing up, it might have an influence on the direction of its neighbor. In ferromagnets, this interaction leads spins to all point in the same direction.

We can make a simple model for this interaction by considering that the magnetization M itself is like a magnetic field. In this case, we say the spins create an effective magnetic field $B_{\text{eff}} = JM/N$, where J is some coupling constant for interaction between spins.

Using this B_{eff}, we start from the result we had for the non-interacting system:

$$M = N \tanh(mB/kT)$$

If we say that the external magnetic field is zero, but the spins do react to the magnetic field generated by the magnetization. Thus, we say that $B = B_{\text{eff}} = JM/N$ and we get

$$M = N \tanh(mJM/NkT)$$

This equation can be solved iteratively on a computer, but is perhaps most easily done graphically. To do so, I'd suggest rewriting the equation with $x = mJM/NkT$ and thus $M/N = xkT/mJ$. We can think of x the way we do M since they're related by constants. Thus, we get

$$xkT/mJ = \tanh(x)$$

Now, plot $\tanh(x)$ vs different lines xkT/mJ depending on the slope of these lines (i.e. depending on kT/mJ), we'll see several different solutions to the equation (i.e. points where the two curves intersect). At high temperature, there will be one solution at $x = 0$ (corresponding to $M = xkT/mJ = 0$). This is the paramagnetic phase, where entropy dominates and there is no ordering. As we lower temperature (decrease the slope of xkT/mJ), we see that there are three solutions, one at positive x and one at negative x and one at solution. These non-zero solutions for x are two different possible free energy minima corresponding ferromagnetic phases (the $x = 0$ solution corresponds to a free energy maxima).

A more mathematical analysis. We can analyze this more mathematically by looking at $xkT/mJ = \tanh(x)$ at small x. Using the Taylor expansion $\tanh(x) = x - x^3/3 + \cdots$, we get

$$\frac{kT}{mJ}x = x - \frac{x^3}{3}$$

One solution to this equation is $x = 0$. We can simplify this by dividing by x to get two more solutions

$$x = \pm\sqrt{3}\left[1 - \frac{kT}{mJ}\right]^{1/2} = \pm\sqrt{3}\left[1 - \frac{T}{T_c}\right]^{1/2}$$

It is natural to define a critical transition temperature $T_c \equiv mJ/k$. We see that at high temperature $T > T_c$, only the $x = 0$ solution is a real number. For $T < T_c$, we have three solutions: $x = 0$ and $x = \pm\sqrt{3}[1 - T/T_c]^{1/2}$. These three phases are the same as those discussed above – instead of solving the equation by graphing, we've simply done so by a Taylor series approximation.

Note that there are two ferromagnetic solutions! One for positive and one for negative magnetization. This is important and is the result of an important **symmetry**: the Ising system has no preference for up or down. Thus, if there is some magnetization due to the peer pressure of spin-spin interaction, while the whole group will agree on some direction, the direction (up vs down) is arbitrary. As long as they all agree, the energy is the same.

Since we have obtained this by a Taylor expansion for small x, these results are only numerically accurate for small x (i.e. small M), although one can numerically solve the equations above with a computer to obtain better numerical results if that is desired – the Taylor approximation is useful for our understanding of the nature of these phases and these results do not change.

9.5 Appendix: Probability

Since many students have not formally taken a class in probability, here are some comments to more better flesh out some issues relating to probability.

9.5.1 Definitions and preliminary remarks

Much of the basics aspects of probability is probably familiar to you. Here's a brief review for completeness and notation.

1. We call all the possible outcomes of an event the **microstates** of the system. For example, for a coin flip, the microstates are heads and tails. For a die, the 6 microstates are numbers 1-6.
2. Often it is useful to group microstates together into **macrostates** based upon some common properties of the microstates. For example, we could imagine in the dice case, two macrostates being odd and even outcomes of the die roll, each macrostate consisting of 3 microstates.
3. We can assign **probabilities** to events with particular microstates as outcomes. For example, for a fair die, each microstate is equally likely and thus we say that they have equal probability. The probability is related to the experimental outcome of events. For example, if we flip a coin N times, we expect it to be heads $p_{\text{heads}}N$ times, where p_{heads} is the probability of the heads microstate.

   Clearly, the following properties must hold (and can be either reasoned, or taken axiomatically)

   (a) *Positivity*: The probability of event T must be non-negative: $p(E) \geq 0$.

   (b) *Normalization*: Since the number of events corresponding to microstate i is $N_i = p_i N$ and since $\sum_i N_i = N$, we must have $\sum_i p_i = 1$.

   (c) *Additivity*: if A and B are disconnected events, then $p(A \text{ or } B) = p(A) + p(B)$. Thus, since each microstate are disconnected outcomes, the probability of a macrostate is the sum of the probabilities of its constituent microstates.

9.5.2 Single variable distributions

In the previous section, I gave examples using discrete random variables (eg the 6 discrete outcomes of rolling a die). Now, let's consider continuous random variables. Consider a continuous set of microstates, each with a different value of x and $-\infty < x < \infty$.

We can define some fundamental relationships.

1. We can consider the **probability distribution function** (**PDF**) $p(x)$ to be the probability of an outcome microstate with value x. $p(x)$ is the continuous equivalent to p_i; for example, the discrete normalization $\sum_i p_i = 1$ has a natural integral equivalent $\int_{-\infty}^{\infty} dx p(x) = 1$ in the continuous case. An example of a continuous PDF is the probability of an event happening if in time t the rate is k: $p(t) = k \exp(-kt)$ and $\int_0^\infty dt p(t) = 1$.

   Note that $p(x)$ is not unitless, but rather has the same units as $1/x$. This is clear due to the normalization criteria $\int dx p(x) = 1$. For this reason, we should technically call $p(x)$ a probability density, whereas $p(x)dx$ is a true (unitless) probability, corresponding to the fraction of microstates of value x within a range dx. This distinction is not needed in discrete distributions, where p_i is a true probability.

2. We can define the **cumulative probability function** (**CPF**), $P(x)$ as the probability that a given outcome that is less than x:
$$P(x) = \int_0^x dx' p(x)$$
Using the time probability example above, we can calculate the probability that the event has happened by time t as $P(t) = \int_0^t dt' k \exp(-kt) = 1 - \exp(-kt)$. As one would expect, $P(t \to \infty) \to 1$. Unlike the probability distribution function, the cumulative probability function is unitless.

3. The **weighted average** (or "expectation value") of any function, eg $f(x)$ can be calculated as
$$\langle f(x) \rangle = \int_{-\infty}^{\infty} p(x) f(x)$$
With our rate example, we can calculate the average time to be $\langle t \rangle = \int_0^\infty dt k \exp(-kt) t = 1/k$ (i.e. the inverse of the rate, as we would expect).

While we often think of PDFs in simple models as Gaussians or delta functions, PDFs can be complex. Thus, we need some systematic means to characterize them. A natural way to do so is by using a cumulant expansion. I will not go into greater details of cumulants, other than mentioning the first four, which are familiar to most students. The first four cumulants are called the **mean**, **variance**, **skewness**, and **curtosis** of the distribution, and can be obtained from the moments as respectively

$$\begin{aligned}
\langle x \rangle_c &= \langle x \rangle \\
\left\langle x^2 \right\rangle_c &= \left\langle x^2 \right\rangle - \langle x \rangle^2 \\
\left\langle x^3 \right\rangle_c &= \left\langle x^3 \right\rangle - 3 \left\langle x^2 \right\rangle \langle x \rangle + 2 \langle x \rangle^3 \\
\left\langle x^4 \right\rangle_c &= \left\langle x^4 \right\rangle - 4 \left\langle x^3 \right\rangle \langle x \rangle - 3 \left\langle x^2 \right\rangle^2 + 12 \left\langle x^2 \right\rangle \langle x \rangle^2 - 6 \langle x \rangle^4
\end{aligned}$$

For example, for a Gaussian PDF, i.e.

$$p(x) = (2\pi\sigma^2)^{1/2} \exp[-(x-\lambda)^2/2\sigma^2]$$

we have a mean of $\langle x \rangle_c = \lambda$ and a variance of $\langle x^2 \rangle_c = \sigma^2$. It turns out that the higher order cumulants are zero: $\langle x^3 \rangle_c = \langle x^4 \rangle_c = 0$ and that the Gaussian can be compactly described simply by its mean and variance.

10 Phases and phase transitions

10.1 What is a phase and a phase transition?

10.1.1 Qualitative defintion

We have talked about phases throughout this course, but perhaps not directly given a definition. A phase describes a particular form of matter (eg liquids, gases, solids, solutions). Typically, differences in phases are not of chemical nature, but physical. What differentiates liquids from gases is how the molecules arrange themselves.

Phases are something for which thermodynamics is particularly well suited since phases arise due to a balance between energy (enthalpy) and entropy. For example, at high temperature, entropy dominates the free energy and one typically finds a gas, since the gas phase has greatest entropy. Similarly, at low temperature, typically one finds a crystal, since crystalline phases are precisely arranged in order to minimize the interaction energy.

Phase transitions are, well, transitions between phases. Phase transitions have common forms, such as ice melting or water boiling, but there are many systems which are phase transitions which you may not suspect (eg protein folding or ligand (drug) binding). These less familiar cases also must obey the laws of thermodynamics and thus what we have learned will apply to them too.

Perhaps the greatest strength of thermodynamics is the fact that it is inherently quite robust. By this I mean that we can make simple models and still get good results. Raoult's law, Henry's law, and ideal gases, are good examples of very simple models which can work remarkably well. Simple models work well since the essence of thermodynamics is getting the enthalpy and entropy correct. Often, this does not require a microscopic understanding of the underlying mechanism, but rather a general idea of the thermodynamic forces at work.

Thermodynamics is also robust due to the existence of state functions. State functions allow us to calculate or measure thermodynamic properties in potentially unusual ways, but get the same result. This invariance with respect to path makes thermodynamics invariant to small perturbations (like small errors in a model). Thus, while thermodynamics is used to describe something truly complicated, there is the hope that a simple model may capture the essence of the thermodynamics and give us a good understanding of the system.

10.1.2 Ehrenfest classification of phase transitions

The **Ehrenfest classification** of phase transitions distinguishes discontinuous phase transitions from continuous ones. Ehrenfest proposed that phase transitions could be classified as "nth order" if any nth derivative of the free energy with respect to any of its arguments yields a discontinuity at the phase transition.

For example, in the van der Waals equation for $T < T_c$, we saw that there was a discontinuous jump in the volume. This jump typically means that there is a kink in the equilibrium free energy vs temperature. When we take the first derivative of the free energy (with respect to temperature, for example), we find that the first derivative is discontinuous due to this kink. Thus, we call these transitions **first order phase transitions**.

On the other hand, there is no such discontinuity for the case $T = T_c$ in a vdW fluid. In this case, the first derivative is continuous. Such transitions are typically called **second order phase transitions**, but this name is typically includes all transitions which are continuous in the first derivative (and thus includes third order, fourth order, etc). Since the name "second order" is a bit misleading, the prefered term is a **continuous phase transition**, but old habits (and nomenclature) are hard to break.

Finally, we can ask, mathematically, where does this discontinuity come from? If we look at the free energy or the partition function, they are just sums of exponentials, and thus look like they should converge and not lead to singularities, eveb in their derivatives. Where does this singular behavior come from? Interestingly, we should keep in mind that there is one singular nature of functions like the partition function or the free energy, namely the thermodynamic limit $N \to \infty$. Mathematically, it is the thermodynamic limit which leads to singularities of the partition function or free energy. Since these singularities are associated with phase transitions, we come to the result that *phase transitions only truly occur in the thermodynamic limit!*

With that formal statement said, clearly nothing in the universe is formally in the thermodynamic limit and thus, in a pratical sense, we say that $N \to 1$mol is sufficiently close to observe phase transitions. However, this is not as clear once one looks at much smaller systems, such as polymers, nanocrystals, proteins, etc (which could have as few as 100's of atoms).

10.2 Landau theory

In order to describe phase transitions in a simple, elegant, yet powerful manner, Lev Landau (one of the greatest physicists of the 20th century) introduced a simple, phenomenological means to study phase transitions which is now called **Landau theory**. This model is **phenomenological** since it does not make any attempts to address all microscopic aspects of the material in question, but rather tries to incorporate only the most important and most relevant aspects.

In Landau theory, one first chooses some appropriate **order parameter**. An order parameter is the name given to the state variable used to differentiate ordered from disordered phases[14]. For example, since the gas phase has a much larger volume than the liquid, one could use the volume V as an order parameter in the gas-liquid transition. In this Ising model, the magnetization $\mathcal{M}$ is a natural order parameter, since it discriminates the paramagnetic from the ferromagnetic phase.

Next, one makes an argument about the nature of the free energy vs this order parameter. In particular, one typically assumes that the order parameter is small and writes a Taylor expansion for the order parameter, making some arguments about the nature of the various coefficients of the expansion from symmetry or other physical arguments. The science here lies in the explanation of why one chooses certain properties for these coefficients. For this reason, Landau theory may seem simple on the surface, but is actually fairly subtle and often considered to be a sophisticated means to address phase transitions.

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[14] Actually, one way to define a phase is as the ensemble of states near ("in") the free energy minima along the order parameter.

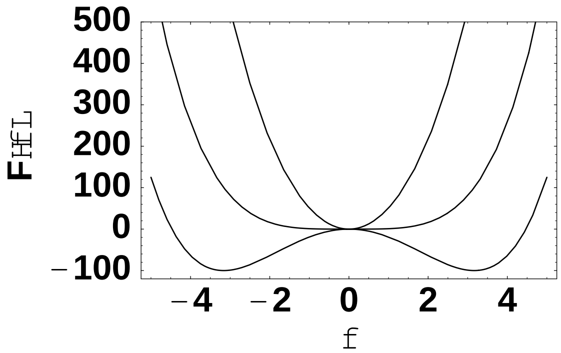

Figure: Landau free energy for an Ising system at three different temperatures.

10.2.1 Landau theory for Ising systems

For example, let's first consider the Landau theory for an Ising ferromagnet. It is natural to choose the magnetization as the order parameter. In the common notation, one typically uses ϕ as the order parameter in Landau theory. Next, we write the free energy vs ϕ in a Taylor expansion for small ϕ. This much is simple:

$$F = a\phi + b\phi^2 + c\phi^3 + d\phi^4 + \mathcal{O}(\phi^5)$$

Now the science lies in the values of these coefficients (and the knowledge that we can keep terms just up to $\mathcal{O}(\phi^4)$). What do we know about the symmetries of this system? If there is no external field ($B_0 = 0$), then there is no preference for the direction the spins will align to. At low temperatures, they should align in the same direction, but that direction is arbitrary: it could be either up or down and there would be no difference in the free energy.

This means that only terms which are invariant to a flip of the overall magnetization should remain in our free energy. Such terms are ϕ to a positive power. The negative power terms will flip sign when ϕ flips sign and thus they are not invariant (they vary!). Thus, we are left with

$$F = b\phi^2 + d\phi^4$$

Next, we have to make an argument about the values of b and d. The ϕ^2 term is much like the ρ^2 term we talked about in the vdW energy: it deals with the interaction between two particles (in this case spins). What is the interaction between these two particles? At high temperature, one would expect that entropy would dominate and thus there would be a repulsive interaction between these spins. At low temperature, there should be an attractive interaction. These two values should be balanced out at the transition temperature T_c. Thus, we can write

$$b = b_0 \frac{T - T_c}{T_c}$$

since this has the desired properties ($b > 0$ for $T > T_c$; $b < 0$ for $T < T_c$; and $b = 0$ for $T = T_c$). b_0 is a positive constant.

Now, we have to choose a value for d. For simplicity, we can simply say that d is a positive constant. We know that it will be hard for 4 spins to agree (especially at small magnetizations – recall that we are doing a Taylor expansion in $\mathcal{M} = \phi$).

If we put this together, we get

$$F = b_0 \frac{T - T_c}{T_c} \phi^2 + d\phi^4$$

What does this look like? For $T > T_c$, there is one free energy minima at $\phi = 0$ and at $T < T_c$, there are two free energy minima at $|\phi| > 0$.

Thus, we see that there is a phase transition at $T = T_c$.[15] One important point is that this phase transition occurs gradually: at $T = T_c$, $\phi = 0$. As we lower T, the free energy minima value of $|\phi|$ gradually increases. We can see this easily by calculating the equilibrium condition

$$\frac{dF}{d\phi} = 2b_0 \frac{T - T_c}{T_c} \phi + 4d\phi^3 = 0$$

and thus

$$\phi_{\text{eq}}^2 = \frac{-2b_0(T - T_c)/T_c}{4d} \quad \text{and thus} \quad \phi_{\text{eq}} = \pm\sqrt{\frac{2b_0(1 - T/T_c)}{4d}}$$

So, for $T = T_c$, we find that $\phi = 0$ and $|\phi|$ increases as we decrease temperature. This type of phase transition (i.e. in which the order parameter gradually, continuously changes) is called **second order**. **First order** transitions occur with a spontaneous jump in the order parameter, which we will see in the next example below.

Of course, we got these results due to the restrictions we put in for the coefficients based upon the symmetries of the problem. There are two powerful results of this:

1. The results we get for this system will be identical to any other system with similar symmetries. We will not talk about other systems in too much detail here, but I will mention that the statistics of random walks has the same symmetries as that of the Ising model. Thus, Ising results also apply to random walks (and thus many polymeric systems).
2. With this simple Landau free energy, we can calculate all of our thermodynamic friends and interpret them in terms of the very simple parameters of our model: T_c, b_0, and d.

We can calculate essentially many other thermodynamic properties from $F(\phi)$. For example,

$$C_V = T\frac{\partial S}{\partial T} = -T\frac{\partial^2 F}{\partial T^2}$$

For $T > T_c$, $\phi_{\text{eq}} = 0$ and $F(\phi_{\text{eq}}) = 0$. Thus, it has zero heat capacity. For $T < T_c$, we calculate

$$C_V = -T\frac{\partial^2}{\partial T^2}F(\phi_{\text{eq}}) = -T\frac{\partial^2}{\partial T^2}\left[b_0\frac{T - T_c}{T_c}\frac{-2b_0(T - T_c)/T_c}{4d} + d\left(\frac{-2b_0(T - T_c)/T_c}{4d}\right)^2\right]$$

Thus, we get

$$C_V = \begin{cases} T \geq T_c & 0 \\ T \leq T_c & (3b_0/2d)(T/T_c^2) \end{cases}$$

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[15] Hopefully, you will see now why we stopped at ϕ^4 terms. We did not need to go any higher in order to describe our system.

10.2.2 First order transitions

How can one create a first order transition? A simple means is to somehow break the symmetry of our problem. For example, consider the Ising system described above. If we break our spin flipping symmetry, then we would have to add in the odd powered ϕ terms. For example, consider including the $c\phi^3$ term. In this case, we get

$$F = b\phi^2 + c\phi^3 + d\phi^4$$

We calculate equilibrium for this case to be

$$\frac{dF}{d\phi} = 2b\phi + 3c\phi^2 + 4d\phi^3 = 0$$

We find three solutions for this cubic equation:

$$\phi = 0 \ , \quad \phi = \frac{-3c \pm \sqrt{9c^2 - 32bd}}{8d}$$

If we plot $F(\phi)$ at different temperatures, we see how these free energy minima become relevant. We see that at very high temperatures, there is only one minima at $\phi = 0$. However, as T is lowered, another minima appears (at $T =?$). At $T =?$, the two minima have equal free energy and for $T <?$, the second minima has lower free energy. When one minima passes the other, the equilibrium value of ϕ jumps from one minima to the other and thus there is a discontinuous (first order) transition.

First order transitions occur throughout biology. For example, (my favorite example) protein folding is a first order transition. We can ask why this might be biologically favorable? In this case, the order parameter would distinguish the folded from the unfolded phases. If the protein gets mutated a little bit, then the free energy of the folded state increases a little bit, but the system is still in the folded state. If the free energy changes too much, the system jumps to the unfolded state and the protein gets eaten up by proteases (biology's disposal system). Thus, proteins are tough enough to withstand some damage, but when they "break" they break completely, in a discontinuous all-or-none manner.

11 Statistical Thermodynamics: a molecular basis for thermodynamics

11.1 The microscopic world: Energy levels

Often, we think of thermodynamic properties, such as matter or energy, as being continuous. However, one of the most fundamental lessons from quantum mechanics is that this is not the case, but rather on a microscopic (atomic) scale, the world is **quantized**. By this, we mean that almost all quantities used to describe matter (energy, position, momentum, etc) take on discrete values when we look at individual atoms. Each permitted state is written in terms of **quantum numbers** which have integral (or sometimes half-integral) values.

For example, for a particle confined to a cubic box of length l, the energy levels can be written as

$$\epsilon = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

where m is the mass of the particle, h is Planck's constant, and n_x, n_y, and n_z are the quantum numbers of motion in the x, y, and z directions. The n values are restricted to be integers and thus there are only certain permitted values of the energy.

The above result only considered the motion of the particle (the **translational energy**). In general, polyatomic molecules also have other types of energy. In general (to a good approximation) we can write

$$\epsilon_{\text{total}} = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{int}}$$

where the new terms correspond to the rotational, vibrational, and interaction energies of the molecules. Theses energies are also quantized.

Often these energies (especially the translational energies), while formally discrete, are so close together that they act like they are continuous. This is why in our everyday world, we often don't see this quantized nature of reality. Also, for many thermodynamics applications, we can ignore this aspect and treat these quantities as being continuous.

Finally, with a knowledge of how many particles n_i are in a particular energy state ϵ_i, one can calculate the total energy simply by

$$U = \sum_{\text{states}} \epsilon_i n_i$$

As we will see in the later sections, simply knowing ϵ_i and n_i will also let us calculate all other thermodynamic properties. Before we get to that, we must get a better sense of what we mean by "states" in the summation below and in general learn how the microscopic world is connected the macroscopic one in which we live.

11.2 From the microscopic to the macroscopic world

11.2.1 Microstates, Macrostates, and Phases: new names for familiar concepts

First, at the very most fundamental level are **microstates**. Microstates correspond to the re-arrangements we talked about when we gave a microscopic interpretation of the entropy. The entropy of something is the ln of the number of microstates. For example, consider a set of 2 coins. In this case, there are 4 possible microstates:

$$\uparrow\uparrow \qquad \uparrow\downarrow \qquad \downarrow\uparrow \qquad \downarrow\downarrow$$

and in general, for N coins, there are 2^N total microstates. For an ideal gas, each microstate would correspond to a particular arrangement of particles in the box.

Next, often there is a logical (thermodynamic) way to group microstates, based upon some (typically) macroscopic parameter. This ensemble of microstates is called a **macrostate**. The concept of a macrostate is particularly useful since we typically measure, calculate, and think in terms of macroscopic properties, and we don't care about the underlying microscopic states (microstates) which comprise the macrostate, but rather the properties of the macrostate.

For example, in the coin system, we could choose the number of coins with tails as a means to group microstates. In our coin spin example, we have

$$\mathcal{M}(\uparrow\uparrow) = 2\,, \quad \mathcal{M}(\uparrow\downarrow) = \mathcal{M}(\downarrow\uparrow) = 0\,, \quad \mathcal{M}(\downarrow\downarrow) = 2$$

Thus, the macrostate for $\mathcal{M} = 0$ consists of two microstates ($\uparrow\downarrow$ and $\downarrow\uparrow$) while the other macrostates consist of only one microstates. The ln of the number of microstates in a macrostate is the entropy of that macrostate. For an ideal gas, for example, we could choose the volume V as our macroscopic parameter used to define macrostates. While there certainly will be microstates which have small volume, the entropy of the macrostate with maximal (box filling) volume will have the most microstates (i.e. the most entropy).

Thus, if the energy of macrostates are the same (as they are for an ideal gas), then the macrostate with the greatest entropy will be the equilibrium macrostate. This is nothing more than what we've said earlier about entropy, energy, and equilibrium, except now we have introduced the concept of a macrostate and its relationship to microstates.

Finally, we have mentioned phases several times in previous lectures. If we calculate the free energy (F or G, depending on the relevant conditions) vs our macrostate parameter M (which was $\mathcal{M}$ for the Ising system or V for a gas in our previous discussion), we will often see free energy minima in $F(M)$. These free energy minima correspond to phases. Thus, a **phase** often consists of several values of M, which corresponds to possible fluctuations of the phase in M.

11.3 Connection to the equilibrium constant

To see how our understanding of the equilibrium constant connects to stat mech concepts, let's look at the equilibrium constant under two special cases.

11.3.1 Special case 1: $\Delta U = 0$

Recall that in the reaction $A \rightleftharpoons B$, we said that the relative concentrations of A and B could be written as

$$\frac{\rho_A}{\rho_B} = \exp(-\Delta F/kT)$$

Let's look at this expression a little more carefully. Let's say that there is no energy difference $\Delta U = 0$. Thus, $\Delta F = \Delta U - T\Delta S = -T\Delta S$. Using the microscopic interpretation for entropy, i.e.

$S = k \ln \Omega$ and thus $\Omega = \exp(S/k)$ (where Ω is the total number of configurations available), we get

$$\frac{\rho_A}{\rho_B} = \exp(-\Delta F/kT) = \exp(T\Delta S/kT) = \frac{\exp(S_A/k)}{\exp(S_B/k)} = \frac{\Omega_A}{\Omega_B}$$

where we have used $\Delta S = S_A - S_B$, $\Omega_A = \exp(S_A/k)$, and $\Omega_B = \exp(S_B/k)$.

Let's think about what this means. We've said before (when we were talking about vdw fluids) that the concentration ρ is much like the probability of finding the system in a given state. This is a good way to think of the formula above. Let's say that there are $\Omega = \Omega_A + \Omega_B$ ways of arranging the system in general. Then, in the case where energy differences are zero, we simply want to know what's the probability that we'll find the system in A vs B. These probabilities are

$$p_A = \frac{\Omega_A}{\Omega}, \qquad p_B = \frac{\Omega_B}{\Omega}$$

If the entropy difference is zero ($\Delta S = 0$), then we know that we should expect to find A and B in equal quantities. This makes sense when we think of things probabilistically, since we say that the two have equal probabilities.

11.3.2 Special case 2: $\Delta S = 0$

Now let's consider the case where $\Delta S = 0$. In this case

$$\frac{\rho_A}{\rho_B} = \exp(-\Delta F/kT) = \exp(-\Delta U/kT)$$

or equivalently in terms of probabilities

$$\frac{p_A}{p_B} = \exp(-\Delta F/kT) = \exp(-\Delta U/kT)$$

We see that the system has a greater probability of being in the state with the lower energy. If the energies are equal, then so are the probabilities. Just as we wrote the probabilities for the case above, we can also write

$$p_A = \frac{\exp(-U_A/kT)}{Z}, \qquad p_B = \frac{\exp(-U_B/kT)}{Z}$$

Note that this preserves the ratio $p_A/p_B = \exp(-U_A/kT)/\exp(-U_B/kT) = \exp(-\Delta U/kT)$. Instead of Ω, we have a normalization constant Z. We will see that just as Ω has a clear physical interpretation (total number of states), so does Z.

11.3.3 Looking closer at Z

This form for the probabilities ($p_i = \exp(-U_i/kT)/Z$) is attributed to Boltzmann and the quantity $\exp(-U_A/kT)$ is called the **B**oltzmann weight. Since we know that the probabilities of all the states in the system must sum to 1, we can say that

$$\sum_i p_i = 1 = \sum_i \frac{\exp(-U_i/kT)}{Z}$$

Here, the i's label the different microstates. Since Z is a constant, we can pull it out to get

$$Z = \sum_i \exp(-U_i/kT)$$

11.3.4 What are Boltzmann weights?

We found that if macrostates have the same energy, then the entropy of a macrostate decides which macrostate will dominate equilibrium. However, what should we do if the energies aren't the same? In order to consider the role of energy on the probability of finding a given state, we need to consider the concept of a Boltzmann weight, named after Ludwig Boltzmann the father of statistical mechanics. (Note that the discussion below assumes constant temperature).

Simply put, Boltzmann weights say that relative probability of finding two microstates is related to their energy difference:

$$\frac{P_1}{P_2} = \exp[-(\epsilon_1 - \epsilon_2)/T]$$

where P_1 and P_2 are the probabilities of finding states 1 and 2 in equilibrium, ϵ_1 and ϵ_2 are their energies, and T is the temperature.

Note that microstates cannot have entropy since entropy is the ln of how many microstates there are — microstates are a fundamental unit of re-arrangement possibilities. With this said, the above should look very familiar. Recall, we said that

$$\frac{c_1}{c_2} = \exp[-(G_1 - G_2)/T]$$

from arguments about chemical equilibrium between two substances 1 and 2 ($1 \rightleftharpoons 2$). In the case where we are working at constant volume and since microstates have no entropy, we get

$$G_i \to \epsilon_i$$

Also, let's think about what we mean by "the probability of finding state i." One way to think about this is to imagine that we have lots of copies of a given system and we look to see what state these systems are in. The fraction of systems which are in state i at any given time is the probability of finding the system in state i. This is analogous to the concentration of particles with state i, i.e.

$$c_i \to P_i$$

Thus, we get Boltzmann weights from our original results on chemical equilibrium.

Boltzmann weights are the fundamental building block of any statistical mechanical analysis – they connect energies with probabilities. As we will see, typically we will start our analysis of a problem by looking at the relevant microstates and then consider the probabilities of finding these microstates.

11.3.5 A brief tangent: why are Boltzmann weights of this form?

Why are Boltzmann weights of this form? In the discussion below, we will see that this form is the result of just a few simple assumptions, namely:

1. There is no absolute zero of energy that is meaningful (all that is important is the relative energy difference)
2. Relative probabilities are related to energy differences

Thus, this very fundamental part of statistical mechanics rests on very simple and pure roots (and is thus very broadly applicable).

Let's say we have two microstates 1 and 2 with energies U_1 and U_2, respectively. We expect that this relative probability has to do with the energies of the microstates. If something has really high energy, we expect it to be unstable, much like in the mechanical examples we discussed early in the class. Certainly, we can write the relative populations of these two microstates as a function of their energies

$$\frac{a_2}{a_1} = f(U_1, U_2)$$

Note that one can think of the a_i's as a concentration c_i or as being proportional to the probability $a_i \sim P_i$.

In general, the zero point of energy is arbitrary and in fact, all we care about in life is energy differences, so

$$\frac{a_2}{a_1} = f(U_1 - U_2)$$

Any change in the zero point in energy would cancel. Now the equation above should be valid for any three microstates, i.e.

$$\frac{a_3}{a_1} = f(U_1 - U_3) \quad \text{and} \quad \frac{a_3}{a_2} = f(U_2 - U_3)$$

Mathematically, we can write

$$\frac{a_3}{a_1} = \frac{a_2}{a_1} \times \frac{a_3}{a_2}$$

And thus, our unknown function f must satisfy

$$f(U_1 - U_3) = f(U_1 - U_2) \times f(U_2 - U_3)$$

What types of functions have this form? Exponentials do. In fact, recall that

$$e^{x+y} = e^x e^y$$

If we say that

$$f(U) = e^{\beta U}$$

where β is a constant. To verify that this form for f does indeed satisfy our requirements, we can plug it in

$$e^{\beta(U_1 - U_3)} = e^{\beta(U_1 - U_2)} e^{\beta(U_2 - U_3)}$$

and thus, we find that

$$\frac{a_2}{a_1} = e^{\beta(U_1 - U_2)}$$

Finally, we see that this allows us to write the population of an arbitrary microstate j as

$$a_j = e^{-\beta U_j}$$

Thus, from these simple assumptions, we have arrived at Boltzmann weights.

11.4 The statistical approach

Now that we have made some connections between the microscopic and macroscopic world, it is time to get down to business and do some calculations.

11.4.1 Partition functions

We have found that the number of molecules in a given state is given by

$$\frac{n_i}{n_0} = \exp(-\epsilon_i/kT)$$

We can use this to calculate the properties of interest. For example, the total energy is

$$U = \sum_i n_i \epsilon_i = \sum_i \epsilon_i \exp(-\epsilon_i/kT)$$

and the average energy per molecule is

$$\frac{U}{N} = \frac{\sum_i n_i \epsilon_i}{\sum_i n_i} = \frac{\sum_i \epsilon_i \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

It is convenient to identify the denominator as the **partition function** Z:

$$Z = \sum_i \exp(-\epsilon_i/kT)$$

We can regard it as the *effective number of energy states accessible to the system*. This makes sense since in our average, it is the normalization (and the normalization in the average is typically the number of things you are averaging).

There is another important relationship to keep in mind with partition functions. Since energies of a system are additive (eg $\epsilon_{\text{total}} = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{int}}$) and often the states of a system can be decomposed into translational, rotational, vibrational, etc degrees of freedom, one can break down the partition function

$$Z = \sum_i \exp[-(\epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{int}})/kT]$$

into several parts

$$Z = \sum \exp(-\epsilon_{\text{trans}}/kT) \sum \exp(-\epsilon_{\text{rot}}/kT) \sum \exp(-\epsilon_{\text{vib}}/kT) \sum \exp(-\epsilon_{\text{int}}/kT)$$

and thus, we can write

$$Z = Z_{\text{trans}} \times Z_{\text{rot}} \times Z_{\text{vib}} \times Z_{\text{int}}$$

This is very useful since it allows us to break up our problem into manageable parts.

11.4.2 Entropy

To think about the entropy, let's consider that the system has N particles. Each of these particles are in certain states. Indeed, the n_i indicate how many of these particles are in state i and the sum of these $\sum_i n_i = N$ is the total number of particles N.

The entropy is the ln of the number of rearrangements of these particles within these energy levels. For example, if all of the particles are in the ground state, then $n_0 = N$ and $n_{i>0} = 0$. In this case, there is only one arrangement (all in the ground state). However, if half are in the ground state $n_0 = N/2$ and half are in the first excited state $n_1 = N/2$ then there are a lot of ways of arranging these particles. How many? Think of it as the number of ways of arranging particles in boxes. For two boxes, this is

$$W = \frac{N!}{n_0! \times n_1!}$$

and for many boxes this generalizes to

$$W = \frac{N!}{n_0! \times n_1! \times \cdots}$$

Since the entropy is related to the number of arrangements W by

$$S = k \ln W$$

then we need to calculate

$$\ln W = \ln N! - \ln n_0 - \ln n_1 - \cdots = \ln N! - \sum \ln n_i$$

If N and n_i are large, we can use Stirling's approximation

$$\ln N! \approx N \ln N - N$$

(which by the way is remarkably accurate and can give good results for even small N). Thus, we find that

$$\ln W = N \ln N - N - \sum (n_i \ln n_i - n_i)$$

but since $N = \sum n_i$, we get

$$\ln W = N \ln N - N \ln n_i = N(\ln N - \ln n_i) = N \ln(N/n_i) = -N \ln(n_i/N) = -\sum n_i \ln(n_i/N)$$

and thus

$$S = -Nk \sum \frac{n_i}{N} \ln \frac{n_i}{N} = -Nk \sum p_i \ln p_i$$

We derived a similar result when we talked about the mixing entropy. One way to think about this very fundamental result is that $\Delta S = \ln n_i$ for state i and the probability of finding state i is p_i and thus it is not surprising to find an entropy of this form.

11.4.3 Partition functions and free energy

Finally, let's use our result for the energy and entropy to derive the relationship between the partition function and the free energy. We know that $F = U - TS$. Let's solve this for the entropy: $S = U/T - F/T$. Now let's write S in terms of Z. To do this, we say that

$$S = -Nk \sum p_i \ln p_i$$

and that the probabilities are given by Boltzmann weights

$$p_i = \frac{\exp(-\epsilon_i/kT)}{Z}$$

Taking the ln we get

$$-\ln p_i = \frac{\epsilon_i}{kT} + \ln Z$$

Substituting this in, we get

$$S = -Nk \sum p_i \ln p_i = Nk \sum p_i \left(\frac{\epsilon_i}{kT} + \ln Z \right) = Nk \left(\frac{1}{kT} \sum p_i \epsilon_i + \ln Z \sum p_i \right)$$

Since $\sum p_i = 1$ and $\sum p_i \epsilon_i = \langle \epsilon \rangle = U/N$, we get

$$S = Nk \left(\frac{U}{NkT} + \ln Z \right) = \frac{U}{T} + Nk \ln Z$$

But since $S = U/T - F/T$ we immediately see that

$$F = -NkT \ln Z$$

Thus, we see that F is directly related to the partition function. We are now in a position to think about how all of this comes together. We can think of the partition function $Z = \exp(-F/kT)$ as the weight of the system, just as $\exp(-\epsilon/kT)$ is the weight of a single microstate. In the case of the system

$$Z = \exp(-F/kT) = \exp[-(U - TS)/kT] = \exp(-U/kT)\exp(S/k) = \exp(-U/kT)\Omega$$

where $\Omega = \exp(S/k)$ is the number of arrangements ($S = k \ln \Omega$). We see that the Boltzmann weight ($\exp(-U/kT)$) and the number of arrangements (Ω) join together in the partition function just as the energy and entropy join in the free energy. Thus, the system can be likely to be found due to low energy (and thus high Boltzmann weight) or high entropy (and thus high Ω).

Moreover, when we have talked about equilibrium, we said that the free energy reaches some minima (eg with respect to some desired macroscopic property such as volume or magnetization). In this case, we are comparing the free energies of different macrostates (eg $F(V)$) and seeing which macrostate is more likely.

It is important to stress that here Z is the **single particle partition function**. In non-interacting systems, we can write the total partition function of the whole system as the product of N single-particle partition functions (just as we divided Z into translational, vibrational, etc parts)

$$Z_N = Z \times Z \times \cdots = Z^N$$

for an ideal solid and

$$Z_N = \frac{1}{N!} Z \times Z \times \cdots = \frac{1}{N!} Z^N$$

for an ideal gas.

11.4.4 Deriving *everything* from the partition function

I said earlier that with the knowledge of just n_i and ϵ_i we can calculate all thermodynamic properties. One of the easiest way to see this is via the partition function. Moreover, knowledge of the partition function allows us to make even more connections than we could with just thermodynamics. This makes sense, since there is more information in the partition function — information about the microscopic properties, which is lacking in a thermodynamic description.

For example, let's consider some derivative tricks with the partition function. We can write U in terms of the partition function by noticing that if we say that $\beta \equiv kT$ then

$$\frac{U}{N} = \langle \epsilon_i \rangle = \sum_i \epsilon_i P_i = \epsilon_i \frac{\exp(-\beta\epsilon_i)}{Z} = -\frac{\partial}{\partial\beta}\frac{1}{Z}\sum_i \exp(-\beta\epsilon_i) = -\frac{1}{Z}\frac{\partial}{\partial\beta}Z = \frac{\partial(-\ln Z)}{\partial\beta}$$

where we have used the mathematical identity $d(\ln y)/dx = (1/y)dy/dx$. Perhaps this is no big surprise, since we can relate U to F/T via derivatives of $1/T$ using thermodynamics.

We can use similar thermodynamic relationships to derive other quantities. For example:

$$S = -\frac{\partial F}{\partial T} \qquad C_V = \frac{\partial U}{\partial T}$$

etc.

We will use these thermodynamic relationships to quickly calculate these quantities from the free energy (which we will get from the partition function).

11.5 Examples and applications

11.5.1 Ideal gases: the translational partition function (classical style)

Classically, we would say that since an ideal gas just models particles wandering around a box, but does not model their interaction, we could say that the energy of the ideal gas is just its kinetic energy:

$$\epsilon = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

where m is the mass of the particle.

To calculate the partition function in this case, we need to sum over all of the microstates. When we discussed microstates, we talked about how they include all of the possible configurations. In terms of entropy, we purely refer to configurations in terms of positions of particles. However, to calculate partition functions, one must include all of the relevant degrees of freedom to describe these particles. This must include the momenta of the particles.

Since the movement in the x, y, and z directions are not correlated, we can treat each independently. We calculate the partition function as

$$Z = \sum_v \sum_x \exp[-\epsilon(v,x)/kT]$$

Now, we know that the energy only depends on the velocity and has the form (in one-dimension) $\epsilon = \frac{1}{2}mv^2$. Thus, we find

$$Z = \int dv \int dx \exp[-mv^2/2kT]$$

We have written the sums as integrals to make the math easier. This is physically reasonable since there will essentially be a continuous spectrum of positions and velocities. We find

$$Z = \int dv \exp[-mv^2/2kT] \int dx = \int dv \exp[-mv^2/2kT] l = \left(\frac{\pi kT}{2m}\right)^{1/2} l$$

Note that the integral $\int dx = l$, where l is the length of the box and we have used the integral

$$\int dv \exp(-v^2/a) = \frac{\sqrt{\pi a}}{2}$$

where $a = 2kT/m$ above.

In three dimensions, we say that

$$Z = Z_x Z_y Z_z = \left[\left(\frac{\pi kT}{2m}\right)^{1/2} l\right]^3 = \left(\frac{\pi kT}{2m}\right)^{3/2} V$$

where $l^3 = V$ is the volume of the box.

Ok, let's calculate the free energy and dissect what we've got here:

$$F = -NkT \ln Z = -NkT \ln V - \frac{3}{2} NkT \ln\left(\frac{\pi kT}{2m}\right)$$

Well, there are some familiar terms. Recall that the entropy went something like $-NT \ln V$ and we see that here, but what about this other junk? Let's calculate the energy first:

$$U = \frac{d(F/T)}{d(1/T)} = Nk \frac{d \ln Z}{d(1/T)} = \frac{3}{2} Nk \frac{d}{d(1/T)} \ln\left[V\left(\frac{\pi k}{2m(1/T)}\right)\right] = \frac{3}{2} NkT$$

Moreover, this 3 comes directly from the 3 dimensions (or 3 degrees of freedom). For d degrees of freedom ($Z = (Z_x)^d$), we get

$$U = \frac{d}{2} NkT$$

Which is the result we talked about earlier with heat capacities.

The entropy is a bit more strange. We can calculate the entropy by

$$S = -\frac{dF}{dT} = Nk \ln V + \frac{3}{2} Nk \ln\left(\frac{\pi kT}{2m}\right) + \frac{3}{2} Nk$$

This equation is called the **Sackur-Tetrode** equation. We see the familiar term $Nk \ln V$ but there are other terms. These other terms comes from the kinetic energy contributions — something that we neglected in our thermodynamic calculations.

To finish the job, we can calculate

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V}\left[-NkT \ln V - \frac{3}{2} NkT \ln\left(\frac{\pi kT}{2m}\right)\right] = \frac{NkT}{V}$$

and thus we find that $PV = NkT = nRT$ as we would have expected.

11.5.2 Ideal gases: the translational partition function (quantum style)

We can also do this calculation from a purely quantum mechanical point of view. When done quantum mechanically, there is no mystery about why we should include velocities into the partition function. We find that the translational energy can be written as

$$\epsilon = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

Again, we can solve the problem in one-dimension and then multiply partition functions. Thus, we need to calculate

$$Z = \sum_{n_x=1}^{\infty} \exp(-n_x^2 h^2/8ml^2kT)$$

However, since the energy levels are very close together, we can approximate this sum with an integral over n_x

$$Z = \int_0^{\infty} dn_x \exp(-n_x^2 h^2/8ml^2kT)$$

Note that this integral is remarkably similar to the classical version! Again, we use

$$\int dv \exp(-v^2/a) = \frac{\sqrt{\pi a}}{2}$$

where in this case $a = 8ml^2kT/h^2$ and we find that

$$Z = \frac{(\pi)^{1/2}}{2}\left(\frac{8ml^2kT}{h^2}\right)^{1/2} = \left(\frac{2m\pi kT}{h^2}\right)^{1/2} l$$

This form is very similar to the classical version. Indeed, both are of the form

$$Z = (AkT)^{1/2}\, l$$

This is the most important aspect. Indeed, the A constant will drop out of many thermodynamic quantities (eg P, U, and C_V) and we get the same answer. Why should there be a difference in values of A? The quantum mechanical calculation is more accurate about the quantization of momenta and this is what leads to a difference in the constants.

In particular, since the equation of state is calculated by $P = -dF/dV$, the most important part of the free energy (in terms of the equation of state) is the volume dependence. This is independent of A.

11.6 Compuational methods for calculating thermodynamic quantities

We have spent much time talking about how to mathematically calculate thermodynamic properties of a system. In principle, this can be done for any system. In practice, it is often difficult to calculate partition functions or any other thermodynamic quantity. Instead, we often use computer simulations.

Simulations serve as a means to directly test whether our explanation of reality (in terms of a model) is correct. In particular, one can often measure anything one would want in a simulation and thus one can both compare simulation result to experiment, as well as use simulations to further interpret experimental data.

There are several ways in which simulations are used in thermodynamic calculations. Here I will present three common approaches.

11.6.1 Exact enumeration

In many systems, one can simply calculate the partition function exactly on the computer (even though it may be hard to do this mathematically). For example, consider a spin system with N spins. We could have the computer run through all of the 2^N spin possibilities and directly calculate the partition function

$$Z = \prod_{i=1}^{N} \sum_{s_i=\pm 1} \exp(-\epsilon/kT)$$

This method is in particular useful when we say that there are interactions between the spins. Interaction is difficult to calculate mathematically, but much more straightforward computationally.

Another example is in polymer systems. For a polymer chain of N monomers, one can try to enumerate all of the possibilities. Often, due to particular aspects of the chemistry of the polymers under study, only particular bond angles and dihedral angles (isomerations) are possible. This allows one to think of the space of polymer arrangements as being discrete (due to the discrete number of isomers) and thus enumerate all of the configurations.

Enumeration is a great means to do calculations since we have directly included all of the microstates into our calculation of the partition function. However, since the number of microstates exponentially increases with the system size N [16], enumeration is often only practical for small systems.

11.6.2 Monte Carlo

It would be great if would only need to sample some subset of all of the microstates and still get good thermodynamic results. This would be fine if we could sample microstates based upon their Boltzmann weights: states with high probability would be sampled a lot (since they are a major contribution to the thermodynamic calculations) and states with low proabability are sampled infrequently (which should be ok, since these do not matter that much anyway). This is much like trying to poll voters.

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[16] We know that this must be the case since entropy is extensive. In this case, we can write $S = Ns$, where s is the entropy per particle. Since $S = k \ln W$, we get $W = \exp(S/k) = \exp(Ns/k)$, i.e. we get an exponential relationship between the number of microstates W and the system size N.

TV news predicts elections based upon small, *but representative* subsets of the total electorate. If we pick such as representative subset, then we can avoid doing a complete enumeration.

But how are we going to do this? Well, let's try to use our knowledge of thermodynamics to our advantage. In particular, we know from thermodynamics that in order to calculate state functions, the path is irrelevant. For this reason, it makes sense to choose a path which is easy to calculate (why make life tougher than it has to be?). Thus, a Monte Carlo calculation is broken up into two parts: (1) choosing "moves" which define the path; and (2) calculating whether the move is accepted or rejected.

Let me illustrate this with an example. Consider trying to study a gas. We can say that in our simple model of a gas, the gas "particles" stick to a lattice. In this case, our "moves" are naturally chosen to be moving one lattice space in each possible direction.

In terms of evaluation of moves, one typically uses the **Metropolis criterion.** This criteria goes as follows: calculate the original energy of the system E_o. Next, make a move (eg choose one of the directions at random) and then calculate the energy of the new configuration E_n. If $E_n < E_o$, then we accept the move. If $E_n > E_o$, we pick a random number R with $0 \leq R \leq 1$. If $R < \exp[-(E_n - E_o)/kT]$ then we also accept the move, otherwise we reject it. What we're doing here is choosing moves with a Boltzmann weight. This is important since it is this property which ensures that we are making moves which are thermodynamically reasonable.

What we get out from these simulations is thermodynamic data, such as free energies, heat capacities, energies, entropies, etc. Since thermodynamics does not depend on the path (for state functions), simple moves (and often simple models) can give good, quantitative results. This is a good example of how thermodynamics concepts really helps in research, even if we aren't using thermodynamics directly.

11.6.3 Molecular dynamics

Finally, instead of appealing to thermodynamic arguments, we can also just think about the natural dynamics of our problem and try to simulate how our system actually works. One way to do this is to directly simulate Newtonian dynamics. By this I mean, we can write Newton's equations of motion for each particle i:

$$F = -\nabla U = m_i \frac{d^2 \vec{r}_i}{dt^2} = ma$$

where U is the potential energy, m_i is the mass of i, $\vec{r}_i$ is the position of i, and t is the time.

One can rewrite this differential equation in many ways in order to numerically solve it. I won't go into too much more detail on how this is done, but I will mention that thermodynamics results do come naturally from these calculations as well, since Newton's equations are certainly consistent with the laws of thermodynamics. In many ways, the real challenge of these simulations is to start with particles and Netwon's equations and to try to extract out some deeper understanding, much like when we found that it was entropy that "pushed" an ideal gas to expand to fill the entire volume possible. *Thus, reproducing nature is only (at best) half of the battle: understanding it is the real challenge!*

A Review

To end the class, I want to review what we have learned. I think you have done a great job understanding most of the important concepts, so here I'll try to touch on those aspects which seemed to give people the most trouble on the problem sets and exams as well as a few things which I think most people have trouble with in general.

A.1 Top 10 confusions/surprises/difficulties with thermodynamics

10. **Legendre transforms**

    For example, we can define new potentials from the Gibbs by saying that $dG = dw_{\mathrm{add}}$ then

$$dG' = dG - \left(\frac{dG}{dX}\right) X = dG - \left(\frac{dw_{\mathrm{add}}}{dX}\right) X$$

9. **Pairwise interaction**: Since the density ρ acts like a probability, we can say that $U/V = a\rho^2$

8. **Electrochemical equilibrium**: $\mu(\alpha) = \mu(\beta)$ not $\mu'(\alpha) = \mu'(\beta)$

7. **Statefunctions**: independent of path (reversible or irreversible)

6. **Entropy can act as a force**:

$$P = -\frac{dF}{dV} = -\frac{dU}{dV} + T\frac{dS}{dV}$$

    Also: consider what "pushes" an ideal gas to fill the whole volume?

5. **Micoscopic interpretation of entropy**: entropy (S) is related to the ln of the number of microstates (W) by $S = k \ln W$. A single microstate "has" only one microstate and thus has no entropy $\ln 1 = 0$.

4. **Equilibrium is found by minimzing the appropriate statefunction** (eg $dF/dx = 0$ for constant N, V, and T) but we can always calculate that statefunction (just doesn't have the same meaning).

    Minimizing means $dF/dx = 0$ not $F = 0$.

3. **Reversible systems are always at equilibrium.**

2. $\Delta U = 0$ **for an ideal gas only at constant temperature.** In other words, U depends only on temperature. In fact, we found that $U = (d/2)nRT$ where d is the number of degrees of freedom.

1. **Work on the system vs work by the system.** Keep the minus signs straight!

A.2 Top 11 important equations

These certainly aren't the only important equations, but if you can just remember these, you'll be in pretty good shape throughout your career in chemistry.

11. $Z = \sum_i \exp(-\epsilon_i/kT) = \exp(-F/kT)$ (link between free energy and partition function)
10. $p_i = \exp(-\epsilon_i/kT)/Z$ (Boltzmann probabilities)
9. $S = -Nk \sum_i p_i \ln p_i$ (stat mech view of entropy)
8. $\mu = \mu^0 + RT \ln(P/1\mathrm{atm})$ (pressure dependence of μ)
7. $P = xP^*$ (Raoult's law)
6. $\Delta U = q + w$ (1st law, conservation of energy)
5. $dS = dq_{\mathrm{rev}}/T \geq dq/T$ (2nd law)
4. $\Delta G = -RT \ln K$
3. $\mu_i = (dG/dn_i)$ (definition of chemical potentials)
2. $C = dq/dT$ (definition of the heat capacity)
1. $G = H - TS$ (definition of Gibbs free energy)
1. $F = U - TS$ (definition of Helmholtz free energy)

A.3 Top 10 important concepts

It's hard to summarize a course into a top ten list, but here goes.

1. Equilibrium
2. Reversibility
3. Statefunctions and Thermodynamic potentials
4. Free energy
5. Entropy
6. Work and Heat
7. First law: best you can do is break even
8. Second law: You can only break even at $T = 0$, otherwise $\Delta S > 0$ and lose something to entropy
9. Phases, phase transitions, and phase equilibrium
10. Statistical interpretation of thermodynamics