CHEM-203 Survey of Physical Chemistry

Lecture summaries for the Second Law of Thermodynamics

Bryan Sanctuary

McGill University

Reading from Laidler, Meiser, Sanctuary: Physical Chemistry

Chapter 3
Sections 3.1 up to and including 3.7; 3.10 (skip Refrigeration and liquefaction, and Chemical Conversion).

Chapter 4
Sections 4.1 up to and including 4.3; 4.6.

Problems:
Chapter 3:
The Carnot Cycle: 3.1-3.5
Entropy Changes: 3.7-3.20, 3.25-3.36
Gibbs and Helmholtz energies: 3.37-3.48

Chapter 4:
Equilibrium Constants 4.1 - 4.15
Equilibrium Constants and Gibbs Energy Changes 4.16 - 4.24
Temperature Dependence of Equilibrium Constants 4.25 - 4.32

Start of Material for second midterm examination.

Chapter 3:

Chapter 4:

Note that the First Law, covered in the first midterm, is NOT directly covered in the second midterm. However, of course, you need to know the First Law to understand the Second Law.

Summary Lecture 14 (Top)

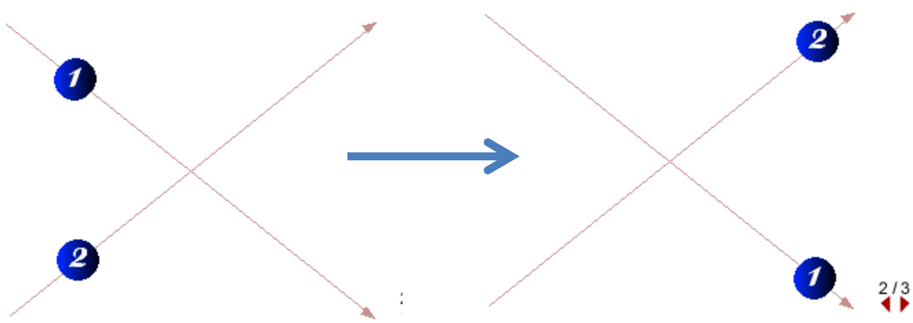
I finished up the reversible ideal gas calculations from Chapter 2.6 for and adiabatic process. You should know:

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$ adiabatic reversible process with $T_1 \neq T_2$
$P_1V_1 = P_2V_2$ isothermal reversible process with $T_1 = T_2$

I finished up by pointing out the for all these processes the enthalpy and internal energy are always given by

$$\Delta U = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

But this is special for an ideal gas. Recall the kinetic molecular model assumes elastic collisions and I pointed out that elastic collisions conserve energy and momentum and can be ignored. Elastic collisions, like billard balls, are like the collision never took place:



But real gases have forces and inelastic collisions. Real molecules attract and repel each other, so if the volume decreases then the molecules are closer together and the forces can play a role that is absent in idea gases. We can express this generally using Thermodynamics by writing a total derivative,

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

We know the first term already and we used it for the ideal gas. The second term reads: $\left(\frac{\partial U}{\partial V}\right)_T$ at constant temperature, the internal energy of a system changes as the volume changes, as it does for real gases, liquids, solids and anything with intermolecular forces, which is pretty much anything, but not for an ideal gas.

Chapter 3 covers the Second Law of Thermodynamics

We will cover a good deal of all sections except 3.8 which will be skipped.

Energy: can use it to heat and do work

Entropy: a qualitative measure of the randomness of a system.

Things randomize spontaneously and the drive to randomize is a natural driving force behind many processes that can happen, even though the energy might increase. We mentioned examples of melting and freezing water; denaturing DNA, and the endothermic reaction:

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

Note here that we have to break two bonds to dissociate $\mathrm{N_2O_4}$, so we have to put energy into the system. Hence the process is endothermic but is still spontaneous (at high enough temperatures) because on the LHS there is one mole of gas and on the RHS there are two. Hence the RHS is more random than the LHS and so the entropy increases. This drives the process and overcomes the need for energy to be absorbed to break bonds.

I will use a number of ways of expressing the Second Law, and one of these states that for all spontaneous processes in an isolated system the entropy must increase. Since the Universe is an isolated system we can write,

$$\Delta S_{\mathrm{Universe}} \geq 0$$
$$\Delta S_{\mathrm{System}} + \Delta S_{\mathrm{Surroundings}} \geq 0$$

The second lines recognizes the universe can be divided into a system and its surroundings, so there is nothing wrong if the system decreases in entropy, (like a biological entity, or the freezing of water, etc.) as long as the surroundings compensates. A living system is very ordered and organized and so has low entropy. This molecular order was attained by randomizing the surroundings (eating) which leads to much greater disorder and satisfies the Second Law.

The equality signs hold for reversible processes (which of course we can never fully realize but we can imagine them). A good definition of a reversible process is $\Delta S_{\mathrm{System}} = -\Delta S_{\mathrm{Surroundings}}$.

The Second Law combines both energy and entropy into two fundamental functions:

The Helmholtz energy: $A = U - TS$

The Gibbs energy: $G = H - TS$

We will come back to these. However let me add here that A and G can always have values under any conditions, and are different ways of looking at the same system. However at constant T and V (and only at constant T and V) the Helmholtz energy is a minimum at equilibrium. At constant T and P the Gibbs energy is a minimum at equilibrium.

These simple statements are critical to deciding if a process will take place or not.

Note the minus sign. If entropy change is positive, it makes A and G more negative and drives them to a minimum. The energy, U or H are negative for exothermic processes, they too help A and G become more negative, again driving the process to a minimum. Play with the signs of energy and entropy in the above to see how changes are spontaneous or not depending on the temperature.

I will say these things many times.

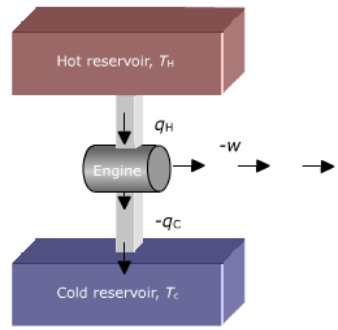
Note that entropy has the units of $[S]=\mathrm{JK^{-1}mol^{-1}}$.

Whenever we have a process that is driven by disorder, we have to do work is we wish to order the system again. Recall that work is the ordered use of energy and heat is the disordered use of energy. So if we disorder something we must do work if we wish to reverse the process and try to get back to the same state: Humpty Dumpty syndrome.

Summary Lecture 15 (Top)

Thermodynamic entropy.

We will use the Carnot cycle to mimic the four strokes of a steam engine. The steam engine is a heat engine. It draws in hot matter, steam, which pushes cylinders and cools as the work is done. Then it exhausts cold steam into the environment.



- The hot reservoir is the heat we pay for.
- The engine is the system and energy is measured relative to it.
- The cold reservoir is the outside environment.

Heat q_H goes into the system and heat $-q_c$ goes out. In the process $-w$ work is done by the engine. The difference between the heat in and out is the work out,

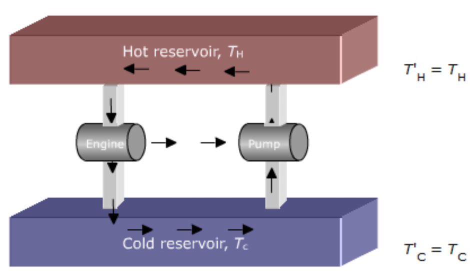
$$-w = q_H - (-q_c)$$
$$-w = q_H + q_c$$

Since we pay only for the hot heat, efficiency is how much work we can get out for the heat in,

$$\varepsilon = \frac{-w}{q_H}$$

Before doing the Carnot cycle, I mentioned a few things. The first steam engines with one cylinder were about 3% efficient; two cylinders about 8% efficient. Today they are about 40% efficient. Heat exchanges are more efficient today. Heating a house with a boiler is now 94% efficient. Efficiency drove the development of thermodynamics.

We looked at the reverse of a heat engine which is the heat pump. You could couple a heat engine to a heat pump and try to get perpetual motion. It is impossible to attain because of engine loses like from friction. However we can come to a logical conclusion because there is a maximum theoretical efficiency that we will get to. The observation is:



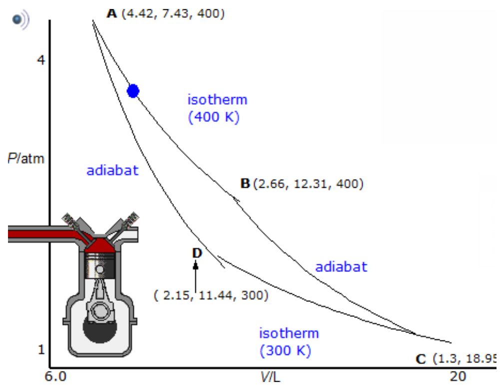
The maximum efficiency of heat engines operating between the same heat reservoirs must be the same.

It will turn out that the maximum efficiency of a heat engine depends only on the difference in temperatures between the hot and cold reservoirs. The theoretical efficiency is 100% when the cold reservoir is at 0 K.

Note also that if a state function, like ΔU, is not zero around a cycle then we could create energy from nothing. This violates the first law.

The fact that we cannot extract work from the surroundings without disturbing it is another way of stating the second law.

The Carnot Cycle



We will relate the Carnot cycle to the four strokes of a steam engine and idealize it to reversible isotherms and adiabats. Around the cycle we will use an idea gas and calculate the heat and work. From this we will discover a new state function. That is of interest. By calculating that new state function we observe: in our experience that whenever a process is spontaneous, this new state function increases, and vice versa. By doing enough examples we come to the formulation of the Second Law.

Both the first and second laws are extremely concise and apply to all macroscopic processes we know.

Summary Lecture 16 (Top)

In this lecture we went around the Carnot cycle for an ideal gas and calculated the internal energy, heat and work change for each stroke of the heat engine. I will not repeat this and it is giving in section 3.1.

These calculations are straight forward and you should be comfortable with the values obtained and what they mean:

Isothermal expansion→ adiabatic expansion→isothermal compression→adiabatic compressions

Summary Lecture 17 (Top)

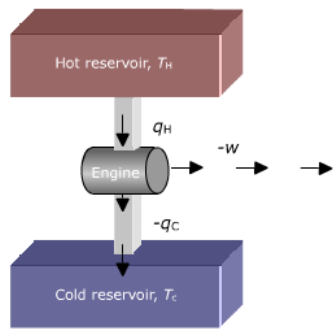
This is the hardest lecture of the course. I suggest you make sure you understand the consequences physically. The difficulty is with the signs and keeping them straight. Energy is positive if the system absorbs it and vice versa.

After studying the Carnot cycle some results emerged based upon trying to understand the efficiency of the heat engine. The engine has been idealized by assuming the four strokes can be approximated without losses (reversible) and that the energy balance is

$$-w = q_H + q_C$$

Efficiency:

$$\varepsilon = \frac{-w}{q_H}$$



State function (discovery of entropy) That is, the heat divided by the temperature around a closed cycle is zero (the details are in the book or my lectures):

$$\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$$

Maximum efficiency (Eq.(3.20) of the book needs a minus sign before the work). You will feel much happier about this if your follow the derivation and agree with each step below:

$$\varepsilon = \frac{-w}{q_H} = \frac{q_H + q_C}{q_H} \overset{\text{reversible Ideal gas}}{=} \frac{T_H - T_C}{T_H}$$

(Then re-arrange the above to get $\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$)

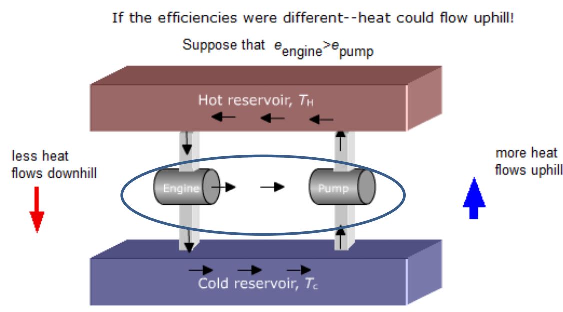
The maximum efficiency for a heat engine depends only on the difference of temperature between the hot and cold reservoir: the bigger the difference the greater the efficiency. Warm cars run more efficiently than those not warmed up.

Kelvin temperature scale: Efficiency cannot be negative or greater than 1. For greater than 1 it shows that the temperature difference must be positive. There is no efficiency for heat flowing from a colder to a hotter.

For efficiency of 1, $T_C = 0$. Since efficiency cannot be greater than 1, this sets the absolute zero of temperature so this was calculated by various experiments and found to be -273.15 C which is defined as 0 K.

Carnot's theorem: the maximum efficiency between two heat engines depends on the temperature difference between the hot and cold reservoirs. In another way: the maximum efficiencies of two heat engines operating between the same reservoirs must be equal.

The proof is to assume the efficiencies are unequal and find a contradiction, and that contradiction is: heat flows from a colder to a hotter, which is beyond our experience.

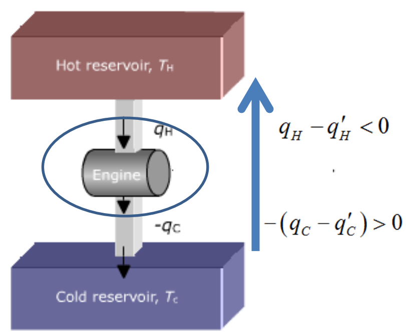


The maximum efficiency of heat engines operating between the same heat reservoirs must be the same. This is called Carnot's theorem.

Suppose (make sure you see how to get the second line—see book):

$$\varepsilon_A > \varepsilon_B$$
$$q'_H - q_H = q_C - q'_C > 0$$

where the primed heats refer to engine B and the unprimed to engine A. Since A is driving B then heat flows into A (q_H) and pumps less heat up from engine B (- q'_H),(we expect that less heat flows up than down), then it should follow that $q_H - q'_H > 0$ but it is opposite. That is more heat is flowing up, $-q'_H$ than flows down, q_H .



Since A is more efficient, we would expect that more heat is absorbed into the less-efficient than the more-efficient engine and so uses, $-(q_C - q'_C) > 0$, but it is opposite in the above. This is enough to show that the two efficiencies must be equal.

Another way to see this is to consider A and B as one engine. The arrows pointing down indicate our experience: heat flows from hot to cold, (the circled two engines are one with no work output: A drives B). However by assuming that the engine A is more efficient than B, we are led to the opposite result: the heat from the hot reservoir is negative $q_H - q'_H < 0$ so heat is not going into the engine, but flowing up to the hot reservoir out of the engine. We also see that the heat exhausted from the engine is $-(q_C - q'_C) > 0$ but is positive so heat is not exhausted, but taken in, *i.e.* flowing up the exhaust pipe! In summary if we assume the maximum efficiencies of two heat engines operating between the same heat reservoirs are different, we come to the wrong conclusion: heat spontaneously flows from the colder to the hotter. We have never experienced this so it must be wrong.

Hence the two efficiencies must be the same.

Perpetual motion is impossible:

- First kind, creates energy from nothing and violates the first law;
- Second kind, allows heat to flow uphill and violates the second law.

We also showed, Book Eq.(3.33)-(3.36) that entropy change is independent of the path taken which is a property of state functions.

I also did the irreversible paths in section 3.2. I will not repeat the equations but the main idea is the irreversible paths are not as efficient as reversible ones, so

$$\frac{q_H^{irr}+q_C^{irr}}{q_{H}^{irr}} < \frac{T_H - T_C}{T_H}$$

And from this follows the **Inequality of Clausius**:

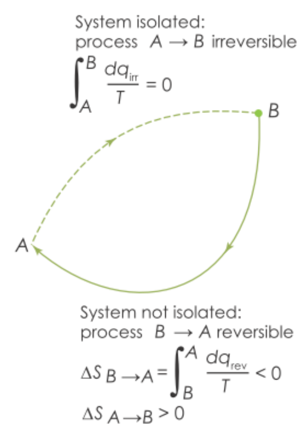
$$\oint \frac{dq^{irr}}{T} < 0$$

(Please go through it and see that it makes sense). The notation $\oint$ means $\int_A^A$ but going around a cycle.

If the cycle is reversible, then the result the state function called the entropy,

$$\Delta S = \oint \frac{dq^{rev}}{T} = 0$$

Going around a cycle where the process is spontaneous from A → B using an irreversible path (take it as adiabatic) and then going back B → A using a reversible path, shows that for a spontaneous process A → B, the entropy must increase (Figure 3.6), (the derivation is in the text: you will feel good when you understand it and may say to yourself, "yeah, makes sense.", "cool", "Its actually quite simple.", "That's why entropy always increases!" (why? By the way: because irreversible process are always less efficient that the reversible process), and so you understand the following equation:



$$\Delta S_{A\to B} > 0$$

greater than zero for all spontaneous processes, reversible or not.

In the next lecture I will summaries these ideas again. They are at the core of the second law which we have seen stated in a number of ways. The conclusion is that for any spontaneous process the entropy increases. Since the universe is an isolated system then the entropy of the universe is increasing—it gives a direction to spontaneity, a direction to time.

The entropy change for a system can be obtained from the reversible path and we find that for any <u>spontaneous</u> process that

$$\int_A^B \frac{dq_{rev}}{T} = \Delta S_{A \to B} > 0$$

We will then do calculations which are based on these ideas and this will give us deeper insight into the second law by studying the applications.

Summary Lecture 18 (Top)

I always think it is best to read the book after studying the material from other points of view. First you should understand what I am saying in class. Then there are problems to do. They really help to cement the material in your head. Use the solution manual of course, but be able to do the questions, eventually, without looking at the solutions. Do not rely on the solution manual because you will not have it for the final exam. Then you have my summaries of the lectures here. By the time you have gone through all that, reading the book will pull things together and give you an overview.

In studying the second law we have covered a good portion of chapter 3. After the introduction there is the Carnot cycle and the calculation around the cycle. Then we got to Carnot's theorem about maximum efficiency depending on the temperature only. We then talked about new state function, entropy, and found that we can always calculate it for the reversible path (Thermodynamic entropy),

$$\int_A^B \frac{dq_{rev}}{T} = \Delta S_{A \to B} > 0 \qquad \text{spontaneous}$$

This brings us up to section 3.3 which is the Molecular Interpretation of Entropy. I went into more detail because I want you to understand Boltzmann's formula (Statistical entropy)

$$S = k \ln W$$

The next thing to do is to use these expressions for the entropy and study it. That is calculating it in different cases. After that we get to the free energy.

I will not repeat the calculations I did in class. Basically they are from the book examples, 3.2 to 3.7. These include calculating entropy for various situations: mixing hot and cold water; a phase transition; the temperature dependence of entropy; freezing super cooled water. These illustrate how entropy of the universe increases when in our experience the process is spontaneous.

Please note how the entropy of the super cooled water and the surroundings at -10 C was calculated. Both the entropy and the enthalpy of fusion must be found at -10 C by "going around the loop". Then the heat lost in the freezing at -10 C is gained by the surroundings, also at -10 C. In most cases we consider the surroundings as a vast heat sink and so pumping heat in and out of the system will not change the temperature of the surroundings.

Please look at the values of the energy and entropy changes and understand the differences between the calculations at 0 C and -10 C. (Good idea for an exam question!) Glad I now have your attention!

The examples 3.2 to 3.7 are the types of calculations you should know. Note that we are always talking about the system and the surroundings. How they couple determines spontaneity. The more the entropy of the universe increases in a process, the greater the drive behind that process. We will find it useful to combine the energy and entropy into one equation for the free energy. You will want to understand the word "free".

In the remainder of this lecture I talked about the statistical entropy and related it to the thermodynamic entropy for an isothermal expansion. I will put it in the next lecture.

Summary Lecture 19 (Top)

In the next lecture I will show some movies of entropy of systems and talk about entropy some more. Entropy can be studied in two ways: discover it in thermodynamics (macroscopic). We did this and discover a new state function by studying the Carnot cycle. Experience which we obtain by calculating this new state function and this leads us to the Second Law: in any spontaneous process this new function increases. Call it the entropy.

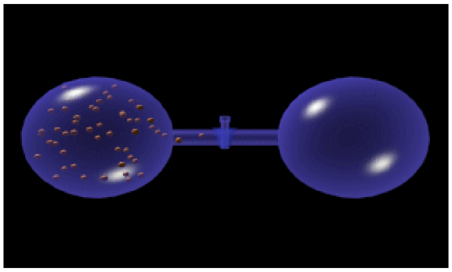
The second is the statistical entropy that comes from Statistical Mechanics. Equilibrium stat. mech. is a beautiful theory and applied to thermodynamics, called statistical thermodynamics, and with it all the thermo functions can be understood from microscopic processes.

But we will not study statistical mechanics. What we will do next time is show how Boltzmann used his expression for the statistical entropy to find that the overwhelmingly dominant states in a system are totally random, so much so that we can ignore all the ordered states. This is an important result and his equation can be found on his tombstone in Vienna,

$$S = k \ln W$$

Where k is the Boltzmann constant, $k = 1.38065 \times 10^{-23}\,\mathrm{JK^{-1}molecule^{-1}}$ which is a fundamental constant in Nature. The term W is an integer and represents the total number of states available to a system. It is a huge number as I will show.

Before discussing entropy (the second law) from thermodynamics, I want to give a physical understanding of what it means. In this and the next lecture that is the goal. Then we will turn to the Carnot cycle and understand it as an idealized process of repeated reversible cycles that extract the maximum work from heat.



The statistical description of the second law explains why when a system couples to another and a spontaneous process occurs. That is the system is driven to occupy all those accessible states in a totally random way.

An example of this is the bulb whence the particles on the LHS are constrained by the stopcock. Open the stopcock and the constraint is lifted so that many more states are suddenly available to the gas and it moves to occupy those states for no other reason except the drive to disorder.

There is a non-zero chance that the system could stay on the LHS. It is a possible and available state, but in your experience this has never happened. The chance that it would happen is so small that we can safely neglect it for the life of the universe. The second law says that will not happen.

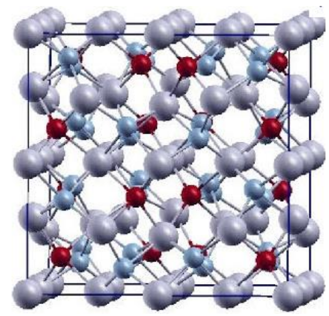
Using Boltzmann's equation, we see that the entropy increases when W increases,

$$\Delta S = S_2 - S_1 = k \ln \frac{W_2}{W_1}$$

And, similar to the two bulbs above, the number of accessible states on the LHS is W_1 with the stopcock closed, and this increases when the stopcock is opened to W_2. (You can see here that there is a relationship between the volume and the number of accessible states.) So when $W_2 > W_1$ the entropy increases.

Summary Lecture 20 (Top)

Because W is the number of accessible states, it is an integer and starts at 1. Then since $S = k\ln 1 = 0$ we start to count entropy from W=1. There is only one state at absolute zero for a perfect crystalline solid. If you know where one atom is, then every other atom in the crystal is predictable. The only motion at absolute zero is called zero point energy for vibration due to the Heisenberg Uncertainty Principle.



The Third Law of thermodynamics states that the entropy of a perfect crystalline solid at absolute zero of temperature is zero.

Hence entropy is quantitative and absolute (has a zero).

However the number of accessible states, W, increases enormously with temperature, size and other constraints. I gave the example of the size of W for a system with entropy of 200J K^{-1}.

$$S = k\ln W \rightarrow W = \exp\left(\frac{S}{k}\right) = \exp\left(\frac{200\ \text{JK}^{-1}}{1.38\times10^{-23}\,\text{JK}^{-1}}\right) = 10^{6.3\times10^{22}}$$

The number of accessible states mean things like all the places a particle can move to; if it can rotate, vibrate, absorb energy and emit it, change quantum states subject to constrains like temperature, pressure, volume, number of moles and any other factors like electric and magnetic fields.

Let us summarize this and say formally that:

A system rearranges itself and moves in to occupy all the states available to it.

To this I will add: the most random states is the most probable (subject to constraints).

Random states are so much more probable that any state that has order (like the gas staying in the LHS bulb) has a probability is so small that it can be neglected. This means that

$$W = W_{\text{ordered}} + W_{random} \cong W_{random}$$

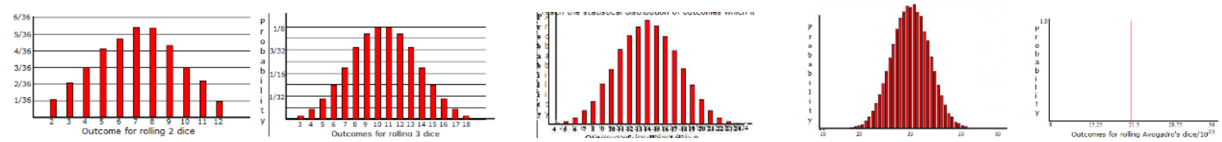
Order is knowledge. The more disorder there is, the less we know. A deck of 52 cards has 52!=8.06 x 10^{67} different ways to shuffle. If we define one order of the cards so we know from one card all the others, this is the perfect arrangement with total knowledge. Move one card and there are 52 ways you can put it in the deck, so you have less knowledge. The chance of a random shuffle giving you the perfect arrangement is 1/52! and improbable.

These examples and rolling dice have only a few states. Imagine if you have Avogadro's constant of dice.

We saw in rolling dice that the frequency that an outcome arose was greatest number of arrangements. There are 6 ways to roll a 7 and only 1 to roll a 2 or 12. The total number of arrangements is 6x6=36, so there is 1/36 chance of a 2 and 1/6 chance of a 7.

Formally would say: "There are six arrangements of two dice constrained to give an outcome of 7"

We can say the same for a system constrained to one mole, and a certain temperature, pressure and volume.

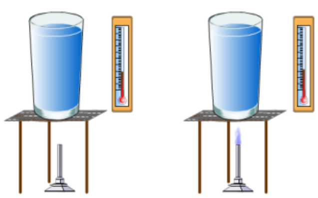


2 dice 3 dice 4 dice 10 dice 10^{23} dice

As the number of accessible states goes up, 6^n for *n* dice, the distribution sharpens showing that the most random disordered arrangments are most probable. For 10^{23} dice, the distribution is so sharp that only the random states can arise. The chance of deviations is small and called fluctuations.

Examples of disorder increasing:

solid liquid gas more vs fewer molecules more degrees of freedom



Cold vs. hot

In all spontaneous processes, constraints are being removed; systems are coupling and getting bigger; and in all these events, the randomness always increases. That is the main idea of randomness.

Entropy is useful in understanding chemical processes.

Summary Lecture 21 (Top)

We have already talked about the statistical entropy, $S = k\ln W$, and I hope that you have a feeling about its meaning-- $W = W_{\text{ordered}} + W_{\text{random}} \cong W_{\text{random}}$ as the number of accessible states (good definition to know for an exam!!) increase, so entropy is a measure of randomness.

In any spontaneous process W increases and so does the entropy. In other words, for spontaneous processes systems couple to each other and so W keeps increasing. As the number of accessible states increase, so does the entropy.

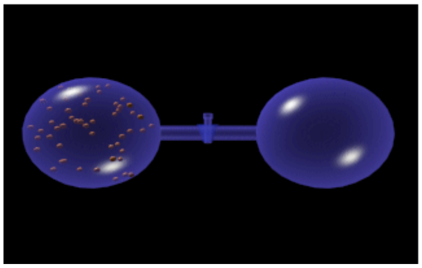
I wanted to show in this lecture is that the statistical entropy and the thermodynamic entropy are consistent. Let us isothermally and reversibly expand and ideal gas from one volume to another. The thermodynamic entropy is

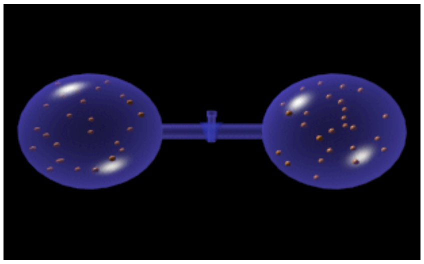
$$\text{isothermally and reversibly: } -w = q = RT\ln\frac{V_B}{V_A} \rightarrow S_{AB} = \frac{q}{T} = R\ln\frac{V_B}{V_A}$$

so

$$S_{V_1 \rightarrow V_1+V_2} = R\ln\frac{V_1+V_2}{V_1} \qquad (**)$$

In the figure we see the gas on the Left Hand Side (LHS) in volume V_1. Then at the end of the expansion the volume is $V_1 + V_2$ as seen in the second image to the right. Before the gas expands, its entropy depends on the number of states on the LHS and after the expansion; the number of states increased because the volume is larger.





Consider this case. We open the stopcock. The instant before the gas expands all the particles are still in the LHS. We can ask what is the probability that ONE molecule is on the LHS when the stopcock is opened? It is (make sure this makes sense)

$$P_{LHS} = \frac{V_1}{V_1+V_2}$$

Now the probability of N molecules being on the LHS is,

$$\left(P_{LHS}\right)^N = \left(\frac{V_1}{V_1+V_2}\right)^N$$

(Note that if the volume doubles ($V_1 = V_2$)then the probability that all the particles are on the LHS is

$$\left(P_{LHS}\right)^N = \left(0.5\right)^{6\times 10^{23}} \approx 0$$

This is why you never find all the particles on the LHS when the whole volume is available to them.)

Back to the expansion: now the chance of a particle being in both volumes is 100% or 1. Therefore we can use the statistical entropy and write it as the ratio of the probability the particles are in both volumes somewhere compared to the probability that they are all in their initial state on the LHS,

$$S_{V_1 \to V_1 + V_2} = k \ln \frac{W_1 + W_2}{W_1} = k \ln \frac{\left(W_1 + W_2\right)/\left(W_1 + W_2\right)}{W_1/\left(W_1 + W_2\right)} = k \ln \frac{1}{\left(P_{LHS}\right)^N}$$

Now simply substitute the probability and get the same result as an isothermal expansion of the ideal gas:

$$S_{V_1 \to V_1 + V_2} = k \ln \frac{1}{\left(\frac{V_1}{V_1 + V_2}\right)^N} = k \ln \left(\frac{V_1 + V_2}{V_1}\right)^N = Nk \ln \left(\frac{V_1 + V_2}{V_1}\right) = R \ln \left(\frac{V_1 + V_2}{V_1}\right)$$

This is the same as Equation (**). Hence we have shown that the thermodynamic and statistical entropy are consistent and make physical sense.

This was Boltzmann's thinking when he found his statistical expression. He knew the second law of thermodynamics and he believed that entropy must be a function of the number of accessible states, W. Therefore he wrote in the most general way,

$$S = f\left(W\right)$$

How to find the function? He realized that W is related to the probability as we have seen above, and the probabilities that events occur is a product, *e.g.*

$$\left(P_{LHS}\right)^N = \overbrace{P_{LHS} \times P_{LHS} \times \ldots P_{LHS}}^{N \text{ times}}$$

On the other hand, entropy is an extensive quantity that is additive,

$$S = S_A + S_B = f\left(W_A\right) + f\left(W_B\right)$$

There is only one function that has this property and that is the logarithm, hence Boltzmann surmised,

$$S = a \ln W_A + b$$

(Remember the old problem: a snake population was dying out because they were adders and could not multiply. To save them, the adders were put on log tables, so then they could multiply—groan).

This is the most general form. If we set the entropy to zero at T=0 K then W=1 and

$$S = a \ln W_A + b \rightarrow 0 = a \ln 1 + b \rightarrow b = 0$$

This choice of b is another way to define absolute zero and ensures that temperature cannot be negative. The constant a can be obtained by comparing with thermodynamic calculations. For example above we found

$$S_{V_1 \rightarrow V_1 + V_2} = k \ln \left(\frac{V_1 + V_2}{V_1} \right)^N$$

And from this we can deduce the constant $a = k$.

Summary Lecture 22 (Top)

The temperature dependence of entropy by doing a Hess' law calculation

$$2A \rightarrow B$$

$$S(T) = S^o(298) + \int_{298}^{T} \frac{dq}{T} + \int_{T}^{298} \frac{dq}{T} = S^o(298) + 2C_V(A)\int_{298}^{T} \frac{dT}{T} + C_V(B)\int_{T}^{298} \frac{dT}{T}$$

$$= S^o(298) + 2C_V(A)\ln\frac{T}{298} + C_V(B)\ln\frac{298}{T}$$

the entropy of a phase transition at the normal melting point, T_o,

$$A(s) \rightarrow B(l)$$

$$S_{\text{melting}} = \frac{\Delta H_{\text{melting}}}{T_o}$$

We will do a number of other problems, but now you can start doing problems in the text book. Again please let me know if you find errors in the solution manual. I will check and update the questions as fast as I can.

We will do more examples (problems) later on how entropy changes with volume and pressure. I rushed through an example at the end of the lecture: mix hot (100 C) and cold (0 C) water together, say one mole of each, and the final temperature is 50 C. Calculating the entropy change shows that for this process the entropy increases. This makes sense because mixing hot and cold water is irreversible. The system will not spontaneously separate into hot and cold regions again.

We are almost through the second law. Here is a summary of all the second law points:

- Do text examples 3.2 to 3.7.

The following problems are relevant:

- The Carnot Cycle: 3.1-3.5
- Entropy Changes: 3.7-3.20, 3.25-3.36
- Gibbs and Helmholtz energies: 3.37-3.48.

1. √ Meaning of entropy: randomness: $S = k\ln W$
2. √ Carnot cycle and theorem
3. √ Kelvin scale
4. √ For a spontaneous process we have found that the entropy for a system is,

$$\int_A^B \frac{dq_{rev}}{T} = \Delta S_{A\rightarrow B} > 0$$

5. √ Kelvin scale is defined
6. √ Calculations like the problems above.
7. Third Law and frozen disorder
8. Equilibrium
9. Gibb's energy
10. √ Skip section 3.8 and 3.9
11. √ 3.10 efficiency

We have done (√) 1 to 6 and 10. This lecture I talked about third law entropy.

I then discussed the entropy of mixing as found in the book starting from Eq.(3.58) and I will not repeat that here.

Summary Lecture 22 (Top)

I also pointed out that configurational entropy is really about knowledge. An ordered deck of cards must be defined and you must know it (that is, its configuration one card after another). Then W=1 for that knowledge—perfect order. The entropy changes when shuffling a deck so you have no knowledge. So the change in entropy between the ordered arrangement and the most random is,

$$\Delta S = k \ln \frac{W_{\text{shuffled}}}{W_{\text{ordered}}} = k \ln \frac{(52)^{52}}{1} = 1.12 \times 10^{-19} \text{ J K}^{-1}$$

The power to 52 is because each of the 52 cards can be arranged in any one of 52! ways. The reason the entropy change is so small is that 52 cards is a small number relative to the number of particles in a mole. The Boltzmann's constant is $k = 1.38 \times 10^{-23}$ J K^{-1}. It is a fundamental constant and one can think of it as a "quantum of entropy" because the smallest entropy change is proportional to k. So if W increases by 1 state we have an entropy change of,

$$\Delta S = k \ln \frac{W+1}{W}$$

I ended by saying that the free energy combines the surroundings into the system to obtain the free energy. The following are the steps,

$$\begin{aligned}
&\Delta S_{\text{Univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \\
&\Delta S_{\text{sys}} - \frac{q}{T} \geq 0 \qquad \text{constant } T \\
&\Delta S_{\text{sys}} - \frac{q_P}{T} \geq 0 \qquad \text{constant } T, P \\
&\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0 \quad \text{drop "sys"} \\
&\Delta G \equiv \Delta H - T\Delta S \leq 0 \\
&G = H - TS
\end{aligned}$$

We will come back to this but what we have done is to consider only the system energy and entropy and find that at constant temperature and pressure the Gibb's free energy tends to a minimum. At equilibrium it is a minimum under these conditions. This is a useful state function and you will encounter it many times in your studies. Before that we look at the Third Law of Thermodynamics.

Summary Lecture 23 (Top)

Third Law of Thermodynamics

Using $S=k\ln W$ then a perfect crystalline solid has W=1 and S=0. Careful experiments were done using thermodynamic heat capacities and accurate data, it is possible to get down to almost 0 K (skip the part about trying to attain 0 K). Then one can measure the entropy of a substance from 0 K to 273.15 K. In addition it is possible to start from W=1 and calculate the entropy. The two do not agree and the discrepancy is greater than experimental error.

The reason: as a solid freezes, disorder remains because a molecule might have more than one way of arranging itself in the lattice. This disorder causes "residual entropy"

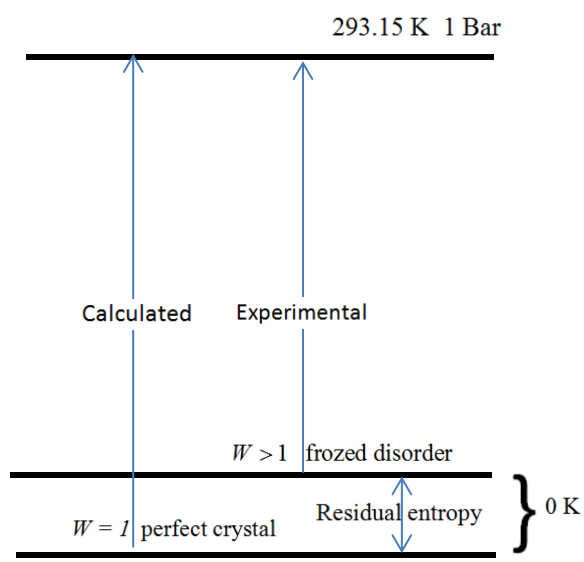
We can calculate in the usual way, using the heat capacities and the latent heats starting at zero degrees and calculating up to 298.15 K,

$$S = \int_0^{T_1^0} \frac{C_P^A}{T} dT + \frac{\Delta_{fus} H_{fus}^1}{T_1^0} + \int_{T_1^0}^{T_2^0} \frac{C_P^B}{T} dT + \frac{\Delta_{fus} H_{fus}^2}{T_2^0} \cdots \int_{T_n^0}^{273.15} \frac{C_P^n}{T} dT$$

This is an absolute number.

Below are the experimental results:

Moleucle	Calculated	>	Calorimetry	Discrepancy
CO	200.05		195.4	4.65
N_2O	222.30		217.4	4.9
NO	213.2		210.16	3.47
H_2O	190.67		187.20	3.47
D_2O	197.26		194.01	3.25
H_2	132.03		125.73	6.3



Carbon monoxide

Frozen disorder comes from equilibrium between two forms,

$$CO \rightleftarrows OC$$

COCOCOCOCOCOCOCO		COOCCOCOCOOCCO
OCOCOCOCOCOCOCOC	→	OCCOOCCOCOCOOC
COCOCOCOCOCOCOCO		OCOCOCCOOCCOOC
OCOCOCOCOCOCOCOC		COCOCOOCCOOCCO
Perfect order W=1		disorder $W=2^N$

Because there are 2^N arrangements, this disorder gives: $S = k\ln W = k\ln 2^N = R\ln 2 = 5.76$ e.u

(entropy unit: e.u.= J $K^{-1}mol^{-1}$)

The same argument works for NNO which is also linear. The reason the value is higher than experiment is that some disorder is frozen in but not all, so not all molecules take two orientations (the deck is not completely shuffled).

NO forms a dimer. The same argument follows except that Nitric Oxide forms a dimer,

$$2NO \leftrightarrow N_2O_2$$

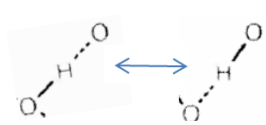
So the units that can exchange are halved

NO ↔ ON
ON NO

There are half as many dimers as monomers per mole, so $S = k\ln W = k\ln 2^{N/2} = 2.88$ e.u

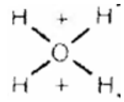
---

Ice takes a tetrahedral structure. Now every proton (H) can take two positions relative to the oxygen. It can be bonded to the oxygen (O-H) or it can be hydrogen bonded to oxygen (H----O):

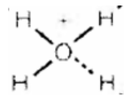


That is, each proton in a water molecule can take two positions. Since there are two protons for every water molecule, then each water molecule has 2^2=4 possible ways of arranging O-H bonds and H-bonds. Hence for N molecules there are $(2^2)^N$ arrangements possible. However only the neutral structures are stable and have two O-H bonds and two hydrogen bonds. If all the structures are kept, then some of the $(2^2)^N$ structures will not be neutral:

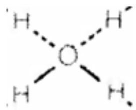
1. Zero H-bonds, four O-H bonds   Extra +2 charge



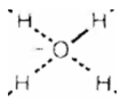
2. One H-bond, three O-H bonds   Extra +1 charge



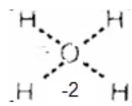
3. Two H-bonds, two O-H bonds   Neutral



4. Three H-bonds, one O-H bond   Extra –1 charge



5. Four H-bonds, zero O-H bonds   Extra -2 charge



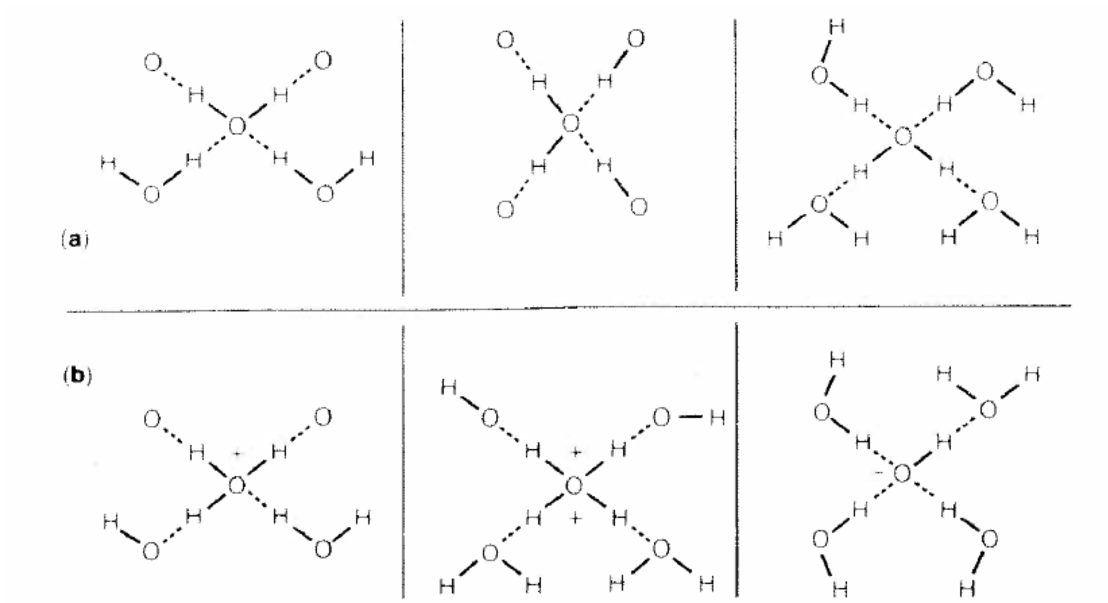
Now if we count up all the possible arrangements of ice using the above cases we count a total of 16 structures. However of these 16 only 6 are neutral. The other 10 are charged and are considered to be eliminated at low temperatures because they are higher energy than the neutral structures. This leaves a fraction of 6/16 that survive at T=0 K.

$$\text{W} = \overbrace{\text{(number of ways H swaps between H-bond \& O-H bond)}}^{\left(2^2\right)^N} \times \overbrace{\text{(fraction of structures that are neutral)}}^{\left(\frac{6}{16}\right)^N}$$

$$W = \left(2^2\right)^N \times \left(\frac{6}{16}\right)^N = \left(4 \times \frac{6}{16}\right)^N = \left(\frac{3}{2}\right)^N$$

$$S = k \ln W = k \ln\left(\frac{3}{2}\right)^N = R \ln\left(\frac{3}{2}\right) = 3.37 \text{ e.u.}$$

The experimental residual entropy is 3.30 e.u. so agreement is good. Here are a few of the 16 structures: the upper three are all neutral and the lower three are charged.



Ortho and para hydrogen: H_2 exist. These are two separate and distinct form of hydrogen: Ortho hydrogen has spin 1 (triplet) and para has spin 0 (singlet))

In fact the conversion between para and ortho is very slow in the absence of a catalyst, so once made ortho and para hydrogen are stable and do not interconvert. (You can make para-Hydrogen, put it in a bottle and in a year hardly any is converted into ortho-hydrogen). It will quickly convert to an equilibrium mixture with a catalyst. Platinum and palladium cause the hydrogen molecule to disassociate on the surface and recombine in a statistical proportion of 3:1.

The statistical proportion is due to the fact that a triplet had three states (0,$\pm$1) and the singlet has only one state (0). Therefore for a mole of hydrogen with equilibrium ratio of ortho and para hydrogen, the number of states is,

$$W = k \ln 3^{\frac{3}{4}N} + \frac{1}{4} k \ln 1$$
$$= \frac{3}{4} Nk \ln 3 + 0 = \frac{3}{4} R \ln 3 = 6.93 \text{ e.u}$$

The Third Law states that the entropy of a perfect crystalline solid is zero. In practice residual entropy is due to frozen disorder.

This shows that the ideas of Boltzmann are correct. Disorder can be frozen in and accounted for by counting the number of different orientations in the crystal. The treatment confirms calorimetry methods for measuring absolute entropies.

Summary Lecture 24 (Top)

Thermodynamics treats different ways a system interacts, or couples, with its surroundings. In Nature cycles are being driven and systems coupled together. Each process is spontaneous and irreversible. All the time then, the number of states accessible is increasing. Suppose you add two systems, and the entropy is the sum of the two:

$$\Delta S = \Delta S_1 + \Delta S_2 = k\left[\ln\left(W_1\right) + \ln\left(W_2\right)\right] = k\ln\left(W_1 W_2\right)$$

Before and after coupling the number of accessible states increases and so does the entropy, *e.g.*

$$W_1 = 10^{20}; W_2 = 10^{20} \text{ then } W_1 W_2 = 10^{40}$$

Condition for equilibrium at constant temperature and pressure:

$$\Delta S_{\text{Univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} = 0 \qquad \text{constant } T$$

$$\Delta S_{\text{sys}} - \frac{q_P}{T} = 0 \qquad \text{constant } T, P$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} = 0 \qquad \text{drop "sys"}$$

$$\Delta G \equiv \Delta H - T\Delta S = 0$$

$$\boxed{\begin{matrix}\Delta G = 0 \\ dG = 0\end{matrix}} \quad \text{conditon for equilibrium}$$

Note that we treat the surroundings as an infinite heat sink or source. Adding or removing energy does not change its temperature.

The same calculation can be done for spontaneous processes at constant volume and temperature:

$$\Delta S_{\text{Univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{sys}} - \frac{q}{T} > 0 \qquad \text{constant } T$$

$$\Delta S_{\text{sys}} - \frac{q_V}{T} > 0 \qquad \text{constant } T, V$$

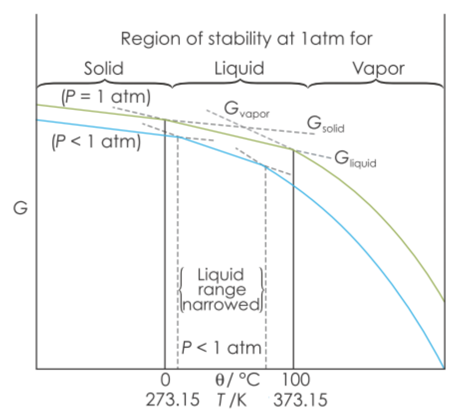
$$\Delta S_{\text{sys}} - \frac{\Delta U_{\text{sys}}}{T} > 0 \qquad \text{drop "sys"}$$

$$\Delta A \equiv \Delta U - T\Delta S < 0$$

$$\boxed{\begin{matrix}\Delta A = 0 \\ dA = 0\end{matrix}} \quad \text{conditions for equilibrium}$$

Figure 5.3

The variation of G with *T* for water. The upper solid line represents the variation of G at 1 atm pressure, and the lower line represents the variation of G at a reduced pressure. The figure shows the narrowing of the liquid range with a decrease in pressure.



If you have different systems, then the system that has the lowest Gibb's energy will exist. Think of a solid, liquid and gas. Here is a figure of the Gibb's energy showing why one phase is replaces the other. Look only at the P=1 atm. curve. All three phases can exist but as the Gibb's energy lines cross, a phase change occurs. The dashed lines correspond to unstable super-cooled or super-heated phases, and they convert to the lower Gibb's energy spontaneously when activated. At the phase transition temperature, two phases are in equilibrium and exist together. The condition for this is,

$$G_S = G_L \text{ at } T_{\text{melting}};\ G_L = G_V \text{ at } T_{\text{boiling}}$$

I will start again in lecture 25 with the discussion of the Gibb's energy and conditions for equilibrium and spontaneity.

Summary Lecture 25 (Top)

With the formulation of the Gibbs and Helmholtz free energies, which combines the First and Second Laws, thermodynamic applications can be developed.
We have

$$\Delta G < 0$$
$$\Delta A < 0$$

Energetics vs. entropics

See example in the book on page 3-56 about the competition between energy and entropy in the formation of hydrogen molecules,

$$2H \leftrightarrow H_2$$

We know that bonds break as the temperature increases. In this case energy and entropy are both negative so in

$$\Delta G = \Delta H - T\Delta S < 0$$
$$\quad <0 \qquad <0$$

So at high temperatures the entropy term eventually makes the free energy positive, so reaction is not spontaneous at high temperatures.

$$\Delta G = \Delta H - T\Delta S < 0$$

ΔH	ΔS	
<0	>0	always spontaneous
<0	<0	spontaneous at low temp.
>0	>0	spontaneous at high temp.
>0	<0	never spontaneous

$\Delta G < 0$ exergonic
$\Delta G > 0$ endergonic

Standard Free energies of formation

Defined at 1 bar, 298.15 K and 1 molar concentration. Use these to obtain the standard free energy change for a reaction,

$$\Delta G^o = \sum \Delta_f G_i^o \left(\text{Products}\right) - \sum \Delta_f G_i^o \left(\text{Reactants}\right)$$

Available work: the "free" part of the Gibbs energy is the amount of energy left over after all the bonds and broken and formed and the entropy is taken into account. This energy is free to do useful work. See the development on Page 3-61 which shows for an isothermal reversible process for an ideal gas that if the volume increases, or the pressure decreases, the entropy increases. For general systems, please see the development on pages 3-62-63 which shows that at constant temperature and pressure the free energy is the non-PV work, Eq.(3.104),

$$dG = dw_{\text{non PV work}}$$

You should be able to read and understand the development leading up to this equation and know what it means.

End of material for Midterm 2.

Summary Lecture 26 (Top)

Chapter 4.

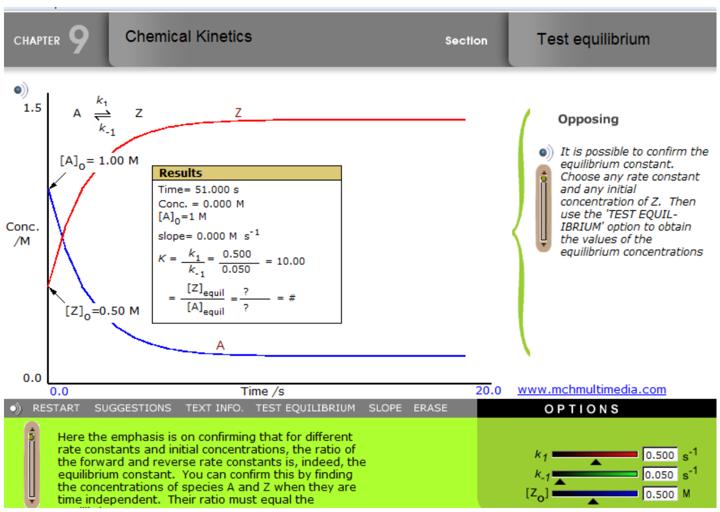
We will not do all of this chapter. The book shows on pages 4-4 to 4-6 that for a reaction,

$$a\text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} z\text{Z}$$

That at equilibrium,

$$K = \frac{[\text{Z}]^z_{\text{equil}}}{[\text{A}]^a_{\text{equil}}} = \frac{k_1}{k_{-1}}$$

in terms of the rate constants for the forward and reverse reactions. You should play with the animation, "Approach to equilibrium" on page 4-28



Pressure dependence

To date we have considered the constraints on the system to be the temperature, pressure and the volume. However in chemical reactions the **number of moles** can change. We have to take that into account. We find that each chemical compound has a certain "potential" to react. This chemical potential is related to the free energy and the more negative it is, the greater the chemical potential and the drive for the reaction to proceed.

Before doing this, first we looked at the **pressure dependence** of the free energy and for the A^{th} species it is given by,

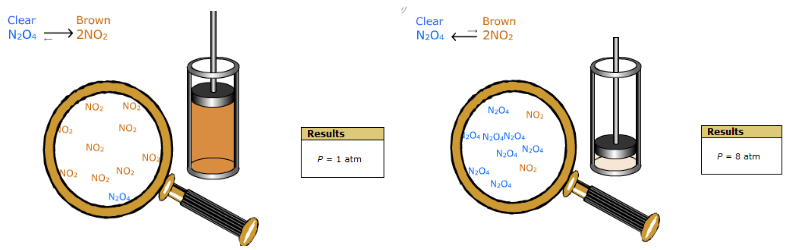
$$\Delta G_A = \Delta G_A^0\left(1\text{ bar}\right) + n_a RT\ln\frac{P_A}{1} = \Delta G_A^0\left(1\text{ bar}\right) + n_a RT\ln P_A^\mu$$

where the "μ" means that the pressure is dimensionless because in exponentials and logarithms the argument cannot have dimensions. Keep this in mind because we are sloppy in keeping this superscript.

We can see an example of Le Chatelier's Principle with the example of a monomer-dimer equilibrium,

$$\underset{\text{high pressure}}{\overset{\text{clear}}{N_2O_4}} \rightleftarrows \underset{\text{low pressure}}{\overset{\text{brown}}{2NO_2}}$$

At low pressure, there is more space for the monomers to move about in but as the pressure increases, the system undergoes a dimerization to reduce the stress of too many monomers. As the pressure increases the entropy decreases so to compensate for this, the dimers form.



The pressure dependence of ideal gases is just the same as we have been using,

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

But it changes for general systems.

Compressibility

It is worthwhile following these equations so you follow the ideas.

Recall that we have the free energy as a function of T and P: $\Delta G(T,P)$ so recall the partial derivatives,

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

Now develop a change of the Gibbs energy. At equilibrium $dG = 0$ at constant T and P, but if they change, so does Gibbs energy. The change depends upon how the volume changes with pressure and how the entropy change with temperature,

$$\begin{aligned}
G &= U + PV - TS \\
dG &= dU + dPV + PdV - dTS - TdS \\
dG &= dq + dw + dPV + PdV - dTS - TdS \\
dG &= \cancel{TdS} - \cancel{PdV} + dPV + \cancel{PdV} - dTS - \cancel{TdS} \\
dG &= VdP - SdT
\end{aligned}$$

Now compare the two and identify:

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$
$$dG = VdP - SdT$$
$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

This is quite general. For constant temperature and an ideal gas we have

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

which we have seen many times. How about liquids and solids? In comparison between gases and liquids and solids, the gases are easily compressed but solids and liquids are not. Thermodynamics has compressibility factors:

An easily compressible substance has a large volume change for a small temperature or pressure change

$$\frac{\Delta V}{\Delta P} \text{ or } \frac{\Delta V}{\Delta T} \text{ or } \frac{\text{Large}}{\text{Small}}$$

An incompressible substance has a small volume change for a large temperature or pressure change

$$\frac{\Delta V}{\Delta P} \text{ or } \frac{\Delta V}{\Delta T} \text{ or } \frac{\text{Small}}{\text{Large}}$$

We express this as a derivative,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Read: *"the derivative isobaric compressibility depends upon the rate of change of volume with respect to temperature at constant pressure."*

The former is the isobaric compressibility factor and the latter is the isothermal compressibility factor. The $1/V$ just makes the two intensive quantities. For an idea gas, plug in the ideal gas law for the volume,

$$\alpha = \frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right)_P = \frac{1}{V}\frac{nR}{P}\left(\frac{\partial T}{\partial T}\right) = \frac{1}{V}\frac{nR}{P} = \frac{1}{T}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial P}\right)_T = -\frac{1}{V}nRT\left(\frac{\partial}{\partial P}\frac{1}{P}\right) = -\frac{1}{V}nRT\left(-\frac{1}{P^2}\right) = -P\left(-\frac{1}{P^2}\right) = \frac{1}{P}$$

Please note that at high temperature α is small and at high pressure κ is small. Under those conditions it is harder to compress a gas so there is a small volume change. Vice versa for low temperature and low pressure.

Summary Lecture 27 (Top)

Pressure dependence of liquids and solids

For solids and liquids the volume does not change much as the temperature and pressure change. We can assume the volume is a constant as the temperature and/or pressure change. We will use this to find the free energy of a reaction at two different pressures, $\Delta G(P_1)$ and $\Delta G(P_2)$. Consider the Hess's law loop,

$$\begin{array}{ccc} A & \xrightarrow{\Delta G(P_1)} & B \\ \uparrow & & \downarrow \\ A & \xrightarrow{\Delta G(P_2)} & B \end{array}$$

Or

$$\Delta G(P_2) = \Delta G(P_1) + \int_{P_2}^{P_1} V_A + \int_{P_1}^{P_2} V_B$$

$$\Delta G(P_2) - \Delta G(P_1) = -V_A \int_{P_1}^{P_2} dP + V_B \int_{P_1}^{P_2} dP$$

$$\Delta G(P_2) - \Delta G(P_1) = -V_A(P_2 - P_1) + V_B(P_2 - P_1) = (V_B - V_A)(P_2 - P_1) = \Delta V \Delta P$$

(Please use the loop to avoid sign errors.)

Superman problem: How hard does superman have to squeeze to change graphite into diamond?

$$\Delta_j G^0(\text{diamond}) = +2.84 \text{ kJ mol}^{-1}$$

Diamond is thermodynamically unstable relative to graphite.

$$\text{C(graphite)} \quad \overset{\Delta_f G=+2.84 \text{ kJ mol}^{-1}}{\rightleftarrows} \quad \text{C(diamond)}$$

We are given the densities of the two:

$$\text{C(graphite)=2.25 g cm}^{-3}$$
$$\text{C(diamond)=3.51 g cm}^{-3}$$

The molar volumes are:

$$\text{C(graphite)=12/2.25 cm}^3 \text{ mol}^{-1} \times 10^{-3} \text{ L cm}^{-3} = 5.33 \times 10^{-3} \text{ L mol}^{-1}$$
$$\text{C(diamond)=12/3.51 cm}^3 \text{ mol}^{-1} \times 10^{-3} \text{ L cm}^{-3} = 3.42 \times 10^{-3} \text{ L mol}^{-1}$$

Assume that the graphite is initially at 1 bar. The free energy is positive at 2.84 kJ mole^{-1}. Take the pressure as the minimum pressure to form diamonds. This will happen when the free energy goes to zero,

$$0 = \Delta G(P) = \Delta G(1) + \left(V_{\text{diam}} - V_{\text{graph}}\right)(P-1)$$
$$0 = 2.84 \text{ kJ mol}^{-1} + (3.42 \ -5.33)\times 10^{-3}(P-1)\,\text{L-atm. mol}^{-1}$$
$$0 = 2.84 \text{ kJ mol}^{-1} \overbrace{-1.91\times 10^{-3}}^{\text{L mol}^{-1}} \overbrace{(P-1)}^{\text{atm.}}\,\text{L-atm. mol}^{-1}$$

We have to change units so both are kJ. We can use the trick of the ratio of gas constants,

$$0 = 2.84 \text{ kJ mol}^{-1} - 1.91\times 10^{-3}(P-1)\,\text{L-atm. mol}^{-1}\,\frac{8.314 \text{ J K}^{-1}\text{mol}^{-1}}{0.08206 \text{ L-atm. K}^{-1}\text{mol}^{-1}}\times 10^{-3}\,\frac{kJ}{J}$$
$$0 = 2.84 \text{ kJ mol}^{-1} - \overbrace{1.94\times 10^{-4}}^{\text{kJ mol}^{-1}\text{atm.}^{-1}} \overbrace{(P-1)}^{\text{atm.}}\,\text{kJ mol}^{-1}$$
$$(P-1) = \frac{2.84}{1.94\times 10^{-4}}\,\frac{\text{kJ mol}^{-1}}{\text{kJ mol}^{-1}}\,\text{atm.} = 14,676 \sim 15,000 \text{ atm.}$$

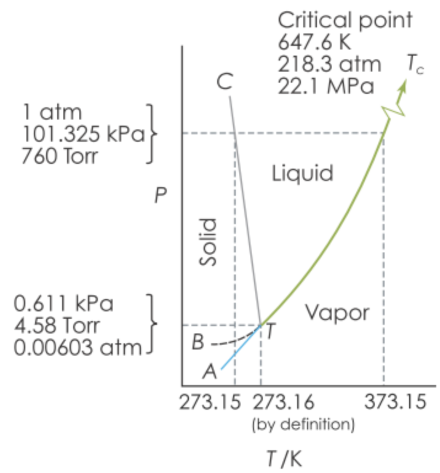
Ignore the 1 atm relative to 15,000 atm.

Next we move onto the relationship to equilibrium

Summary Lecture 28 (Top)

I finished the problem above on crushing graphite into diamond. It is important to know how to change units in such problems and being careful with signs.

I did a bit of a detour to apply to the phase diagram of water (See Figure 5.1 and understand the equations from (5.5) to (5.8). We think of constant *T* and *P*, and so can plot the phases like on the right. A phase is stable if it has lower Gibbs free energy than the other phases. Along the curves, the free energies are equal:



$$G_S = G_L; G_S = G_V; G_L = G_V$$

for respectively freezing-melting; subliming-solidifying; boiling-condensing.

At any pressure or temperature you can find the phase from this graph. The equilibrium between phases is given by the lines along which two phases are at equilibrium. If you draw a line at any constant pressure, you can read off the freezing and boiling points. The figure shows one atmosphere. The triple point is unique and is defined by $G_S = G_L = G_V$ which is where all three phases co-exist at equilibrium.

One property of water is that ice floats. This is important for life because if it sank like most solids, then the oceans would never melt and life is unlikely to evolve. Other examples of floating solid elements are Gallium, Bismuth, Antimony, Germanium and Silicon at standard conditions.

From the phase diagram we see that the L-V curve has a positive slope as does the S-V line. However the S-L line has a negative slope. It is this point that I want to explain:

Along the S-L curve we can write the following (5.5) to (5.8):

$$\begin{aligned}
&dG_S = dG_L \\
&V_S dP - S_S dT = V_L dP - S_L dT \\
&V_L dP - V_S dP = S_L dT - S_S dT \\
&\left[\frac{dP}{dT} = \frac{(S_L - S_S)}{(V_L - V_S)} = \frac{\Delta S_{fus}}{\Delta V_{fus}} \right]
\end{aligned}$$

This says that as you change the pressure and temperature while maintaining the two free energies equal (that is we stay on the line where the two phases are in equilibrium), then the slopes of those curves are given by the latent changes in entropy and volume. Now the entropy change from a solid to a liquid is always positive. So for ice and water the molar volume change is negative, $\Delta V_{fus} < 0$, and so the slope is negative. This is why ice floats, which means the density of ice is less than water. We know that of course but thermodynamics expresses it.

Section 4.1

Chemical potential

Please follow the development (that is, understand the equations) in this section. Consider reactions taking place at constant *T* and *P*. Then for a chemical reaction we study the Gibbs free energy. In a reaction the number of moles of each reacting species will change until equilibrium is reached. At equilibrium there is no change and $dG_{Rx} = 0$. Until then, the number of moles will vary.

Suppose we have a reaction,

$$2A + B \rightleftarrows X + 2Z$$

Then for each compound we can write,

$$G_A = n_A G_A^o + n_A RT \ln P_A^\mu$$
$$\left(\frac{dG_A}{dn_A}\right)_{T,P,n_B,n_C,n_D\ldots} = G_A^o + RT \ln P_A^\mu \equiv \mu_A$$

where the chemical potential, μ_A, is generally different for each compound. The chemical potential is also called a partial molar quantity and it is the Gibbs energy per mole for a compound. Therefore if the chemical potential is large and negative, the compound is reactive, and vice versa.

These combine to give a result like Eq.(4.16), or generally,

$$\Delta G_{Rx} = \Delta G_{Rx}^o + RT \ln Q$$

where the quotient product contains the non-equilibrium pressures. At equilibrium $Q \to K$ (the equilibrium constant) and we have,

$$\Delta G_{Rx}^o = -RT \ln K$$

which relates the value of the Gibbs energy to the equilibrium constant. Please see how large and small values of $Q, K, \Delta G_{Rx}$ are related.

Although the above is for gases, the same works for solutions. We do not ever need to include solids because how much is present does not change the equilibrium. So for solutions, we have concentrations in molar or molal units. However in the event the concentrations are high, then we use activities,

$$K_c = \frac{a_X a_Z^2}{a_A^2 a_B}$$

Generally the activities are related to the concentration by, $a_A = \gamma_A [A]$ where the concentration is in, say, mole per liter and the term, γ_A is called the activity coefficient. For dilute systems the activity coefficient is 1.

This treatment covers all types of equilibrium such as solubility products, K_{sp}, acid dissociation, K_A, base dissociation, K_B, Complex ion formation, Oxidation-Reduction (REDOX) reactions, organic reactions: substitution, elimination, polar and non-polar solvents, etc.

I did a problem in class of the use of the quotient product:

Burn hydrogen gas, the fuel, in a system that exchanges any heat produced with the surroundings leaving the reactants and products at 25 C. Calculate the Gibbs energy in two cases:

a. $P_{O_2} = 10 \text{ atm.};\ P_{H_2} = 10 \text{ atm.};\ P_{H_2O} = 0.01 \text{ atm.};$
b. $P_{O_2} = 0.01 \text{ atm.};\ P_{H_2} = 0.01 \text{ atm.};\ P_{H_2O} = 10 \text{ atm.};$

Balanced chemical reaction:

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O}$$

Calculate the Gibbs energy from tables,

$$\Delta G^o = \Delta G^o_{\mathrm{H_2O}} - \Delta G^o_{\mathrm{H_2}} - \frac{1}{2}\Delta G^o_{O_2} = -228.60 \text{ kJ mol}^{-1} - 0 - 0 = -228.60 \text{ kJ mol}^{-1}$$

Now at different pressures, use the loop,

$$\begin{array}{ccc} \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} & \xrightarrow{\Delta G} & \mathrm{H_2O} \\ \downarrow & & \uparrow \\ \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} & \xrightarrow{\Delta G^o} & \mathrm{H_2O} \end{array}$$

This gives,

$$\Delta G = \Delta G^o + RT\ln P_{\mathrm{H_2O}} - RT\ln P_{\mathrm{H_2}} - \frac{1}{2}RT\ln P_{\mathrm{O_2}}$$

$$= \Delta G^o + RT\ln\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}P_{\mathrm{O_2}}^{1/2}}$$

a. $P_{O_2} = 10$ atm.; $P_{H_2} = 10$ atm.; $P_{H_2O} = 0.01$ atm.;

$$\Delta G = \Delta G^o + RT\ln\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}P_{\mathrm{O_2}}^{1/2}} = -228.60 + 8.314\times10^{-3}\times298.15\ln\frac{0.01}{10\times\sqrt{10}}$$

$$= -228.60 - 19 \text{ kJ mol}^{-1}$$

Note that the 19 kJ is negative, so a low pressure of the products and a high pressure of the reactants helps the reaction proceed.

b. $P_{O_2} = 0.01$ atm.; $P_{H_2} = 0.01$ atm.; $P_{H_2O} = 10$ atm.;

$$\Delta G = \Delta G^o + RT\ln\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}P_{\mathrm{O_2}}^{1/2}} = -228.60 + 8.314\times10^{-3}\times298.15\ln\frac{10}{0.01\times\sqrt{0.01}}$$

$$= -228.60 + 22.8 \text{ kJ mol}^{-1}$$

Note that the 22.8 kJ is positive, so a high pressure of the products and a low pressure of the reactants hinders the reaction proceed.

Temperature dependence of equilibrium constants:

From above with have

$$\Delta G^o = -RT\ln K$$

From this we can write the equation of a straight line,

$$\Delta H - T\Delta S = -RT\ln K$$

$$\ln K = \left(\frac{\Delta S}{R}\right) - \frac{1}{T}\left(\frac{\Delta H}{R}\right)$$

$$f(x) = a + mx$$

However it is only a straight line if the entropy and the enthalpy do not change much with temperature over the range of interest. Let us assume this which can be checked simply by doing the experiment at different temperatures and determining if the line is really straight. If so then the intercept gives the entropy and the slope gives minus the enthalpy.

If so, then at two different temperatures we have

$$\ln\frac{K_2}{K_1} = -\left(\frac{\Delta H}{R}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Will check that the enthalpy and entropy do not change much over a temperature range by looking at some data:

Suppose with have at 0 C and 50 C:

$$K_0 = 1.35\times10^{-10}$$
$$K_{50} = 3.33\times10^{-9}$$

So

$$\ln\frac{K_{50}}{K_0} = \ln\frac{33.3}{1.35} = -\left(\frac{\Delta H}{R}\right)\overbrace{\left[\frac{1}{323} - \frac{1}{273}\right]}^{-5.67\times10^{-4}\ \mathrm{T^{-1}}}$$
$$\Delta H = -\frac{8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\left(\ln\frac{33.3}{1.35}\right)}{-5.67\times10^{-4}\ \mathrm{T^{-1}}} = +47\ \mathrm{J\ mol^{-1}}$$

We also have

$$\Delta G_0 = -R\times273\ln K_0 = 51.6\ \mathrm{J\ mol^{-1}}$$
$$\Delta G_{50} = -R\times323\ln K_{50} = 52.4\ \mathrm{J\ mol^{-1}}$$

If this value of the enthalpy is temperature independent, then we should be able to calculate the entropy and find it also temperature independent,

$$\Delta G_0 = \Delta H - 273\times\Delta S = 51.6\ \mathrm{J\ mol^{-1}}$$
$$\Delta G_{50} = \Delta H - 323\times\Delta S = 52.4\ \mathrm{J\ mol^{-1}}$$

Or

$$\frac{\Delta H - 51.6\ \mathrm{J\ mol^{-1}}}{273} = \frac{(47-51.6)\ \mathrm{J\ mol^{-1}}}{273\ \mathrm{K}} = -16.8\ \mathrm{e.u.}$$
$$\frac{\Delta H - 52.4\ \mathrm{J\ mol^{-1}}}{323} = \frac{(47-52.4)\ \mathrm{J\ mol^{-1}}}{273\ \mathrm{K}} = -16.7\ \mathrm{e.u.}$$

Therefore over this temperature range the major effect of temperature is from the T in $\Delta G = \Delta H - T\Delta S$.

I do suggest that you make your own notes and organize the second law. We covered a lot of ideas but they come together and make sense by organizing the topics and thinking about what they mean in terms of processes you are familiar with. Doing the problems will help.

End of thermodynamics