Lecture 13

I'd like to start our consideration of the **second law of thermodynamics**. There are limitations to the information that the first law gives us. The **first law tells us that certain processes are impossible**, the ones which do not conserve energy. However, it does not tell us the answer to a very important question: which of the processes that are possible will occur spontaneously, i.e., without doing work on the system. It is **the second law that determines which processes are spontaneous** and which are not.

In order to address this broader subject, we're going to start with a narrower question. The question is "What is it that controls the efficiency of a process?" In particular, we are interested in the efficiency of devices that take in energy in the form of heat, and convert it to work, so called heat engines. The pioneers of thermodynamics were immensely practical people who were concerned with issues such as efficiency in boring cannons or getting the most work out of an engine. The model developed to study the work done by a heat engine, the **Carnot cycle**, is not only still practical (it can still be used to determine the maximum efficiency of the engines in our cars or of electrical generators), but instructive. We will find that the considerations that allow us to determine the most efficient conditions for operation of a heat engine lead to the second law of thermodynamics as well.

A heat engine works by drawing heat from a source at high temperature, converting some of it to work, and then dumping the remaining heat energy into a low temperature sink. In the 19th century, Sadi Carnot, a French engineer, developed a thermodynamic cycle that allows us to figure out the most efficient conditions for operating such an engine. The engine requires some kind of "working fluid" which is usually a gas.

Carnot's cycle consists of **four steps**, all of which are **performed reversibly**. In the **first**

step, the gas is placed in thermal contact with a heat source at T_1, the high temperature, and is **expanded isothermally and reversibly** from state A to state B. In the course of this expansion, the work done on the system is w_1 and the system absorbs heat q_1 from the heat reservoir. In the **second**, the gas is **reversibly and adiabatically expanded** from B to C, and does work w_2 on the system. Since this second step is adiabatic, $q = 0$. In the **third step**, the system is put in thermal contact with a heat sink at temperature T_2, the low temperature, and is **isothermally and reversibly compressed** from state C to state D. The work done on the system is w_3 and the heat released to the sink is q_3. Finally, in the **fourth step**, the system is **adiabatically compressed** from state D to our initial state, state A. The work done on the system is w_4, and for this step again, the heat is zero.
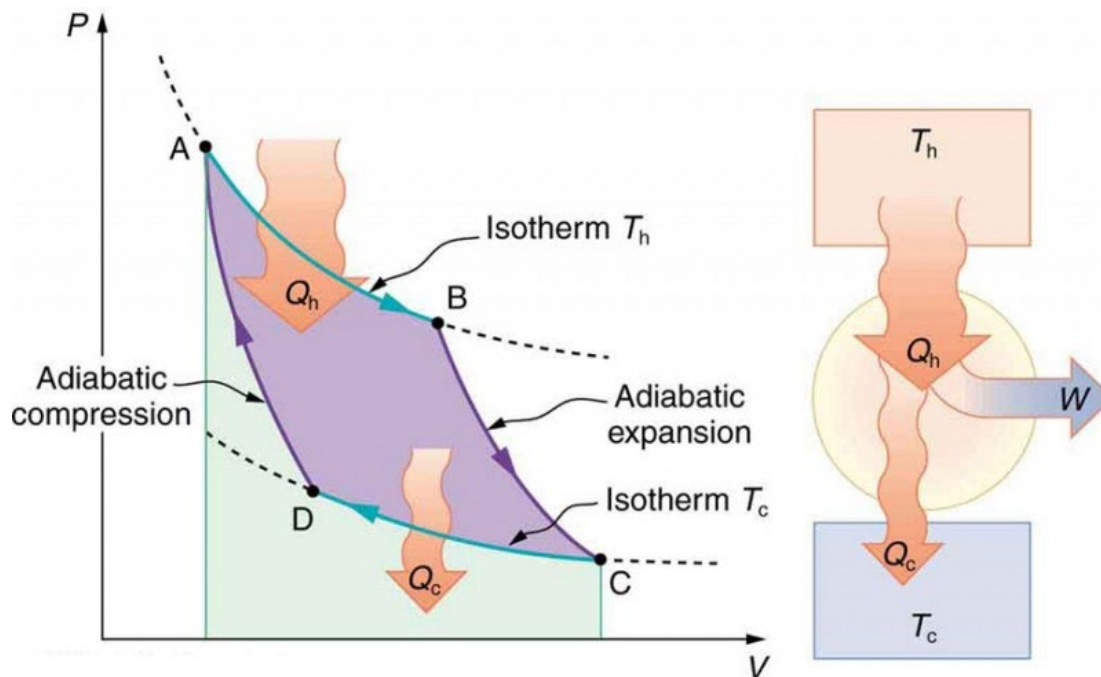

Figure 1This figure comes from the following website: https://courses.lumenlearning.com/physics/chapter/15-4-carnots-perfect-heat-engine-the-second-law-of-thermodynamics-restated/ In this figure $T_h = T_1$, and $T_c = T_2$

The energy changes for the four steps are

$$\Delta U_1 = q_1 + w_1$$

$$\Delta U_2 = w_2$$

$$\Delta U_3 = q_3 + w_3 \text{ and}$$

$$\Delta U_4 = w_4.$$

When we complete the four steps, we have completed a cycle, since we are back in our initial state. WHAT WILL ΔU FOR THE WHOLE CYCLE BE? [Zero] We will find that for all state functions, their change for a cyclic process will always be zero, since the initial and final states are the same. The energy change for the cycle is also given by the sum of the energy changes for the four steps, so we can write

$$\Delta U_{cy} = \left(q_1 + q_3 \right) + \left(w_1 + w_2 + w_3 + w_4 \right) = q_{cy} + w_{cy} = 0 .$$

This tells us that **the work done by a Carnot cycle is equal to the difference between the heat absorbed from the reservoir, and the heat deposited in the sink**.

As I said earlier, Carnot was interested in the efficiency of heat engines. The **efficiency** of such an engine is defined as **the ratio of the work done by the engine divided by the heat absorbed**, i.e., the fraction of the absorbed energy that is converted to work. This is expressed quantitatively as $\varepsilon = \dfrac{-w_{cy}}{q_1} = \dfrac{q_1 + q_3}{q_1}$. The reason for the negative sign is our convention that w is the work done on the system, and -w is the work done by the system. Since Carnot was interested in the work the system did, he had to use -w in the equation for the efficiency. Note that in this equation $q_1 + q_3 \leq q_1$, since q_1 is the energy brought into the system as heat and is a positive number, and q_3 is the energy released from the system as heat and is a negative number. Therefore $0 \leq \varepsilon \leq 1$. We can see from this equation that there are two ways to improve the efficiency of a heat engine. One is to increase the amount of heat absorbed at the high temperature reservoir

(make q_1 large) the other is to decrease the amount of heat released at the low temperature sink

(make q_3 small). If it were possible to reduce the heat released to the sink to zero, then our engine

would be perfectly efficient.

How do we change the amount of heat absorbed in these two steps? Let's see by calculating

ε for an ideal gas. In step one, the isothermal reversible expansion at T_1,

$$\Delta U = q_1 + w_1 = q_1 - nRT_1 \ln V_b/V_a.$$

We've already shown that for an ideal gas U is constant during an isothermal process, so we can

now write $q_1 = -w_1 = nRT_1 \ln V_b/V_a$. For step 3, the isothermal reversible compression at T_2, we

can use the same reasoning to obtain $q_3 = -w_3 = nRT_2 \ln V_d/V_c = -nRT_2 \ln V_c/V_d$. The sum $q_1 + q_3$

is therefore given by

$$q_1 + q_3 = nRT_1 \ln\frac{V_b}{V_a} - nRT_2 \ln\frac{V_c}{V_d}$$

We can simplify this further if we note that V_b and V_c are connected by an adiabatic expansion,

and V_d and V_a are connected by an adiabatic compression. Earlier we showed that for an adiabatic

path,

$$(\frac{T_f}{T_i}) = (\frac{V_i}{V_f})^{\gamma-1}$$

$$Hence, (\frac{T_2}{T_1}) = (\frac{V_b}{V_c})^{\gamma-1} \text{ for step 2 and } (\frac{T_1}{T_2}) = (\frac{V_d}{V_a})^{\gamma-1} \text{ for step 4.}$$

If we set these two equations equal we get

$$(\frac{V_b}{V_c})^{\gamma-1} = (\frac{V_a}{V_d})^{\gamma-1} \text{ or } (\frac{V_b}{V_c}) = (\frac{V_a}{V_d}),$$

which implies in turn that $\frac{V_c}{V_d} = \frac{V_b}{V_a}$. This means that we can rewrite our expression for the total

heat as

$$q_1 + q_3 = nR(T_1 - T_2)\ln\frac{V_b}{V_a}$$

Since $q_1 = nRT_1 \ln V_b/V_a$, for an ideal gas, $\varepsilon = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$. In other words, to change the heat

absorbed, we merely change the difference in temperature between the heat source and the heat

sink. So we see that we can also say that the way to increase the efficiency of an engine is to

increase the temperature of the heat source, or decrease the temperature at the heat sink.

Let's look at an example: Suppose a heat engine absorbs 400J of heat from a high

temperature source at 450K and has its heat sink maintained at 350K. Calculate 1) ε, the efficiency

of the engine, 2) -w the work performed, and 3) q_3, the amount of heat lost to the low temperature

reservoir.

We begin by remembering that

$$\varepsilon = 1 - \frac{T_2}{T_1} = -\frac{w}{q_1}; q_1 = 400J, T_1 = 450K, T_2 = 350K.$$

We can get the answer to our first question merely by plugging in numbers to our equation. Thus

$\varepsilon = 1 - 350K/450K = .222$, so under these conditions the engine is only 22% efficient. To get the

answer to the second question we rearrange our equation to give

$$-w_{net} = q_1 \varepsilon = (.222)\ 400J = 88.8J.$$

Finally to answer the third question we need to use the first law of thermodynamics. What is the

first law? [$\Delta U = q + w$] What is the total q for this process? [$q = q_1 + q_3$] Therefore we can rewrite

our first law as

$$\Delta U = q_1 + q_3 + w.$$

What is ΔU for this process? [0, initial state and final state for the process are identical] Therefore we can solve to get q_3 = -w - q_1 = 88.8 J - 400 J = -312.2J. Why is q_3 negative? [Because it represents energy flowing from the system]

There are two modern devices that are based on using work to reverse the direction of heat flow, i.e. to transfer heat from a low temperature source to a high temperature "sink". These are the heat pump and the refrigerator. Because the goals of these devices, although based on similar principles, are different from that of a heat engine, the efficiency is defined differently for these devices. For the refrigerator we have,

$$\varepsilon_{fridge} = \frac{q_3}{w} = \frac{T_2}{T_1 - T_2},$$

where q_3 is the energy transferred in the form of heat from the low temperature source, the inside of the refrigerator. For the heat pump we have

$$\varepsilon_{heat\ pump} = \frac{-q_1}{w} = \frac{T_1}{T_1 - T_2},$$

where $-q_1$ is the energy in the form of heat transferred from the outside of the house which is at a lower temperature to the inside of the house which is at a higher temperature. There are two important distinctions between these equations and those for the Carnot Cycle. First, both of these processes can have efficiencies substantially higher than one. In other words, for both processes the heat transferred can greatly exceed the work done on the system. In addition, note that unlike the Carnot engine, the efficiency of both devices decreases as the difference between the high and low temperatures increases. These observations explain both the advantages and disadvantages of heat pumps as heating sources for homes. They can be very efficient, and therefore very cost effective. On the other hand, in places where the outside temperature is substantially below room

temperature, the efficiency of traditional heat pumps decreases rapidly.

However, this does not mean that the efficiency of heat pumps is only accessible to those of us living in the South. A new version of the heat pump which combines geothermal and heat pump technologies works by burying the low temperature coils at a depth below the frost layer. Because the ground beyond a depth of about six feet stays at a temperature equal to the average yearly temperature for the area, the difference in temperature between the source and the sink is kept reasonably low, and efficiencies stay high even in the coldest weather.

Lectures 14-15

When we were calculating the efficiency of a Carnot engine, we came up with two different

equations. The first was $\varepsilon = \dfrac{q_1 + q_3}{q_1}$ and the second was $\varepsilon = \dfrac{T_1 - T_2}{T_1}$. Although we used the ideal

gas law to derive this second equation, we will find that it is just as general as our first equation.

Therefore, we can equate these two formulas, to obtain $\dfrac{q_1 + q_3}{q_1} = \dfrac{T_1 - T_2}{T_1}$. A little manipulation

gives us a new equation, $\dfrac{q_1}{T_1} + \dfrac{q_3}{T_2} = 0$. This equation implies the existence of a **new state function**.

To see why let's add up the quantities q_{rev}/T for each of the steps in our Carnot cycle. FOR THE

FIRST STEP, WHAT IS Q? So q_{rev}/T is q_1/T_1. FOR THE SECOND STEP, WHAT IS Q? So q_{rev}/T is zero for

the second step. FOR THE THIRD STEP WHAT IS Q? So q_{rev}/T for the third step is q_3/T_2. WHAT IS THE

VALUE OF Q FOR THE FOURTH STEP? Therefore if we add up q_{rev}/T for the cycle we get $q_1/T_1 + q_3/T_2$,

which our new equation tells us is zero. WHAT WAS THE VALUE OF ΔU FOR THE CYCLE? [Zero]

WHY? [Because the process was cyclic, and the change in any state function for a cyclic process

is zero.] Therefore, since the change in the quantity q_{rev}/T is zero for our cyclic process, we can

conclude that we have a new state function. We shall call this new state function the **entropy**, S,

and will initially define it as $\Delta S = q_{rev}/T$. If we have an infinitesimal heat flow we write this in

differential form as $dS = dq_{rev}/T$. So you see that our consideration of the Carnot Cycle has led to

a new state function, the entropy.

What is important about this new state function, entropy? To understand the importance

of this function, we turn once again to the efficiency of the Carnot Cycle. Remember that in the

Carnot Cycle all the steps are carried out reversibly. Earlier we stated, in a crude way, that the

reversible work is the maximum work that can be done (we will prove this in a couple of weeks). Since $\varepsilon \equiv -w/q_1$, this implies that for any given processes, $\varepsilon_{rev} \geq \varepsilon$. We can rewrite this as

$\dfrac{q_{1,rev} + q_{3,rev}}{q_{1,rev}} \geq \dfrac{q_1 + q_3}{q_1}$. However, our work with the Carnot Cycle showed us that the reversible

efficiency could also be written as $\varepsilon = \dfrac{T_1 - T_2}{T_1}$, so we can rewrite our inequality as $\dfrac{T_1 - T_2}{T_1} \geq \dfrac{q_1 + q_3}{q_1}$

, which in a few steps can be rewritten as $0 \geq \dfrac{q_1}{T_1} + \dfrac{q_3}{T_2}$. For a differential heat flow this sum

becomes, $0 \geq \dfrac{dq_1}{T_1} + \dfrac{dq_3}{T_2}$. This is a version of the **Clausius Theorem**. Since the theorem refers to

cyclic processes, its most general form involves a cyclic integral, $\oint \dfrac{dq}{T} \leq 0$. If you haven't seen a

cyclic integral before don't worry. It's just an integral where the upper and lower limits of integration are the same number. For a state function it will always be zero. For a path function it will depend on the specific path.

What can we learn from this cyclic integral? We know from the Carnot cycle that **when the entire cyclic process is reversible the sum will be zero. If any process is irreversible the sum will be less than zero. Finally, under no circumstances will the sum ever be greater than zero.** Therefore, the value of this cyclic integral is that it allows us to distinguish between reversible and irreversible processes. Why do we care about when a process is reversible or irreversible? Let's think about what reversibility means. A process has to occur slowly enough that the system and surroundings are in equilibrium throughout. It turns out that in order for a process to be truly reversible, it has to occur infinitely slowly. In other words, it is going so slowly that we can say that the process is not spontaneous. Irreversible processes will occur more quickly,

and are therefore spontaneous processes. Therefore, we can say that **this inequality is 0 for reversible processes, and less than zero for spontaneous processes**. There are no processes for which the sum is positive.

This is a new result, because the first law only tells us that for a process to occur it must satisfy energy conservation. Our new result tells us something about when a process will occur spontaneously. It is important here to understand the technical meaning of the word spontaneous. In thermodynamics, to say that a process is spontaneous means that it will proceed without work being done on the system. As an example, heat flows from a hot source to a cold sink without doing any work on the system (it just happens). However, in order to move heat from a cold source to a hot sink (like in a refrigerator) work needs to be done, so we conclude that the process is not spontaneous.

The problem with the Clausius inequality is that it depends on calculation of a path function, heat. It would be much easier if we could predict spontaneity using a state function, whose changes would be much easier to calculate. It turns out that we can do this using the entropy. So, all we need now to complete our development of the second law is to show the relationship of our new state function, the entropy, to spontaneity. Our interpretation of the Clausius Theorem is the key. We begin by considering the following cyclic process:

State 1 $\xrightarrow[\text{irreversible}]{}$ State 2 $\xrightarrow[\text{reversible}]{}$ State 1

According to the Clausius Theorem we have $\int_1^2 \frac{dq}{T} + \int_2^1 \frac{dq_{rev}}{T} < 0$. The second term is dS, the differential of the entropy. Thus the equation now becomes $\int_1^2 \frac{dq}{T} + \int_2^1 dS < 0$. Reversing the limits on the second integral and adding the entropy term to both sides gives us $\int_1^2 dS > \int_1^2 \frac{dq}{T}$ or $dS > \frac{dq}{T}$

. If we remember that dq/T = dS under reversible conditions, this finally becomes dS ≥ dq/T, our most general and useful version of the second law. We have three different cases here. The first is dS = dq/T. This occurs only for reversible processes. The second is dS > dq/T. This occurs for irreversible or spontaneous processes. The third, dS < dq/T never occurs.

To gain even more physical insight, let's consider the entropy of an isolated system. For this case dq/T will be zero. Our three cases now become **dS = 0 for reversible processes, dS > 0 for spontaneous processes, and if dS < 0 the process is impossible and will not occur.**

Now consider the universe. Since it contains everything, it is by definition an isolated system. Therefore we can state our result as **$dS_{univ} = 0$ for a reversible process, while $dS_{univ} > 0$ for a spontaneous process.** This is why the second law is sometimes stated as "The entropy of the universe is always increasing."

A common physical interpretation of entropy is that entropy corresponds to increasing disorder. While crude, this physical idea will later help us in our development of the third law. In statistical mechanics, the entropy is most simply calculated using a formulation derived by Ludwig Boltzmann, $S = k \ln w$. In this equation, S is the absolute entropy, k is Boltzmann's constant, $R/N_0 = 1.38$ x 10^{-23} J K^{-1}, and w is the degeneracy of the system. The degeneracy of a system is the number of energetically equivalent configurations at a given energy. It makes sense that disorder would increase with the degeneracy, because the higher the degeneracy, the more widely the system would be distributed among possible configurations. This is not unlike a deck of cards being more widely distributed when 52 card pickup is played in a large living room than when it is played in a small closet.

Another useful version of the second law is obtained if we divide the universe into system

and surroundings. Then $dS_{univ} = dS_{sys} + dS_{surr.}$ This means that our second law may also be written **$dS_{sys} + dS_{surr} \geq 0.$** We will find that this form of the second law will be the one that we use most often.

Before we go on to specific examples, let's do a quick recap. By using the Carnot Cycle, we introduced a new state function called the entropy. This state function has the property that if the change in its value for a process = 0 for system + surroundings, the process is reversible. If the change in its value for a process is positive for system + surroundings, the process is spontaneous.

Now we have to figure out how to calculate entropy changes. Notice that our definition of the entropy is $dS = dq_{rev}/T$. This means that in order to calculate the entropy change between two states, we need to find a reversible path between the two states. Let's look at the calculation of some entropies.

We'll demonstrate the calculation of entropies and the second law by considering the entropy of the isothermal reversible expansion of an ideal gas. Our calculation of ΔS for isothermal cases is simplified since T is constant and we can pull it out of the integral.

$$\Delta S_{gas} = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T}\int_1^2 dq_{rev} = \frac{q_{rev}}{T}$$

Remember that for an isothermal process in an ideal gas, $dU = C_V\,dT = 0$. Remember also that $\Delta U = q + w$. Therefore, for an isothermal process in an ideal gas, $q = -w$. Since for the isothermal reversible expansion of an ideal gas $w = -nRT\,\ln(V_2/V_1)$, $q_{rev} = nRT\,\ln(V_2/V_1)$. Therefore $\Delta S_{gas} = q_{rev}/T = nR\,\ln(V_2/V_1)$. Note that if $V_2 > V_1$, an expansion, the entropy of the system increases, and if $V_2 < V_1$, a compression, the entropy of the system decreases. However, the second law says that the entropy of the universe should be zero for a reversible process. WHY ISN'T OUR RESULT 0?

[Universe = system + surroundings, must include $\Delta S_{surroundings}$.]

Let's figure out how to calculate $\Delta S_{surroundings}$. Suppose that in an isothermal reversible process the system absorbs an amount of heat q_{rev}. The entropy change for the system is simply $\Delta S = q_{rev}/T$. Where did the heat that is transferred into the system come from? [Surroundings] Therefore, the heat flow for the surroundings will be given by $-q_{rev}$. Now what about the temperature of the surroundings? Remember that in a reversible process, the critical variables for system and surroundings need to be in equilibrium. Since the critical variable for heat transfer is T, the temperature of the system and the surroundings must be equal. Therefore $\Delta S_{surr} = -q_{rev}/T$. Since $\Delta S_{Universe} = \Delta S = \Delta S_{sys} + \Delta S_{surr}$, we have $\Delta S = q_{rev}/T - q_{rev}/T = 0$, which agrees with the second law.

Now let's consider an isothermal irreversible expansion of an ideal gas that connects the same two states as our reversible process. Since S is a state function ΔS_{sys} is independent of path, so $\Delta S_{sys} = nR \ln(V_2/V_1)$. How does the entropy of the irreversible expansion differ from the reversible expansion? First of all, since the same two states of the system are involved, ΔS_{sys} is the same as for our reversible case. However, ΔS_{surr} will differ. Suppose that the expansion is against $p_{ex} = 0$. Then $w = 0$ and since $\Delta T = 0$, $\Delta U = 0$ and $q = 0$. This means the $q_{surr} = 0$ for the irreversible process, and therefore $\Delta S_{surr} = 0$. Note that we cannot use the argument that entropy is a state function for the surroundings, because we do not know enough about the surroundings to define their state. Taken together, our results mean that the overall entropy for the irreversible process is $\Delta S = \Delta S_{sys} + \Delta S_{surr} = nR \ln(V_2/V_1)$, which is > 0 if $V_2 > V_1$, i.e., if an expansion occurs. Therefore, isothermal irreversible expansions into vacuum are spontaneous processes. However, if $V_2 < V_1$, i.e. if compression occurs, then $\Delta S < 0$, and the process will not occur. DOES THIS

LATTER STATEMENT MAKE PHYSICAL SENSE? WHY?

Let's look at the entropy changes of a couple of other types of processes. First let's look at the entropy change associated with a phase transition. Let's start with our definition of entropy. Q: HOW IS AN ENTROPY CHANGE DEFINED? [$dS = dq_{rev}/T$] To calculate dq_{rev}, we postulate that the system is heated infinitely slowly. Remember that **because S is a state function, it doesn't matter whether the actual transition occurs infinitely slowly, because as long as the initial and final states are the same, ΔS will be the same.** Q: NOW SUPPOSE THAT OUR PROCESS IS VAPORIZATION UNDER CONDITIONS OF CONSTANT PRESSURE. WHAT IS DQ FOR THIS PROCESS? [dH_{vap}] From our definition we have $dS = dH_{vap}/T$, and since phase transitions are isothermal, this integrates to $\Delta S_{vap} = \Delta H_{vap}/T$. We can extend this result to all types of first order phase transition by writing $\Delta S_{trans} = \Delta H_{trans}/T_{trans}$. Note that ΔH of vaporization, of fusion and of sublimation are all positive, so for all three of these processes, ΔS will be greater than zero. Q: CAN ANYONE GIVE ME A QUALITATIVE EXPLANATION OF WHY MELTING A SOLID OR VAPORIZING A LIQUID ALWAYS RESULTS IN AN INCREASE OF ENTROPY? [Going from S to l or l to g results in an increase in disorder]

You might guess that for most substances the increase in disorder going from a liquid to a gas would be about the same. This is the essential content of **Trouton's Rule**, which states simply that the entropy of vaporization of most liquids is $\cong 85$ J K^{-1} mol^{-1}. Since $\Delta S = \dfrac{\Delta H}{T}$ for phase transitions, we can use Trouton's rule to estimate the enthalpy of an unknown phase transition, or alternatively the transition temperature.

Now let's consider the entropy change due to heating. Q: WHAT IS OUR DEFINITION FOR CHANGE IN ENTROPY? [$\Delta S = \int \dfrac{dq_{rev}}{T}$] Q: SAY THAT WE'RE AT CONSTANT PRESSURE. WHAT IS

DQ_REV? [$dq_{rev} = C_p \, dT$] Combining these results yields the equation

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T}.$$

Q: IF C_P IS CONSTANT WHAT IS ΔS? [$\Delta S_{heating} = C_p \ln(T_2/T_1)$ at constant p] Q: IF THE HEATING WERE

DONE AT CONSTANT V WHAT WOULD DQ_REV BE? [$C_V \, dT$] So for constant volume, we would have

$$\Delta S = \int_{T_1}^{T_2} C_V \frac{dT}{T}.$$

and for constant C_V,

$$\Delta S_{heating} = C_v \ln\left(\frac{T_2}{T_1}\right)$$

These results are even more important because they can be rewritten as

$$S_2 - S_1 = \int_{T_1}^{T_2} C_p \frac{dT}{T} \Rightarrow S_2 = S_1 + \int_{T_1}^{T_2} C_p \frac{dT}{T}$$

This means that we can **relate the entropies at any two temperatures**, as long as we know C_p.

Let's do a couple of examples.

Example: What is $\Delta S_{H2O(g)}$ when the water is heated from 110°C to 170°C at 1 atm pressure. $C_p(H_2O(g)) = 33.58$ J K^{-1} mol^{-1}.

We begin with the equation $\Delta S = \int C_p \frac{dT}{T}$. Since we are not told otherwise, we assume

that C_p is constant and integrate to get $\Delta S_{heating} = C_v \ln\left(\frac{T_2}{T_1}\right) = 33.58 \ln(443/383) = 48.87$ J K^{-1}

mol^{-1}.

Example 2: What is $\Delta S(H_2O)$ when water is heated from 50 °C to 170 °C at 1 atm.

$C_p(H_2O(l) = 75.29$ J K^{-1} mol^{-1}. Q: CAN WE JUST USE THE EQUATION $\Delta S = \int C_p \frac{dT}{T}$ FOR THIS

PROCESS? [No, phase transition occurs at 100 °C and 1 atm.] Q: WHAT IS THE HEAT CAPACITY AT

A PHASE TRANSITION? [∞, $C_p = \Delta H/\Delta T = q/0$] So for this problem in order to calculate ΔS we need

to break our calculation into three parts. First we heat the water to the boiling point and calculate

its entropy change. WHAT WILL THE CHANGE IN ENTROPY BE FOR THIS PART OF THE PROCESS?

$$\Delta S_1 = \int_{273}^{373} C_p(H_2O(l)) \frac{dT}{T}$$

The second part of the process is to evaporate the liquid at the normal boiling point. WHAT IS ΔS

FOR THIS PART OF THE PROCESS? [$\Delta S_2 = \Delta H_{vap}/373$] Finally we raise the temperature of the vapor

from 100 °C to 170 °C. THE ENTROPY FOR THIS PROCESS IS WHAT?

$$\Delta S_3 = \int_{373}^{443} C_p(H_2O(g)) \frac{dT}{T}$$

The total entropy change is the sum of the three component entropy changes,

$$\Delta S = \int_{323}^{373} C_p(H_2O)) \frac{dT}{T} + \frac{\Delta H_{vap}}{T} + \int_{373}^{443} C_p(H_2O(g)) \frac{dT}{T}$$

If we write this change in entropy as $\Delta S = S_{443} - S_{323}$, we can see that by considering the various

phase transitions and with knowledge of all the heat capacities, that we should be able to calculate

changes in entropy from temperatures as low as zero K. For example, for H_2O this calculation

would be

$$S_T = S_0 + \int_0^{273} C_p(H_2O(s)) \frac{dT}{T} + \frac{\Delta H_{fus}}{273} + \int_{273}^{373} C_p(H_2O(l)) \frac{dT}{T} + \frac{\Delta H_{vap}}{373} + \int_{373}^{T} C_p(H_2O(g)) \frac{dT}{T}$$

To determine an absolute value for the entropy (not surprisingly, called the absolute entropy) we

only need to know the entropy at absolute 0.

There is a problem in doing these calculations. At temperatures below 10K, it is extremely

difficult to measure heat capacities. However, Debye and Einstein came up with a theory of heat

capacity that shows that for low temperatures $C_p \propto T^3$. So to calculate the entropy from 0 to 10K we find the heat capacity at 10K and then use this equation of Einstein and Debye, which is called the **Debye extrapolation**. The real power of the Debye calculation is that if we know C_p of a substance at 10 K, to a good approximation we also know the entropy at 10K. For example, suppose the $C_p(Ar, 10K) = 0.81$ J K^{-1} mol^{-1}. What is ΔS from 0 to 10 K? We use our previous result to write $S_{10} - S_0 = \int_0^{10} \frac{C_p dT}{T}$. Since the temperature is between 0 and 10K we use the Debye extrapolation to estimate the heat capacity, writing $C_p = aT^3$, where a is a constant. This yields

$$S_{10} - S_0 = a\int_0^{10} \frac{T^3 dT}{T} = \frac{aT^3}{3}.$$

Since $C_p(10) = a\,T^3$, $S_{10} - S_0 = 1/3\,C_p(10) = .27$ J K^{-1} mol^{-1}.

Now we have the tools to calculate any entropy relative to the entropy at 0 K. It remains only to determine the **value of the entropy at 0K**. First, I'd like to turn to a **statistical definition of the entropy** since I think it will help our understanding of 0K entropies. We've already stated that **entropy is related to disorder**. A gas is more disordered than a liquid and has higher entropy. A liquid is more disordered than a solid and has higher entropy. Similarly, when we heat an object its disorder increases, because its atoms can move around more and therefore its entropy increases. In 1896, Ludwig Boltzmann came up with a quantitative expression for this relation of entropy to disorder by writing S = **k ln w**, where w is the **degeneracy** of the system at temperature T, and k = R/N_A (N_A is Avogadro's number). The **degeneracy is approximately defined as the number of arrangements of a system at a given temperature.** Let's look at the effect of temperature on this number of arrangements. Say we have a gas of five particles in a volume V. There are many different combinations of positions of these five particles within the volume V, therefore the

degeneracy w is high and S is high. Now we lower the temperature and the gas of 5 particles condenses. The particles are constricted in space, but still have many different configurations, since the condensed liquid, though constrained to the bottom of the container, can still flow. For this case w is smaller, so S is smaller. Now we lower T again so that the liquid becomes a solid. The degree of disorder of the solid is a matter of which particles are moving and how much. For this case w is still smaller and S is smaller yet. As we continue to lower the


GAS   LIQUID   LIQUID   SOLID

temperature, fewer of the particles are able to move. This continues until we reach absolute zero. For a perfect crystal at absolute zero there is only one configuration, w = 1 and since S = k ln W, S = 0.

This is the essential content of the **third law of thermodynamics**, which states "The entropy of perfect crystals of all pure elements and compounds is zero at the absolute zero of temperature." Note that this law very specifically mentions **perfect crystals**. What is a perfect crystal and what is an imperfect crystal?

A perfect crystal is a regular arrangement of atoms or molecules with every particle in it's assigned space. Looking at a two-dimensional example, we see that as long as the atoms are

PERFECT CRYSTAL   NAUGHTY CRYSTAL
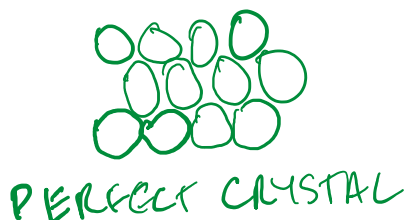
indistinguishable and don't move, there is only one configuration for this perfect crystal. However, crystals sometimes form with imperfections, such as an atom missing from one of its sites. This is one type of imperfect crystal. We can see that with one atom missing there are several (in this case twelve) distinguishable configurations of the crystal, all with identical energies. As an example here are three of the twelve configurations for this 11 atom crystal. Since each of these

THREE IMPERFECT CRYSTAL CONFIGURATIONS

distinguishable configurations has only one empty lattice site, the energies are the same. In fact, a crystal of 1 mol of Ar, with a single missing atom has 6.023 x 10^{23} distinguishable configurations at 0K and therefore has a degeneracy w = 6.023 x 10^{23}. Since the statistical definition of entropy is S = k ln W, we have"

$$S = \frac{8.314J\ K^{-1}mol^{-1}}{6.022x10^{23}} \ln 6.022x10^{23} = 7.56x10^{-22}\ JK^{-1}.$$

The real power of the third law is that since it defines an absolute zero of entropy, it means that unlike the energy and enthalpy, for which we can only calculate relative values, we can calculate absolute values for the entropy. These **absolute entropies** are also called **third law entropies**.

The **standard third law entropy** is defined as follows. "The standard entropy of a substance, S°, is its entropy in its standard state at temperature T."
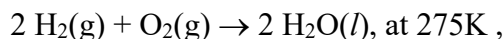
In addition, we can define a standard reaction entropy as

$$\Delta S^0_{rxn} = S°(\text{products}) - S°(\text{reactants})$$

If we use our formulation for a generalized reaction, the **standard entropy of reaction** becomes

$$\Delta S^0_{rxn} = \sum_J \nu_J S^0_J$$

For example in the reaction

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l), \text{ at } 275K\ ,$$

the ν_J's are -2, -1 and +2 respectively and

$$\Delta S^0_{rxn,275} = 2S^0_{275}(H_2O(l)) - 2S^0_{275}(H_2(g)) - S^0_{275}(O_2(g))$$

These absolute entropies are readily obtained from tables, such as those in the CRC Handbook or those supplied by Atkins, DePaula and Keeler.

One last entropy topic. When we first talked about changes in energy, we obtained the equation $dU = -p_{ex}dV + dq$. Notice that this equation consists of terms which are either difficult to measure (dq) or refer to the surroundings. However, for a reversible process we can now develop an equation which describes the energy change in terms of **internal variables only**. Our first step is to replace the work term with a reversible work term, which yields a familiar equation, $dU = -pdV + dq$. Now remember that our definition of a change in entropy is $dS = dq_{rev}/T$, which implies that $dq_{rev} = TdS$. Now our equation for the energy change becomes $dU = -pdV + TdS$. We've succeeded in writing our change in terms of internal variables only. Note that even though the work term and the heat term are reversible, this equation can be used to calculate the change in energy for irreversible changes as well, as long as the initial and final states are the same as in the reversible case. This equation is called the **fundamental equation of thermodynamics**, and has tremendous utility. We will be exploiting it substantially from now on.