

## Chapter 30

# 30 Thermal Properties of Matter 2.1.4, 2.1.5

In this lecture we want to make our study of temperature more mathematical. And we want to consider how energy relates to temperature. The problem is that although we have a strategy for finding  $w$ , the work done as we change temperature. We will start to fill that void in this lecture.

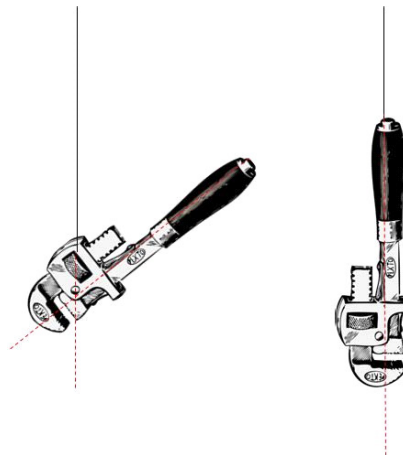
We learned in PH 121 what energy was. We studied work and potential energy, and we studied kinetic energy. But these were always the energy *of* an object. We described these energies in terms of the motion of the center of mass of an object using the particle model. Now we know that there is energy *in* an object. This is different. Particles don't have internal parts, but real things do. Our particle model was an approximation. So we need to go beyond the particle model here. We will call the energy associated with the inside parts of an object *internal energy*. And this internal energy is associated with thermal energy.

To study this, Let's refine our definition of internal energy by saying that it is all the energy of a system that is associated with its microscopic components – atoms and molecules – when viewed from a reference frame at rest with respect to the center of mass of the system. Any motion of the center of mass is our Principles of Physics I (PH121) mechanical energy. Now we want the motion of the parts of the object with respect to the center of mass. Let's review center of mass briefly.

From Principles of Physics I we know the center of mass is given by

$$r_{cm} = \frac{1}{M} \int \mathbf{r} dm \quad (30.1)$$

and we can think of the center of mass as the point an object freely spins around.



For groups of molecules, we remember

$$\vec{r}_{cm} = \frac{\sum_i m_i \vec{r}_i}{M} \quad (30.2)$$

where

$$M = \sum_i m_i \quad (30.3)$$

is the total mass of all the molecules.

You might remember this in one dimension for two masses

$$x_{cm} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \quad (30.4)$$

Now suppose we let all of the masses involved be tied together with spring-like forces. These spring-like forces would allow the masses to oscillate a little. That would change the  $\mathbf{r}_i$  involved in our center of mass calculation. But if the oscillations were random, the actual center of mass would not change. This is the kind of motion involved in internal energy.

By making all the little molecules move, we have changed the energy state of the object, but we have not moved it, so the mechanical energy has not changed. The energy we have described is the thermal internal energy (there is still the nuclear internal energy, but that is a subject for the class called Modern Physics (PH279). Let's consider forms of internal energy in more detail in this lecture.

## Fundamental Concepts

1. Heat capacity relates energy transfer by heat to temperature change in solids and liquids
2. Specific heat is a heat capacity per unit mass

3. A phase change is changing from solid to liquid, or from liquid to gas for a sample of a material
4. Calorimetry is the use of thermal conservation of energy to study a sample of material

## 30.1 Heat

Temperature, in our intuitive model, seems connected to heat. But what is heat? If we can figure this out we might be able to give a better definition of temperature. Let's give heat a symbol,  $Q$ , but in this lecture we want to give a specific definition of heat.

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Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.

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When we “heat” a substance, we add energy from it's surroundings. When the temperature changes, it is energy that is making the temperature change. An object could gain or lose energy *by heat*. We will use the word “heat” for the transfer of energy no matter which direction the energy is flowing. This is a little like using the word “acceleration” no matter whether we are speeding up or slowing down.

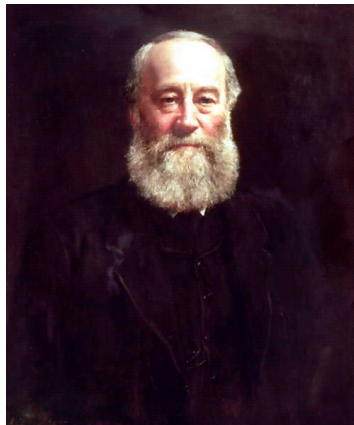
In the dim past, scientists thought heat was a fluid (called caloric). This model of heat is not correct (science changes!). We now define heat as a transfer of energy. But because of this history, we have some left-over names that are not very descriptive of the modern ideas they represent. Examples are “latent heat” and “heat capacity” (we will define these soon).

The thing to remember is that a system *has* a temperature but it can *give* or *receive* energy by heat.

### 30.1.1 Units

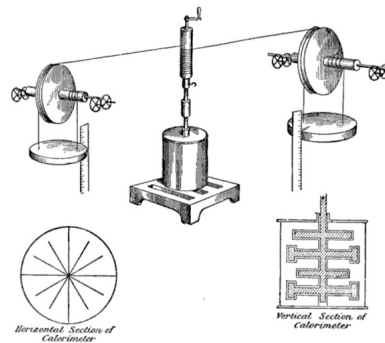
There are several units for heat. The calorie (cal) is the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5 °C (287.65 K) to 15.5 °C (288.65 K). This is somewhat arbitrary, but it works for many things, especially biological systems. The British thermal unit (Btu) is the unit used by refrigeration and heating contractors. One Btu is the amount of energy transfer necessary to raise the temperature of 1 lb of water from 63 °F (290.37 K) to 64 °F (290.93 K). This is an enormous amount of energy being transferred! If you wish to heat an entire building, this is a fine unit, but for us it is a bit large. In the SI system we already have a unit for energy, the Joule. We will try to stick to this nice, medium sized, unit. But let's see where it came from.

### 30.1.2 Mechanical equivalent of heat



James Prescott Joule. (Image in the Public Domain)

The name “Joule” is a person’s name, Joule was an early researcher and is credited with showing that heat transfer is a transfer of energy. Joule was able to build a device to prove that mechanical energy could be converted to heat energy. His device is shown in the picture.



Joule's Water-Churning Apparatus for Determining the Mechanical Equivalent of Heat.

Joule Apparatus (Image in the Public Domain courtesy Gaius Cornelius)

The paddle device was placed in the drum that is sitting behind it. The crank was operated by strings attached to it that were pulled by masses tied to the other end of the string (see the right hand side of the figure). When the masses were released, the paddle wheel stirred a liquid. The friction from the paddle wheel stirring the liquid raised the temperature of the liquid. The masses would lose energy equal to

$$\Delta U = 2mgh \quad (30.5)$$

assuming the masses were equal. By carefully measuring the temperature of the water, Joule found that

$$\Delta U = C \Delta T \quad (30.6)$$

with the proportionality constant approximately

$$C = 4.18 \frac{\text{J}}{\text{g}} ^\circ\text{C} \quad (30.7)$$

which means that 4.18 J of mechanical energy raises the temperature of 1 g of water by 1 °C. (Here  $C$  is a generic symbol for a constant). We have more precise measurements now that set this value at  $4.186 \frac{\text{J}}{\text{g}} ^\circ\text{C}$ . But you can see that Joule did very good for working with what amounts to a fancy butter churn in the 1800's!

Notice that we are considering raising the temperature of 1 g of water by 1 °C. This is the basis of the unit called the calorie. Using the same 4.5 °C (287.65 K) to 15.5 °C (288.65 K) change in temperature, we realize

$$1 \text{ cal} = 4.186 \text{ J} \quad (30.8)$$

which gives us a convenient way to convert from calories to Jules. But more importantly, it shows that heat is really tied to energy, not to some substance. Work can raise a temperature in a system just like “heating” the system with a fire or stove.

Because of this experiment by Joule, this idea that work can be turned into thermal energy is known as the *mechanical equivalent of heat*.

## 30.2 State Variables

As you know, we are at the beginning of a new topic, and we will find that physics did not develop as a cohesive whole. The new topic is called *Thermodynamics* and it developed independently of the theories of oscillation and waves and optics. Thus the language we use will be different, and sometimes old words will need new meanings.

We learned before about solids, liquids, and gases. We learned that the degree of bondedness made the difference between these states. The states of matter are often called *phases* in thermodynamics. This use of the word “phase” has nothing to do with the phase of an oscillator or wave. It is just the condition of being solid, liquid or gas.

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To change from solid to liquid, or from liquid to gas, is called a *phase change*.

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To describe the state of a sample of matter, we use a set of variables like mass, volume, pressure, density, and energy. We have used these throughout Principles of Physics I. Thermodynamics has it's own set of descriptive variables to add to

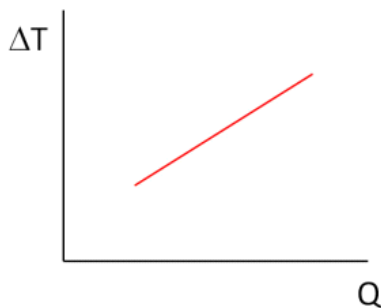
these: moles, number density, and Temperature. These variables, along with our original set, are called *state variables* and together, they describe the conditions of a particular piece of matter. We have hinted that one of these state variables will be the amount of internal energy in our sample of material, let's call that  $\Delta E_{int}$ . Note here the “ $\Delta$ ” means “an amount of” and not a “difference between two amounts of” a substance. So  $\Delta E_{int}$  is an amount of internal energy. We know from our study of thermal expansion that the work,  $w$ , might be such a state variable. And we also know now that energy can be transferred by heat,  $Q$  so maybe heat is a state variable.

It would be good to be able to relate these new variables. So let's try to develop a relationship between  $\Delta E_{int}$ ,  $W$ , and  $Q$  for our samples.

Suppose you are heating something on your stove, say, a sample of steak.



You would expect that as energy is transferred from the hot stove to the cold beef, the temperature of the steak would increase. It makes sense that the more energy you transfer, the more the temperature will rise. Gasses are more complicated, because their volume will change, but the volume of solids does not change much with temperature (we know that it changes a little) so we don't have as many complications as we would with a gas.



We could guess that the temperature increase might be linear in the amount of energy transfer we give to the solid.

$$\Delta T \propto \Delta E_{int}$$

where our only form of increasing the energy here is  $Q$ , since the change in volume of the stake sample is small enough that any work,  $w$ , is negligible. Since  $P$  and  $V$  are not changing much. So to a good approximation

$$\Delta T \propto Q$$

Experimentalists did this experiment and found that for many temperature regions this is true. Of course, we could over heat our sample



changing it's form (from stake to charcoal, and smoke), but then the sample is no longer the same substance. In this case  $\Delta T$  is no longer proportional to  $Q$ . But as long as we don't change the composition of the substance (we stay in the linear regime) , we can say that  $\Delta T$  is proportional to  $Q$ .

Physicists don't like proportionality signs, so they invented a constant with the right units that would make this an equality

$$\Delta T = \frac{1}{K}Q$$

But, they found that the internal structure of the solid mattered. There was a different constant,  $K$ , for every material.

They called the constant,  $K$ , the *heat capacity* of the material. The name is one of our throwbacks from the past, but for us it means the constant of proportionality between  $Q$  and  $\Delta T$  that holds all the specific material properties of that substance that change the slope of the  $\Delta T$  vs.  $Q$  graph.

Of course, the more material we have in our sample, the longer it takes to heat it up. If we have a roast, it takes longer to cook than a small steak. So it is customary to define a heat capacity per unit mass, this is called the *specific heat* of the material.

$$\Delta T = \frac{1}{mc}Q$$

and we often rearrange this equation to give

$$Q = mc\Delta T$$

As an example, it takes 4190 J to raise 1 kg of water by 1 K. So

$$4190 \text{ J} = (1 \text{ kg}) (c) (1 \text{ K})$$

solving for  $c$  yields

$$c_{\text{water}} = 4190 \frac{\text{J}}{\text{kg K}}$$

Which is familiar to us from Joule's work.

Here are a few more substances and their specific heat values.

Substance	$c \left( \frac{\text{J}}{\text{kg K}} \right)$	$c \left( \frac{\text{J}}{\text{mol K}} \right)$
Aluminum	900	24.3
Copper	385	24.4
Iron	449	25.1
Gold	129	25.4
Lead	128	26.5
Ice	2090	37.6
Mercury	140	28.1
Water	4190	75.4

Notice that things that heat up or cool down quickly have small specific heats. Things that heat up slowly or cool slowly have large specific heats. Water in any of its phases has large values of specific heat. This is why living next to a lake or the ocean keeps your temperatures moderate. It takes quite a lot of energy transfer to heat up or cool off the water, so the temperature of the water does not change much.

This is why Buffalo NY temperatures lower when the lake freezes. This is also the source of lake or ocean breezes. In the morning, the land changes temperature more quickly than the water. The warmer air over the land becomes less dense and rises, leaving a lower pressure area. This causes a cool breeze to form from the sea to the land.



Conversely, in a large city, the concrete and blacktop heat up much quicker, so we experience increases in daytime temperature as a city grows.



A specific heat is a per-unit-mass property, but we could just as well define specific heat as a per-unit-mole quantity. Then the specific heat would be the amount of energy it takes to increase the temperature of a mole of material. This incarnation of the idea of specific heat is called a *molar specific heat*, and we will give it the symbol  $C$ .

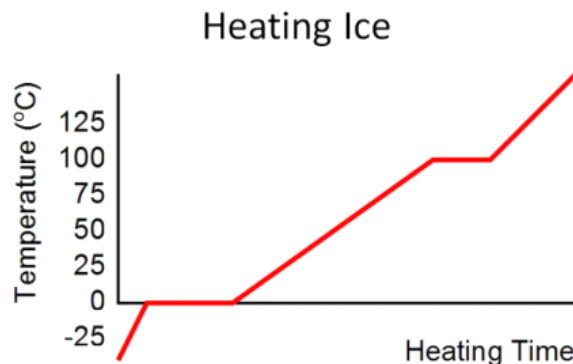
$$Q = nC\Delta T$$

It is worth noting that the molar heat capacities given in the last table are remarkably alike. Except for water, which is a compound, they are all about  $25 \text{ J}/(\text{mol K})$ . This gives us a clue towards understanding what is happening microscopically, but we will have to wait to investigate this clue until a further lecture.

WARNING: Specific heat values are really not constant. They do vary with temperature a little. We know from our study of thermal expansion that the volume of a sample of a material will change a small amount as it is heated or cooled. After all, this is one we found to measure temperature! There is a small amount of work done in changing the volume of the material. Not all of the energy will go into changing the temperature. So our heat capacity will change a little as the volume changes. But if the change in temperature is not too big, we can treat heat capacities for solids and liquids as constants. Oh, but for gasses...we know the volume might change quite a lot as the temperature changes for a gas, so we will find that this analysis needs a few changes for gasses. We will study this in a later lecture.

### 30.3 Phase Changes and Phase Diagrams

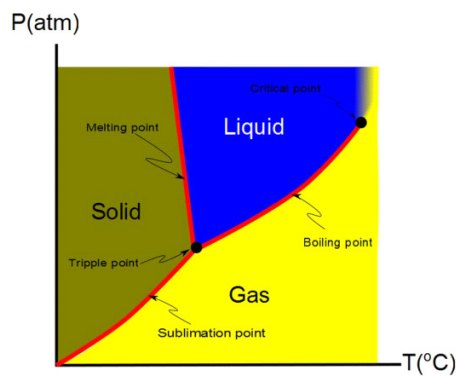
Let's consider heating ice. You take a chunk of ice from outside on a cold February day in Rexburg, Idaho. The ice has a temperature of about  $-25^\circ\text{C}$ .<sup>1</sup> You place it in a pan on your stove and heat it up. Then, being a physics student, you plot the temperature as a function of time. Here is what you get.



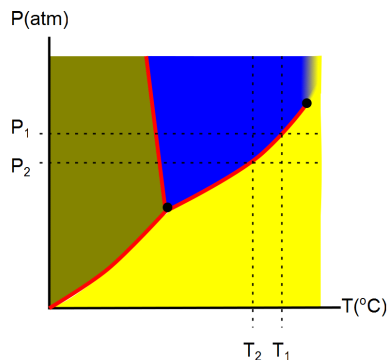
<sup>1</sup>OK, that might be an exaggeration, it only occasionally gets that cold in Rexburg.

Notice the places where you are still transferring energy by heat, but the temperature does not change. These are phase changes. A phase change is like melting and boiling. In our chart, the first is melting, the second is boiling.

One of the things you will notice is that the melted ice does not boil at  $100^\circ\text{C}$  here in Rexburg. This is because we are up so high that the air pressure is less than  $1\text{ atm} = 1.013 \times 10^5\text{ Pa}$ . In the next graph, I have plotted the melting, and boiling point of a substance as a function of pressure. The melting point and boiling point are not single points, but lines on this graph. This is because melting and boiling points depend on pressure. There is also a line for the sublimation point. Along this line, a solid will change directly into a gas. Dry ice does this at normal room temperature and pressure.



If we observe the boiling line, we see that as pressure goes down, the boiling temperature goes down. Look at  $T_1$  and  $T_2$  in the next figure, where  $T_2 < T_1$ . Note that  $P_2 < P_1$ .



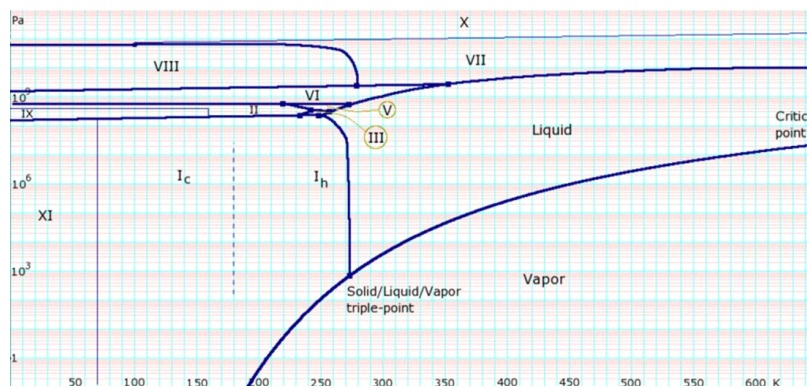
This agrees with our Rexburg boiling point experience.<sup>2</sup> We can see from the graph that melting or boiling depends on pressure, and so does sublimation point.

<sup>2</sup>So if we have a water boil alert here, you have to boil your water longer in Rexburg than you would in NY City in order to make it safe to drink.

The triple point is a special point where all three states are possible at the same pressure and temperature. Ice, steam, and water will all exist in equilibrium, for example, at the triple point of water.

The critical point is where the clear distinction between liquid and gas stops. beyond this boiling the material is in a fluid state, but not clearly liquid or gas. Along each of the lines in our figure, we can say that the material is in phase equilibrium, meaning that both phases from either side of the line are possible and equally probable. Only at the triple point are all three phases equally probable.

Our diagram is rather schematic, and this is on purpose. An actual phase diagram for water is given in the next figure.



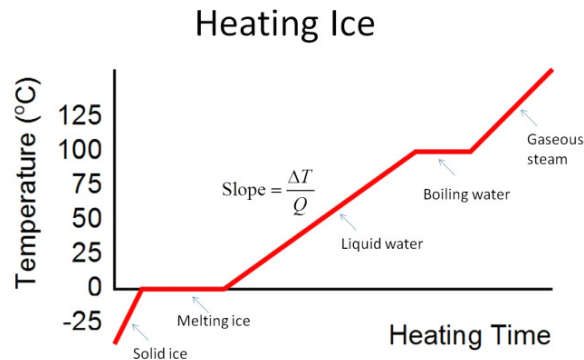
More Complete Phase Diagram for Water (Public Domain Image courtesy Karlhahn)

You can see there are more phases for water than our simple model of solid, liquid, and gas give.

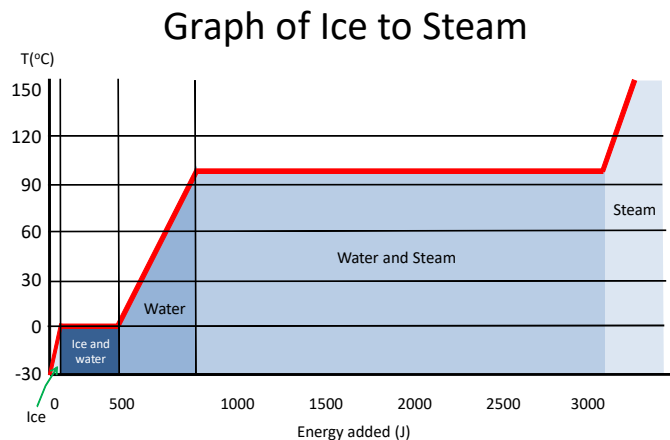
But why do we care about phase changes? Because it takes energy to make a phase change happen. Phase changes direct energy into breaking molecular bonds instead of increasing temperature. So in our graph of temperature vs. heating time the flat parts are where bonds are being broken and a phase change is happening.

## 30.4 Phase changes and heat of transformation

Recall the graph of temperature vs. time for heating a chunk of Rensselaire ice.



Here is the graph again, but this time the horizontal axis is labeled “Energy added” because we realize that we are adding internal energy as we wait and watch the ice.



We see regions of the graph where the ice changes temperature, and we can understand that during these times the temperature gain will be proportional to the amount of energy transferred by heat.

$$\text{Slope} = \frac{\Delta T}{Q} = \frac{1}{Mc}$$

But what about the horizontal parts of the graph? We identified these before as phase changes. The slope is zero during the melting and boiling times.

We have an amount of energy transferred by heat. You might guess that how much energy it takes for the phase change to completely change from one state to the other depends on the strength of the bonds of the material. The added energy is going into breaking those bonds. So the amount of energy it

takes to, say, melt different substances will be different. From experience we know that it takes more energy to heat large amounts of material than small amounts of material. We can express this mathematically as

$$Q = \pm LM$$

where  $L$  is the symbol we give to the constant that expresses the how easily the material melts or freezes. We need at least two of these, one for melting/freezing and one for boiling/condensing. Then

$$\begin{aligned} Q &= \pm L_f M && \text{melt/freeze} \\ Q &= \pm L_v M && \text{boil/condense} \end{aligned}$$

where we call these two constants

$$\begin{aligned} L_f & \text{ heat of fusion} \\ L_v & \text{ heat of vaporization} \end{aligned}$$

generically we call each of these a *heat of transformation* but generally they are still referred to by their old title of “*Latent heat*.”

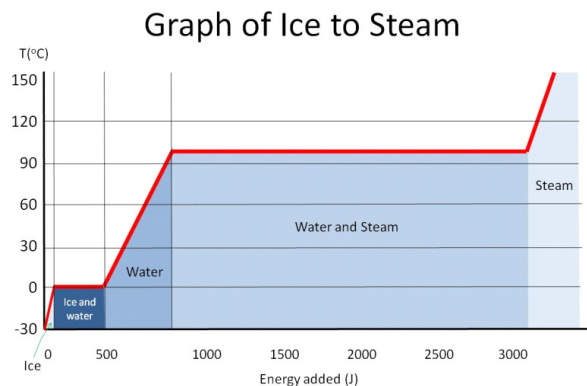
Substance	$T_m$ (°C)	$L_f$ ( $\frac{\text{J}}{\text{kg}}$ )	$T_m$ (°C)	$L_v$ ( $\frac{\text{J}}{\text{kg}}$ )
Nitrogen ( $N_2$ )	−210	$0.26 \times 10^5$	−196	$1.99 \times 10^5$
Ethyl alcohol	−114	$1.09 \times 10^5$	78	$8.79 \times 10^5$
Mercury	−39	$0.11 \times 10^5$	357	$2.96 \times 10^5$
Water	0	$3.33 \times 10^5$	100	$22.6 \times 10^5$
Lead	328	$0.25 \times 10^5$	1750	$8.58 \times 10^5$

Notice that our equations each have a “ $\pm$ ” sign in them. We must supply the sign by context. We need a sign convention like back when we were studying optics!

Let’s choose that energy that leaves is negative and energy that is gained by the system is positive. Also notice that so long as we warm the ice somewhat slowly, that the ice completely melts before the temperature of the water starts to rise.

Let’s do a problem. Suppose we want to increase the temperature of  $1 \text{ g} = 0.001 \text{ kg}$  of ice at  $-30.0^\circ\text{C}$  and change it to steam at  $120.0^\circ\text{C}$ . How much energy transfer by heat is required to do this?

A graph of temperature vs. heat energy is shown. Let’s take it one piece at a time.



**Part A:** Warming up the ice to  $0^{\circ}\text{C}$ .

This part acts as we learned in the last section. We have

$$\begin{aligned}
 Q &= m_i c_i \Delta T \\
 &= (0.001 \text{ kg}) \left( 2090 \frac{\text{J}}{\text{kg}^{\circ}\text{C}} \right) (0^{\circ}\text{C} - (-30^{\circ}\text{C})) \\
 &= 62.7 \text{ J}
 \end{aligned}$$

We can get away with using  $^{\circ}\text{C}$  because we only need  $\Delta T$  and the divisions of the Celsius and Kelvin scales are the same size.

**Part B:** Melting ice

Now the ice changes to water. We have a heat of transformation. To find out what happens we use the equation

$$\begin{aligned}
 Q &= m_i L_f \\
 &= (0.001 \text{ kg}) \left( 3.33 \times 10^5 \frac{\text{J}}{\text{kg}} \right) \\
 &= 333.0 \text{ J}
 \end{aligned}$$

The total energy so far is  $62.7 \text{ J} + 333.0 \text{ J} = 395.7 \text{ J}$ . Note that during Part B the temperature didn't go up!

**Part C:** Warming the melted ice (water)

Again we have the normal case where we can use the specific heat of water (now that the ice has melted)

$$\begin{aligned}
 Q &= m_w c_w \Delta T \\
 &= (1 \text{ g}) \left( 4190 \frac{\text{J}}{\text{kg}^{\circ}\text{C}} \right) (100^{\circ}\text{C} - 0^{\circ}\text{C}) \\
 &= 419.0 \text{ J}
 \end{aligned}$$

The total energy so far is  $62.7 \text{ J} + 333.0 \text{ J} + 419.0 \text{ J} = 814.7 \text{ J}$

**Part D:** Boiling the melted ice (water)

Now we convert the water to steam.

$$\begin{aligned} Q &= m_w L_v \\ &= (0.001 \text{ kg}) \left( 2.26 \times 10^6 \frac{\text{J}}{\text{kg}} \right) \\ &= 2260.0 \text{ J} \end{aligned}$$

The total energy so far is  $62.7 \text{ J} + 333.0 \text{ J} + 419.0 \text{ J} + 2260.0 \text{ J} = 3074.7 \text{ J}$

**Part E:** Warming the steam

Now we have steam, and can use the specific heat of steam (we don't usually do this! we usually use the ideal gas law when it becomes a gas!)

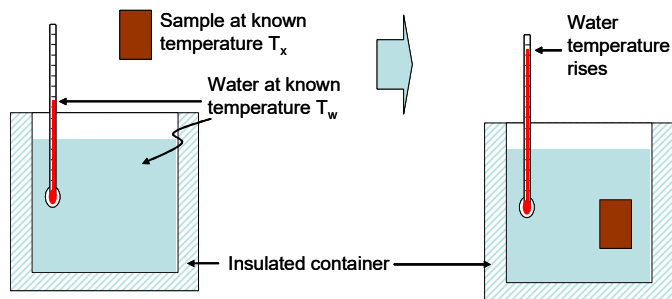
$$\begin{aligned} Q &= m_s c_s \Delta T \\ &= (0.001 \text{ kg}) \left( 2010 \frac{\text{J}}{\text{kg}^\circ\text{C}} \right) (120^\circ\text{C} - 100^\circ\text{C}) \\ &= 40.2 \text{ J} \end{aligned}$$

The total energy transfer required is  $62.7 \text{ J} + 333.0 \text{ J} + 419 \text{ J} + 2260.0 \text{ J} + 40.2 \text{ J} = 3114.9 \text{ J}$

## 30.5 Calorimetry

We can now calculate results for many common thermal experiences. We have all experienced eating something with a large temperature. The solution is to quickly drink something cold. This lowers the temperature. We would like to be able to quantify this. But our mouth is not a great device to use to do quantitative analysis on temperature changes. Let's consider a more suitable apparatus.

Suppose we have an insulated container with a thermometer. We can call this apparatus a *calorimeter*.



Inside of this container let's place a known mass of water and measure the temperature,  $T_w$ . Then we can introduce our sample of hot material. Suppose we know that the hot material has a temperature  $T_x$ .

Let's assume that the container walls are perfectly insulating, then knowing the sample temperature  $T_x$  and the water temperature  $T_w$  with  $T_w < T_x$  we can find  $c$  or  $K$  (or even  $C$ ) for our material. We recognize for this ideal system no energy can leave, because of the insulation. So

$$Q_{\text{cold}} = -Q_{\text{hot}} \quad (30.9)$$

or energy would not be conserved. Then for the water

$$Q_w = m_w c_w (T_f - T_w)$$

and for the sample

$$Q_x = m_x c_x (T_f - T_x)$$

so, using energy conservation

$$\begin{aligned} -Q_x &= Q_w \\ -m_x c_x (T_f - T_x) &= m_w c_w (T_f - T_w) \end{aligned}$$

and we can solve for  $c_x$

$$c_x = -\frac{m_w c_w (T_f - T_w)}{m_x (T_f - T_x)} \quad (30.10)$$

Note the sign convention! If energy leaves the object, the value of  $Q$  is negative. Our denominator is, indeed, negative because for the sample  $T_f$  is less than  $T_x$ . We could use our value of  $c_x$  to identify our material by looking it up in a table of specific heat values.

Let's try a second problem. Suppose we have 2 kg of ice at  $0^\circ\text{C}$  and 1 kg of water at  $50^\circ\text{C}$ . What is the final temperature? This time we could have a phase change, we will need to be careful. We can look up the heat of transformation and the specific heat of ice and water:

$$L_f = 3.33 \times 10^5 \frac{\text{J}}{\text{kg}}$$

$$c_w = 4190 \frac{\text{J}}{\text{kg K}}$$

$$m_i = 2 \text{ kg}$$

$$m_w = 1 \text{ kg}$$

$$T_{ii} = 0^\circ\text{C}$$

$$T_{iw} = 50^\circ\text{C}$$

We still don't expect to lose any energy, so

$$Q_{\text{cold}} = -Q_{\text{hot}}$$



We identify the hot thing as the water this time and the cold thing as the ice. The water only changes temperature, but the ice experiences a phase change. We need to account for all of the energy transferred so for this ice

$$Q_{ice} = Q_{cold} = Q_{melt} + Q_{heat\ up}$$

Then we can put this into our conservation of energy equation

$$\begin{aligned} Q_{ice} &= -Q_{water} \\ Q_{melt} + Q_{heat\ up} &= -Q_{water} \\ L_f m_i + m_i c_w (T_f - T_{ii}) &= -m_w c_w (T_f - T_{iw}) \end{aligned}$$

The final temperature will be the same for both. To find that final temperature we have a little algebra to do. Let's distribute on both sides of our equation.

$$\begin{aligned} L_f m_i + m_i c_w (T_f - T_{ii}) &= -m_w c_w (T_f - T_{iw}) \\ L_f m_i + m_i c_w T_f - m_i c_w T_{ii} &= -m_w c_w T_f + m_w c_w T_{iw} \\ L_f m_i - m_i c_w T_{ii} - m_w c_w T_{iw} &= -m_w c_w T_f - m_i c_w T_f \\ L_f m_i - m_i c_w T_{ii} - m_w c_w T_{iw} &= -(m_w c_w + m_i c_w) T_f \end{aligned}$$

$$\begin{aligned} \frac{L_f m_i - m_i c_w T_{ii} - m_w c_w T_{iw}}{-(m_w c_w + m_i c_w)} &= T_f \\ T_f &= \frac{m_i c_w T_{ii} + m_w c_w T_{iw} - L_f m_i}{(m_w c_w + m_i c_w)} \end{aligned}$$

Really we should do this in kelvin.

$$\begin{aligned} T_f &= \frac{(2\text{ kg}) \left(4190 \frac{\text{J}}{\text{kg K}}\right) (273\text{ K}) + (1\text{ kg}) \left(4190 \frac{\text{J}}{\text{kg K}}\right) (273 + 50)\text{ K} - \left(3.33 \times 10^5 \frac{\text{J}}{\text{kg}}\right) (2\text{ kg})}{\left((1\text{ kg}) \left(4190 \frac{\text{J}}{\text{kg K}}\right) + (2\text{ kg}) \left(4190 \frac{\text{J}}{\text{kg K}}\right)\right)} \\ &= 236.68\text{ K} \\ &= -36.47^\circ\text{C} \end{aligned}$$

Now let's ask, is this reasonable?

The answer is no! We can't end up with a temperature less than the two temperatures we started with. Let's see why this went wrong.

We should have checked in advance to see if all the ice melts. It would take

$$Q = m_i L_f = (2\text{ kg}) \left(3.33 \times 10^5 \frac{\text{J}}{\text{kg}}\right) = 6.66 \times 10^5\text{ J}$$

to melt all the ice. Since the water in the calorimeter is losing energy, we expect that it will have a lower temperature. But it is unlikely that it will all freeze, so

the lowest temperature for the water would be  $0^\circ\text{C}$ . That means the available energy transfer from the water is just

$$\begin{aligned} Q &= m_w C_w (T_0 - T_{wi}) \\ &= (1 \text{ kg}) \left( 4190 \frac{\text{J}}{\text{kg K}} \right) (273 \text{ K} - 323.15 \text{ K}) \\ &= -2.095 \times 10^5 \text{ J} \end{aligned}$$

That is, the warmer water can provide  $2.095 \times 10^5 \text{ J}$ . But since  $2.095 \times 10^5 \text{ J} < 6.66 \times 10^5 \text{ J}$  the warm water does not have enough energy available to melt all the ice. Once the water is all at  $0^\circ\text{C}$ , the ice and water are in thermal equilibrium. No energy will be transferred. So our final temperature of the mixture is  $273 \text{ K}$  or  $0^\circ\text{C}$ .

Of course if our system of ice and water isn't isolated, eventually all the ice will melt. But that would be due to a transfer of energy by heat from the outside environment.

This problem is a bit of a trick, but such a situation can really happen. So it is really important that we stop to consider whether our numerical answers are reasonable once we have done a calorimetry problem.

We have filled in the missing piece of information for solids and liquids. We can say that so long as we don't change the structure of the material,

$$Q = Mc\Delta T$$

or

$$Q = nC\Delta T$$

so we can find  $Q$ ,  $w$ , and  $\Delta E_{int}$  for solids and liquids. But we said gasses will be more difficult. We will take up the relationship between energy transfer by heat and the change in temperature for gasses in our next lecture.