

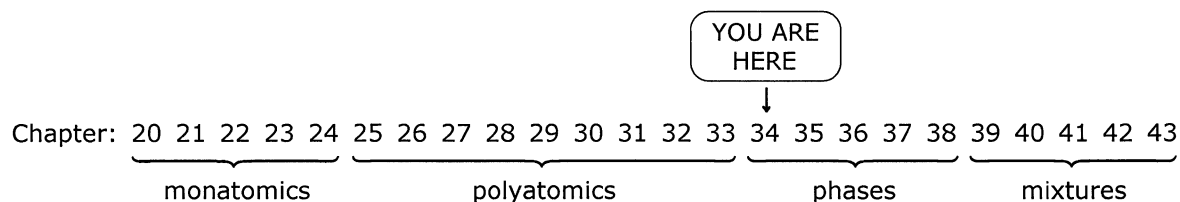
Chapter 34

PHASES, Part 1

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We open with a reminder of where we are at and where we are going.

We have completed fourteen chapters on the study of matter, primarily on the scale of the individual chemical unit. We began with single atoms and then we bonded these to form the rich diversity of polyatomics. Chemical bonds give us compounds; they also give us the molecular and network forms of the elements. Now, from this point, we start into a very different topic: how molecules interact with other molecules. These interactions will involve forces which are quite different and also much weaker than the forces of chemical bonds. The results of these forces are also different: these forces give us the liquid and solid phases and they give us liquid and solid mixtures. With this coverage, we are coming up to the scale of the observable world, where phases and mixtures are so much a part of our normal daily experience.



We begin this part of the journey with the common phases for single compounds. Later, beginning in Chapter 39, we will combine different compounds to form mixtures. There are numerous parts to understanding phases and mixtures. Several of the parts deal with aspects which we have covered so far, and we will be connecting various portions of the Grand Puzzle. We will also be adding quite a few new aspects as we go.

34.1 About phase

Gas, liquid and solid: the common phases. You know them, but what are they? We already covered gas phase back in Chapters 16 and 17, so you already know what that one is. What about liquids and solids? And what about why? Why is one compound a gas at one set of conditions and a liquid or a solid at another set of conditions? Why do different compounds exist in different phases even at the same conditions?

The why parts are very important. We first asked why back in Chapter 10.

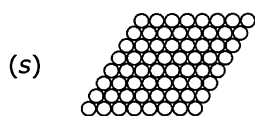
“ Why is one compound a gas and another compound is a liquid under similar conditions? This is a very interesting question, but we're not ready for the details yet. I'll tell you this much now: there is an inherent drive in all of Nature to favor the gas phase out of all three common phases (gas, liquid, solid). This applies to everything. That drive is part of "entropy" but entropy is bigger than this and I'm not going there right now. Simply for now, if a compound is NOT a gas, then something else is going on. In network compounds, this something else is chemical bonds and these bonds keep the atoms closely connected to one another. In molecular compounds, this something else is called "intermolecular forces". Intermolecular forces are the ways by which molecules interact with each other in their immediate surroundings. This can lead to molecules actually clinging to each other; this is how a liquid phase and a solid phase overcome Nature's preference for gas phase. This is all we need for now. We will get into more details regarding entropy and intermolecular forces, and the balance between the two, beginning in Chapter 34. ”

We touched upon this again in Chapter 16.

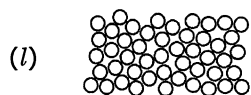
“ The three common phases, solid, liquid and gas, are very much a part of your life. Why are there three? Notice that I said "common" phases. These three phases are common to the surface of planet Earth, given the conditions that exist here. That's what we're used to. ”

These prior points remain very relevant. So also is the subject of orbitals which we have just completed: ORBITALS ARE AN IMPORTANT PART OF THE FORCES WHICH ARE RESPONSIBLE FOR THE LIQUID AND SOLID PHASES. We shall see the role of orbitals in Chapter 37 when we examine the individual types of forces which are involved.

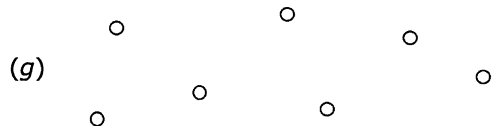
At this time, I want to begin with a few basic features of solid (*s*), liquid (*l*), and gas (*g*) phases so that we can put things into context.



In a typical solid phase, the particles are in some fixed arrangement and they are locked in place. There is some wiggle room and that allows the particles to rotate or to vibrate in that position, but they cannot move out of their fixed location.



In a typical liquid phase, the particles are in loose contact and they are in motion. There is no fixed arrangement overall. In their motions, they constantly bump into each other, and it takes a while for any one particle to move around very far. Although overall movement is slow, they can occupy any location within the volume of the liquid.



In a typical gas phase, the particles are widely separated. Their locations can be anywhere. They move freely relative to each other and at a range of speeds.

These are simple descriptions of the phases, but they do not explain why any particular compound occurs as solid, liquid or gas. In order to understand that, we must look at more fundamentals.

The first quote above (the one from Chapter 10) is extremely important. It contains the most essential aspects for understanding why compounds may be in different phases at different conditions. Half of the story deals with entropy: entropy always favors the gas phase, for reasons we shall see momentarily. If some substance is not gas phase, then there are forces which are operating in order to hold the chemical units together; those forces are the other half of the story. For a substance which exists as a network, then chemical bonds hold the atoms or ions together to form the liquid or solid phase. For a substance which exists as single molecules, then intermolecular forces allow the separate molecules to cling together to form the liquid or solid phase. There are various kinds of intermolecular forces which we shall see in Chapter 37, but for now we simply refer to them collectively as a whole. For now, the important part to understand is that these forces can be strong enough to overcome entropy's preference for gas phase.

Overall then, we have three things to consider for phases: entropy, chemical bonds, and intermolecular forces. Among the three, entropy opposes the other two. For any particular substance under any given set of conditions, its phase is determined by entropy versus chemical bonds and/or intermolecular forces.

ENTROPY	vs.	CHEMICAL BONDS AND/OR INTERMOLECULAR FORCES
This favors gas phase.		These bind and/or attract atoms, molecules and ions together to form liquid and solid phases.

However, one word is missing: balance. You must understand the balance.

Of our three factors, we have already covered the part for networks. Most network compounds are solids due to the strong chemical bonding which extends in the one, two or three dimensions of the network. This strong chemical bonding overcomes entropy and it locks the chemical units in place, thus giving the solid phase. The bonding can be ionic (e.g., NaCl or KI), covalent (e.g., diamond or SiO₂), or metallic (e.g., Fe or Zn). Some network compounds are liquids and these also use chemical bonding. For example, elemental mercury has metallic bonding and it is a liquid. For all network compounds, it is chemical bonding which overcomes entropy. This is all that we need for understanding the phases of network compounds, although we shall see some variations in Chapter 38.

Networks are not our primary concern right now. Our greater emphasis here will involve elements and compounds which exist as molecules (or as single atoms for the elements of Group 18). All of these substances can only form liquid or solid by using intermolecular forces. (Although the term is "intermolecular" forces, the same term is applied to the monatomics of Group 18.) Intermolecular forces are typically much weaker than chemical bonding. Nevertheless, if the grand total of intermolecular forces is strong enough to overcome entropy, then a liquid or solid can be obtained. If not strong enough, then the gas phase is obtained. Overall, we must consider the balance of entropy versus intermolecular forces.

In order to do this, we need a bit more of entropy. We don't need all of entropy right now; we'll just bring in enough for phases.

34.2 Options

Entropy is often described in different ways in different applications by different people. I shall cut to the chase and go for the bottom line.

Entropy is about options. The more the better.

Options? Yes, options. At the most fundamental level, entropy involves the various options for energy. Entropy itself is a mathematical measure of the options for how the energy of a system is distributed among its various molecules and their various bonds and their various motions. Those energies are quantized, so this alone can impose some limits to the options. The fundamental aspects of entropy can get a bit complicated and those aspects are beyond what we need right now. For now, we focus on phases. For now, we keep things on a somewhat simple scale. For now, we just want to know how the energy options on the molecular scale are manifested in the bigger picture of the bulk phase. For now, that's all we need.

A good question for you to consider is why is entropy so important. Well, entropy is important because it is the law. Simply stated, Nature demands higher entropy; all processes must increase entropy, and only those events which increase the total entropy in the universe can occur. We will talk more about this law and about entropy as a mathematical measure of options in Chapter 44 and following Chapters. Entropy is a very big part of Nature and it affects everything. That includes you and everything about you: it includes your life, it includes every cell in your body, it includes everything that you ever do. It is manifested in many ways. These things are part of your world. Whether you know it or not. Whether you understand it or not.

For our discussion of phases, the options we need to consider for entropy are the options for location, orientation and motions of the particles involved. The options for location are related to the volume of the sample: a greater volume allows more options. Orientation relates to direction and whether the molecule is free to face in any direction. Motion can be how fast the particle moves in its phase and in what direction. Motion can also be more subtle things such as how the molecule vibrates along its chemical bonds or how the molecule rotates in three dimensions. All of these involve differing amounts of energies and that allows for more options. The more options, the better.

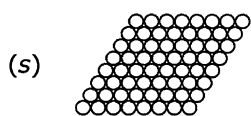
There is another way to look at entropy by looking at its opposite. The opposite of options is restrictions. If molecules are relatively restricted in location or in orientation or in motion, etc., then there is less entropy in the system. If molecules are relatively unrestricted in these aspects, then there is more entropy in the system.

HIGH ENTROPY	LOW ENTROPY
More options	Fewer options
Fewer restrictions	More restrictions

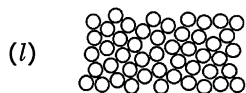
Entropy is important to all aspects of chemistry, not just phases. Entropy is a thermodynamic function and it shares many relationships which we have previously considered for enthalpy (H) and for internal energy (U) along with their changes, ΔH and ΔU ; those things go back to Chapter 18. Entropy is symbolized by S ; for any process or reaction, there is an associated ΔS , which is the final entropy minus the initial entropy, $S_{\text{final}} - S_{\text{initial}}$, for the system. The units for entropy are a bit different, however. Instead of just J's or kJ's as for ΔH or ΔU , entropy units also include a temperature component: the units are J/K. The connection with temperature has important ramifications because the total entropy contribution for a process can depend greatly on temperature. Our focus here involves the qualitative aspects of phases, and I don't want to get into the numbers and the units and the math of entropy yet. Later, beginning in Chapter 44, we will get into more details of entropy and we'll include quantitative (numerical) aspects and this business about increasing the entropy of the universe. I'm not interested in the universe right now. Right now, we're just doing phases.

Although I'm delaying numbers and calculations for entropy for now, we will be dealing with numbers and calculations for ΔH as applied to the energy (enthalpy) associated with a change of phase. We had talked about this back in Chapters 18 and 19 when we were talking about vaporization and such. Right now would be a good time for you to go back and look over that stuff.

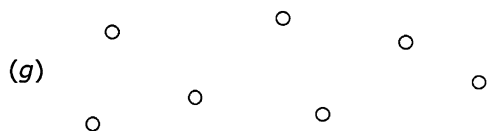
Let's return to our three phases and evaluate their relative entropies based on qualitative considerations of the options for their particles.



The solid phase does not have a lot of options. The particles are in fixed locations. They can vibrate in position and many can rotate in position to another orientation; these provide for some options but that's about it. There are a lot of restrictions within the solid phase. Overall, there is little entropy.



The liquid phase has numerous options (fewer restrictions) because the particles are able to move around a bit. There are options in terms of location and orientation. There are options in terms of motions involving speed and direction, as well as vibration and rotation. The motions will be a bit limited due to the close contacts, but at least there are some. Overall, there is moderate entropy in the liquid phase.



The gas phase has the most options and least restrictions. The particles are distributed over a much greater volume with zillions of possibilities for location and orientation. The speeds and directions of the particles are highly variable. The particles are free to vibrate or rotate in any direction. This is the best. By far, the entropy of the gas phase is the greatest of our three phases.

Thus, based only upon entropy and upon Nature's drive to more entropy, the gas phase is the best; after that, the liquid phase is better than the solid phase.

As noted earlier, solid and liquid phases are obtained when intermolecular forces are strong enough to overcome the entropy preference for gas phase. These intermolecular forces favor the opposite order of the phases: intermolecular forces most favor the solid phase, then liquid phase, and then gas phase. Actually, for an ideal gas, there are no intermolecular forces at all! That was part of the conditions for an ideal gas. On the other hand, real gases can have some small interactions. If you're rusty on this, go back and read Reality check in Chapter 17.

As we go along here, I am going to start abbreviating "intermolecular forces" as IFs (plural) or IF (singular). It's just easier that way.

Now we come to an all-important summary. The gas phase has a lot of entropy but very weak (if any) intermolecular forces; it is the favored phase by entropy alone. If IFs are strong enough to overcome entropy and to hold the molecules in close proximity, then the liquid phase can be obtained; this has moderate entropy, although much less than gas phase. If the IFs are yet stronger, and if they are strong enough to overcome the moderate entropy of the liquid phase, then the solid phase is obtained. The solid phase has the least entropy. Here's a schematic illustrating those relationships.

phase:	(s)	(l)	(g)
entropy, S :	little	moderate	a lot
IFs:	stronger	somewhat strong	very little (if any)

These relationships are extremely important. They explain a lot about phases and why one compound is one phase or another. We'll see this as we go.

Let me point out something in the above schematic. Notice the uneven spacing between the phases. That shows another important point regarding the differences in the phases. Let me redraw the schematic with this emphasis.

phase:	(s)	(l)	(g)
entropy, S :	little	moderate	a lot
IFs:	stronger	somewhat strong	very little (if any)
	—— gap ——		———— big gap ———

There is a gap between solid and liquid, but there is a big gap between liquid and gas. That is important: for both entropy and for intermolecular forces, the gap between gas and liquid is bigger than the gap between liquid and solid. The difference in the gaps can be considerable although it will depend on the specific compound and the specific conditions. For example, at normal temperatures, the big gap can be three, four, or more times the smaller gap.

The above diagram furthermore conveys very important thermodynamic information for changes between the phases.

The gaps for entropy reflect the size of ΔS for any change between any two phases. The gaps for IFs reflect the size of ΔH for any change between any two phases.

Notice that IFs are related to ΔH . The ΔH for a change between phases is dominated by the energies of making and breaking the intermolecular forces which are involved. THIS IS VERY IMPORTANT! Let me say this again.

THE ΔH FOR A CHANGE BETWEEN PHASES IS DOMINATED BY THE ENERGIES OF MAKING AND BREAKING THE INTERMOLECULAR FORCES WHICH ARE INVOLVED.

You need to know this.

Alright, we have our basics in place for enthalpy and entropy. With this much, we now begin our next chunk of material coverage: phase changes. The study of phase change is very much a part of the study of phases themselves. We'll spend the rest of this Chapter and the next two Chapters covering aspects of phase changes. After that, in Chapter 37, we'll finally talk about the actual kinds of intermolecular forces which are available. We will be able to use phase change information to evaluate the total strength of IFs among different compounds. We will begin to see why some compounds are gases or liquids or solids at what kind of conditions. In Chapter 38, we'll talk about the properties of liquid and solid phases on the big picture scale.

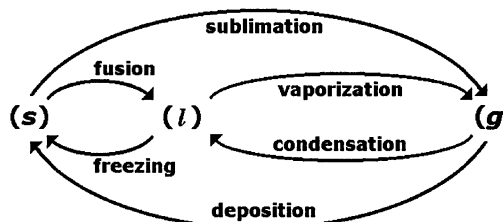
34.3 A change of phase

First, we need some terminology.

Given the three phases of solid, liquid and gas, there are six possible changes between any two. Each of the six possible transitions has its own specific term.

- (s) \rightarrow (l) The change from solid phase to liquid phase is called melting or fusion.
- (l) \rightarrow (s) The change from liquid phase to solid phase is called freezing.
- (l) \rightarrow (g) The change from liquid phase to gas phase is called vaporization.
- (g) \rightarrow (l) The change from gas phase to liquid phase is called condensation.
- (s) \rightarrow (g) The change from solid phase to gas phase is called sublimation.
- (g) \rightarrow (s) The change from gas phase to solid phase is called deposition.

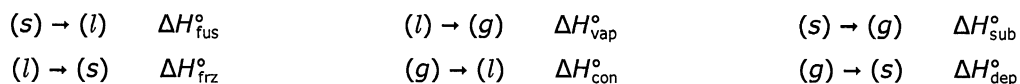
Here's a diagram which relates all of these terms and which shows the gap/big-gap relationship. Keep the terms in mind.



Without any doubt, the one substance on Earth which most commonly demonstrates all of these processes is water. The phase transitions of water are all part of your world.

- (s) \rightarrow (l) Ice cubes and icebergs melt. Although "melting" is the normal word, the word "fusion" is also used for this phase change. Either word is fine.
- (l) \rightarrow (s) You place liquid water into the freezer to make ice.
- (l) \rightarrow (g) Water left open to air will evaporate. On a hot stove, it will boil. Evaporation and boiling are both examples of vaporization.
- (g) \rightarrow (l) On a hot, humid day, water vapor from the air condenses on the outside wall of a cold drink.
- (s) \rightarrow (g) Freezer burn involves foods losing moisture due to sublimation. You may also come across long-lost ice cubes in your freezer which have shrunk in size due to sublimation. As another example, snow and frost can disappear without melting by subliming back into the air.
- (g) \rightarrow (s) Speaking of frost, where did it come from? Water vapor from the air deposits on your car windows as ice. The next time you're scraping frost off your windows, you can thank deposition.

Each phase transition is associated with some enthalpy change, ΔH . If the conditions start at standard and end at standard, then we have ΔH° . When you want to specify the enthalpy for a particular transition, you can give the transition as a subscript, which is commonly abbreviated. This leads to the following notations for transition enthalpies.



We used some of this notation back in Chapter 19 when we talked about $\Delta H_{\text{vap}}^{\circ}$ and $\Delta H_{\text{con}}^{\circ}$ for water. Keep in mind that these were all defined for one mole. And don't forget Important Aspect 2 from the very beginning of Chapter 19: of our six phase changes, three are reversals of the others. That means we have the following relationships.

$$\Delta H_{\text{fus}}^{\circ} = -\Delta H_{\text{frz}}^{\circ} \qquad \Delta H_{\text{vap}}^{\circ} = -\Delta H_{\text{con}}^{\circ} \qquad \Delta H_{\text{sub}}^{\circ} = -\Delta H_{\text{dep}}^{\circ}$$

Because of these relationships, it is very common for references to show only the first of each pair, namely $\Delta H_{\text{fus}}^{\circ}$, $\Delta H_{\text{vap}}^{\circ}$ and $\Delta H_{\text{sub}}^{\circ}$. The others are found from these.

Each phase transition is also associated with a change in entropy, ΔS or ΔS° . You can write analogous descriptions for ΔS° as for ΔH° above.

$$\begin{array}{lll} (s) \rightarrow (l) & \Delta S_{\text{fus}}^{\circ} & (l) \rightarrow (g) \quad \Delta S_{\text{vap}}^{\circ} & (s) \rightarrow (g) \quad \Delta S_{\text{sub}}^{\circ} \\ (l) \rightarrow (s) & \Delta S_{\text{frz}}^{\circ} & (g) \rightarrow (l) \quad \Delta S_{\text{con}}^{\circ} & (g) \rightarrow (s) \quad \Delta S_{\text{dep}}^{\circ} \\ \Delta S_{\text{fus}}^{\circ} = -\Delta S_{\text{frz}}^{\circ} & & \Delta S_{\text{vap}}^{\circ} = -\Delta S_{\text{con}}^{\circ} & \Delta S_{\text{sub}}^{\circ} = -\Delta S_{\text{dep}}^{\circ} \end{array}$$

Although we can set up these relationships for ΔS° , as stated earlier, I am postponing ΔS° calculations until Chapter 44. We will be doing ΔH° calculations, however, so we will be crunching numbers for ΔH° even though numbers for ΔS° will wait.

As noted previously, intermolecular forces are a major part of ΔH° for phase changes. Let's return to the gap/big-gap picture.

phase:	(s)	(l)	(g)
entropy, S:	little	moderate	a lot
IFs:	stronger	somewhat strong	very little (if any)
	—— gap ——		———— big gap ———

For now, we focus only on the IFs, as reflected in ΔH° . Here's how it boils down.

- Fusion/freezing

In order to melt a solid to liquid, you must pay to overcome the stronger IFs of the solid phase. This is a payment of energy into the system, so fusion is endothermic ($\Delta H_{\text{fus}}^{\circ}$ is positive). The cost is some modest amount of J's.

phase:	(s)	(l)	(g)
IFs:	stronger	somewhat strong	very little (if any)
	—— gap ——		

$$\Delta H_{\text{fus}}^{\circ} = \text{a modest amount of J's}$$

Conversely, whenever a liquid freezes to a solid, it releases a modest amount of J's as the stronger IFs kick in. Thus, freezing is exothermic ($\Delta H_{\text{frz}}^{\circ}$ is negative).

- Vaporization/condensation

In order to vaporize a liquid to gas phase, you must pay to overcome the IFs of the liquid phase; vaporization is endothermic ($\Delta H_{\text{vap}}^{\circ}$ is positive). The cost is large compared to melting.

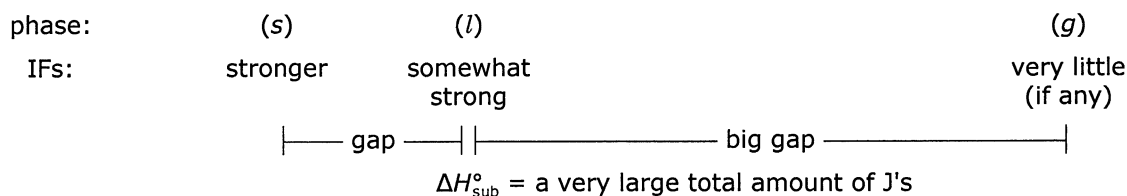
phase:	(s)	(l)	(g)
IFs:	stronger	somewhat strong	very little (if any)
		———— big gap ———	

$$\Delta H_{\text{vap}}^{\circ} = \text{a large amount of J's}$$

Conversely, when you condense from gas to liquid, the IFs kick in and their energy is released; condensation is exothermic ($\Delta H_{\text{con}}^{\circ}$ is negative).

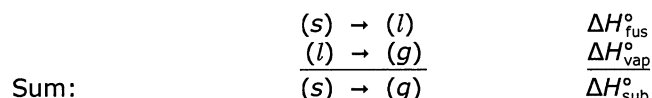
- Sublimation/deposition

In order to sublime a solid to gas phase, you must pay to overcome all IFs all at once; sublimation is endothermic ($\Delta H_{\text{sub}}^{\circ}$ is positive) and the cost is very large.



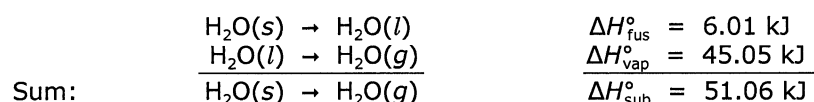
Conversely, when a gas deposits as a solid, the J's are released; deposition is exothermic ($\Delta H_{\text{dep}}^{\circ}$ is negative).

The gap/big-gap relationship immediately tells us the relative sizes of $\Delta H_{\text{fus}}^{\circ}$, $\Delta H_{\text{vap}}^{\circ}$ and $\Delta H_{\text{sub}}^{\circ}$: the smallest is $\Delta H_{\text{fus}}^{\circ}$, $\Delta H_{\text{vap}}^{\circ}$ is larger, and $\Delta H_{\text{sub}}^{\circ}$ is the largest. In fact, $\Delta H_{\text{sub}}^{\circ}$ is the sum of the other two. You can see this from above but it also ties into the additivity of reactions (Important Aspect 4 in Chapter 19).



Keep these various relationships in mind as we go.

Let's take a look at some numbers for water at standard conditions at 0. °C.



For one mole of solid water (ice) to melt at 0. °C, the cost ($\Delta H_{\text{fus}}^{\circ}$) is 6.01 kJ. That's not a lot to pay. For one mole of liquid water to vaporize at 0. °C, the cost ($\Delta H_{\text{vap}}^{\circ}$) is 45.05 kJ, which is a lot more. These two values, 6.01 kJ vs. 45.05 kJ, clearly show the relative sizes in the gap/big-gap relationship, although water is more drastic in this comparison than many other compounds. If you want to sublime solid water to gas at 0. °C, then the cost ($\Delta H_{\text{sub}}^{\circ}$) is 51.06 kJ (6.01 kJ + 45.05 kJ).

Notice that the enthalpies of phase change are much smaller than the enthalpies of chemical reactions. Chemical reactions involve making and breaking chemical bonds. As we have seen since Chapter 18, enthalpies of reactions which involve making/breaking chemical bonds can be in the hundreds or thousands of kJ's. IFs are typically much weaker than chemical bonds. Making and breaking IFs will typically involve only up to several dozens of kJ's, although some can go higher.

If you've reviewed Chapters 18 and 19, then you might have noticed that I gave the value of $\Delta H_{\text{vap}}^{\circ}$ as 44.00 kJ back then whereas here I used the value 45.05 kJ. I'm just being picky right now. 44.00 kJ is for 25 °C and 45.05 kJ is for 0. °C. Enthalpies of phase transitions vary a bit with temperature, so the numbers can change a little. For general approximations, some instructors simply use 25 °C values throughout. That's fine. Just be aware that different values may apply for different temperatures.

34.4 Some number-crunching

Alright, let's get deeper into some numerical calculations involving J's. For purposes of illustration and for purposes of tying together various aspects here and from Chapters 18 and 19, we shall consider the simple phenomenon of heating a solid. Our solid will be an ice cube at some cold temperature. We'll heat this sample and watch it change until we've converted it to a gas at 100. °C.

Here are the details. The ice cube has a mass of 15.0 g. We'll start at -40. °C, which is much colder than most ice cubes. Only water is present in our system; no air or anything else will be present. We'll stay at one atm pressure throughout, so all phases are to be at one atm. We'll let the volume change but we won't worry about its numbers; that's another kind of calculation which we don't need here. We will need to note the melting point as 0. °C and the boiling point as 100. °C. We'll start heating the sample, which means that we'll be adding J's to the sample. Back in Section 18.5, we summarized that there are two and only two things that can happen when you add J's to a system: the J's will pay for an endothermic process to occur or the J's will raise the temperature. As done at that time, the calculation of J's for an endothermic process is a stoichiometry problem; raising the temperature is a heat capacity problem.

Let's begin. We'll break this into four Parts.

► Part 1.

As we add heat to the ice cube beginning at -40. °C, the ice cube will simply warm up. There's nothing else that it can do until it hits its melting point of 0. °C. So, for Part 1 here, we calculate

how many J's are needed to warm the sample from $-40.^\circ\text{C}$ until $0.^\circ\text{C}$. This calculation uses the old heat capacity equation.

$$q = \Delta T \times \text{mass} \times c$$

The temperature change is from $-40.^\circ\text{C}$ to $0.^\circ\text{C}$. For ice in this temperature range, the value of c is $2.0 \text{ J}/(\text{g} \cdot ^\circ\text{C})$. Plug these in, along with the 15.0 g for mass.

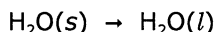
$$q = [0.^\circ\text{C} - (-40.^\circ\text{C})] \times 15.0 \text{ g} \times 2.0 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} = 1,200 \text{ J or } 1.2 \text{ kJ}$$

This tells us that it takes 1.2 kJ to warm the ice cube from $-40.^\circ\text{C}$ to $0.^\circ\text{C}$.

OK, now we have an ice cube at $0.^\circ\text{C}$. We continue to add heat to it. Then what? It melts. That's the next Part.

► Part 2.

Melting is a phase change, which we can write as follows.



How much energy will this cost? For water at $0.^\circ\text{C}$, $\Delta H_{\text{fus}}^\circ = 6.01 \text{ kJ}$. That's for one mol, but we have 15.0 g . This means that we have a stoichiometry problem. Here's the setup.

$$15.0 \text{ g H}_2\text{O} \times \frac{\text{mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{6.01 \text{ kJ}}{\text{mol H}_2\text{O}} = 5.00 \text{ kJ}$$

This tells us that 5.00 kJ are required to melt the 15.0 g ice cube. That will leave you with 15.0 g of liquid water.

Notice that we're still at $0.^\circ\text{C}$. We added heat energy to ice at $0.^\circ\text{C}$ and we got liquid water at $0.^\circ\text{C}$. The temperature didn't go up in Part 2 because all the J's paid for the melting process.

Let's continue to add more heat. It's finished melting, so the liquid will simply get warmer until the next phase change at $100.^\circ\text{C}$.

► Part 3.

We can calculate the total heat energy needed to get the liquid from $0.^\circ\text{C}$ to $100.^\circ\text{C}$. This is another heat capacity calculation.

$$q = \Delta T \times \text{mass} \times c$$

The temperature change is from $0.^\circ\text{C}$ to $100.^\circ\text{C}$. For liquid water in this temperature range, an average value of c is $4.2 \text{ J}/(\text{g} \cdot ^\circ\text{C})$. Plug everything in.

$$q = [\text{_____ } ^\circ\text{C} - \text{_____ } ^\circ\text{C}] \times \text{_____ g} \times 4.2 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} = \text{_____ J or _____ kJ}$$

If you do all this, it tells you that it takes 6.3 kJ to warm the liquid water from $0.^\circ\text{C}$ to $100.^\circ\text{C}$.

By the way, some of you may be wondering about evaporation here: why doesn't some of this water evaporate while it goes through the temperature changes? Well, the simple answer is that the design of the problem does not allow for it. If some volume of gas (such as air) were present, then evaporation could occur, but we specified water to be the only compound present. We also specified one atm pressure throughout and water cannot give a gas phase by itself at one atm until we hit the boiling point of $100.^\circ\text{C}$. So there's no gas phase yet.

That's about to change. You have 15.0 g of liquid water at $100.^\circ\text{C}$. As you continue to heat it, it will undergo vaporization. That's next.

► Part 4.

Vaporization can be written as follows.



How much will this cost? In order to find that, we need the enthalpy of vaporization at $100.^\circ\text{C}$ which is 40.65 kJ . Plug this value into a stoichiometry string similar to the one in Part 2 above. You do it, in the space below.

Be sure you get 33.8 kJ; that's what's required in order to vaporize the 15.0 g of water. Now you have 15.0 g of water vapor at 100. °C.

We could continue adding heat to the system, in which case the $\text{H}_2\text{O}(g)$ would get hotter. That's another heat capacity problem if you're interested, but that was not requested in the current series.

► Summary

All in all, to take 15.0 g of ice at $-40.$ °C to gas at 100. °C, the total cost is 46.3 kJ.

warming the ice from $-40.$ °C to 0. °C:	1.2 kJ
melting the ice at 0. °C:	5.00 kJ
warming the liquid from 0. °C to 100. °C:	6.3 kJ
vaporizing the liquid at 100. °C:	33.8 kJ
	<hr/>
	46.3 kJ

This concludes the calculations for this illustration.

Before closing here, let me point out two things.

First: compare the cost to melt (5.00 kJ) versus the cost to vaporize (33.8 kJ). That reflects the difference in the gap/big-gap relationship for the IFs of the phases. It costs more to vaporize than to melt.

Second: in this series, we started with ice and we added heat until it was gas. You can also consider the opposite direction: begin with gas phase and remove heat (cool it down) until the water is frozen. In this case, the system releases J's and all enthalpy changes are negative. If you use the same amount of water as in the illustration above, you simply reverse all signs but keep the same numbers. Thus, if you begin with 15.0 g of H_2O vapor at 100. °C and place it in a very cold freezer at $-40.$ °C, then you have the following.

condensing the water vapor at 100. °C:	-33.8 kJ
cooling the liquid from 100. °C to 0. °C:	-6.3 kJ
freezing the liquid at 0. °C:	-5.00 kJ
cooling the ice from 0. °C to $-40.$ °C:	-1.2 kJ
	<hr/>
	-46.3 kJ

The numbers are the same for each step and for the total, but now the processes are exothermic and the signs are negative. The water is losing heat to its surroundings (the freezer).

OK, that's enough calculations for right now. From here, we'll start into the picture of what's actually happening as phase changes occur.

Problems

- True or false.
 - For a given compound, its liquid phase has less entropy than its solid phase.
 - Of the three common phases, intermolecular forces are strongest in the solid phase.
 - An ideal gas has no intermolecular forces.
 - Condensation is endothermic.
 - Ice cubes left open in a freezer will shrink over time.
- True or false.
 - For any given substance, $\Delta S_{\text{sub}}^{\circ}$ is greater (more positive) than $\Delta S_{\text{vap}}^{\circ}$.
 - Freezing releases more energy than condensation.
 - Deposition is favored by entropy.
 - Of the three common phases, the gas phase has the most entropy.
 - Liquid and solid phases can exist when intermolecular forces are strong enough to overcome the natural tendency to maximize entropy.

3. Which of the following relationships are NOT correct?
- $\Delta H_{\text{vap}} = -\Delta H_{\text{con}}$
 - $\Delta H_{\text{fus}} > \Delta H_{\text{vap}}$
 - $\Delta H_{\text{frz}} = -\Delta H_{\text{fus}}$
 - $\Delta H_{\text{sub}} > \Delta H_{\text{fus}}$
 - $\Delta H_{\text{vap}} > \Delta H_{\text{sub}}$
4. a. Using enthalpies of formation, calculate $\Delta H_{\text{vap}}^{\circ}$ (in kJ) for methyl alcohol, CH_3OH , at 25 °C.
b. How many kJ's are required to vaporize 28.6 g CH_3OH at standard conditions?
5. Consider the following physical properties for benzene, C_6H_6 .
- | | |
|-----------------------------|--|
| melting point = 5.5 °C | $\Delta H_{\text{fus}}^{\circ} = 9.87 \text{ kJ}$ |
| boiling point = 80.1 °C | $\Delta H_{\text{vap}}^{\circ} = 30.72 \text{ kJ}$ |
| c of solid = 1.5 J/(g • °C) | c of liquid = 1.8 J/(g • °C) |
- A 12.0 g sample of solid benzene at -12.7 °C was heated until finally reaching gas phase at its boiling point.
- How many kJ's were required to heat the sample to its melting point?
 - How many kJ's were required to melt the sample?
 - How many kJ's were required to heat the liquid to its boiling point?
 - How many kJ's were required to vaporize the liquid?
 - How many kJ's were required for the total process?
6. For H_2O at 0 °C, the standard enthalpy of fusion is 6.01 kJ and the standard enthalpy of vaporization is 45.05 kJ. How many kJ are required to sublime 8.63 g H_2O at 0 °C?