

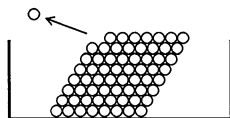
We now proceed to the other phase transitions.

### 36.1 Sublimation/deposition

Of our phase changes, sublimation and deposition may be the ones which many people are least familiar with, although these are actually quite common. As already noted in Chapter 34, water in a freezer or outside in the winter time provides the most obvious and most common examples of sublimation and deposition. Other compounds do this as well. Dry ice is solid  $\text{CO}_2$ ; it sublimates. Elemental iodine is a deep, dark purple solid; it sublimates, producing a faint purple vapor. Every time you can smell a solid, it's because of sublimation. For example, you may know the smell of mothballs. For many decades, those were composed of naphthalene,  $\text{C}_{10}\text{H}_8$ , a solid which sublimates readily but slowly. In somewhat more recent decades, *p*-dichlorobenzene,  $\text{C}_6\text{H}_4\text{Cl}_2$ , has also been used in mothballs; it, too, is a solid and it sublimates readily but slowly. *p*-Dichlorobenzene has also been used in restroom sanitizers/deodorizers. (You find these often as chunks of solid in or hanging around a toilet.) Both naphthalene and *p*-dichlorobenzene have environmental and toxicity (not just to moths!) issues, and other compounds have also been used. As another example of sublimable solid, phenol,  $\text{C}_6\text{H}_5\text{OH}$ , has been used as a mild antiseptic in various applications such as some throat sprays and lozenges. (Phenol was the first antiseptic in surgical applications; that was back in the 1860s by a surgeon whose name would later be applied to a commercial product. It's not used for those applications anymore, although some replacements are derived from it.) Pure phenol is a solid and it has a very characteristic smell.

Sublimation and deposition are very much like vaporization and condensation. There's really not much new to this. Basically, we just apply the same principles from last Chapter. I'll briefly cover the necessary aspects.

Consider a molecular solid phase at some temperature in some container open to air, which I illustrate at right. (No, it's not drawn to scale again.) The particles in the solid phase are held in place by intermolecular forces. They're stuck in their positions, not able to move around any. They can wiggle (very forcefully at times) and some can rotate a bit, but that's all. There are not a lot of options to the motions. As the temperature increases, the particles' average energy increases; as such, wiggling and rotating increase, but there's still no overall moving around within the solid.

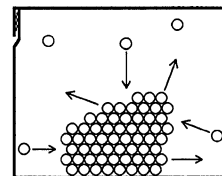
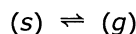


If a particle on the surface of the solid possesses a sufficiently high energy, then it can escape the intermolecular forces and venture out into the gas phase. This represents the simplest act of sublimation. Typically, depending on conditions, huge numbers of particles are escaping in any given moment of time. Depending on their concentration and the temperature of the gas phase, these vapor particles will exert some vapor pressure.

Like vaporization, sublimation is endothermic. Compared to vaporization (and as noted in Chapter 34), sublimation is more endothermic because there are stronger IFs to overcome.

Open to air, the usual motions of the gas phase will take the vapor particles well away from the solid and the solid can eventually sublime completely away. In the vicinity of the solid, however, the gas particle can collide with the surface and be recaptured. That's deposition. Deposition is exothermic, more so than condensation because stronger IFs are kicking in and more energy is released.

In a closed container, the concentration of gas particles will increase and deposition will get faster. At some point, the speed of deposition will equal the speed of sublimation, and the system will be in dynamic equilibrium. At equilibrium, enthalpy and entropy are in balance. We can depict the equilibrium generically as follows.



Deposition need not occur at the same place where sublimation had occurred. Thus, the shape of the solid can change over time. Deposition can even occur at a different spot in the container, thus growing a new piece of solid.

Since the speed of deposition and the speed of sublimation are the same at equilibrium, the concentration of the gas phase particles will stay constant; thus, the vapor pressure will stay constant,

and this is the equilibrium vapor pressure. EVP will depend on temperature: at higher  $T$ , more particles will have more energy to escape to the gas phase, and a higher EVP will result. Here are some numbers for water (ice).

$T$ :	-40. °C	-30. °C	-20. °C	-15 °C	-10. °C	0. °C
EVP (Torr):	0.096	0.29	0.77	1.24	1.95	4.58



The general variation of EVP and  $T$  for different compounds is shown at left. This curve is similar to the curve in Chapter 35 for vaporization/condensation but the curvature is different. The math relationship is again a logarithmic function. We saw in the last Chapter that such curves describe the pressure and boiling point relationship for compounds. Here, instead of boiling point, we use "sublimation point"; this is the temperature at which a compound's EVP has some specified pressure. For example, at 0.77 Torr, water's sublimation point is -20. °C. The curve shows a general

pressure and sublimation point relationship for many typical compounds; different compounds will have a different curvature and will lie in a different range of  $P$  and  $T$ .

In the last Chapter when we did boiling point, we noted that the term normal boiling point is for the specific case where EVP is one atm. Unfortunately, this same notation is not always encountered with sublimation point and the term "normal sublimation point" is not always used. That can lead to ambiguity. Many references only list sublimation points for the specific case of one atm, which means they are really normal sublimation points. For example, you may find the sublimation point of  $\text{CO}_2$  to be listed as -78 °C. Well,  $\text{CO}_2$  sublimates at other temperatures, too, all the way up to -57 °C, but its EVP is one atm only at -78 °C. Be aware that various sources may list "sublimation points" which are really "normal sublimation points".

The discussion from last Chapter on relative humidity also applies for sublimation/deposition with water as ice. At RH = 100%, the air is saturated. At RH < 100%, the air is unsaturated; more solid can be lost to gas phase. At RH > 100%, the air is supersaturated; water vapor can form more ice. Jack Frost comes into the picture by taking advantage of the EVP and  $T$  relationship, just as in dewpoint. Let me explain this part. During some wintry day, there's some  $P(\text{H}_2\text{O})$  of water vapor in the air which is less than EVP for that daytime temperature. At night and into the wee morn, the air temperature drops and therefore EVP drops. When EVP equals the actual  $P(\text{H}_2\text{O})$ , then the air is saturated. This temperature is the frost point. As cooling continues, air-borne water molecules deposit onto grass, vehicles and other surfaces. In this way, you have both rime and reason.

Calculations for RH are the same as in the last Chapter. Here's an example for you: calculate the RH at -20. °C if the water vapor pressure is actually 0.24 Torr. Fill it in below.

$$\text{RH} = \frac{0.24 \text{ Torr}}{\quad} \times 100\% = \quad \%$$

Everything from the last Chapter about drying also applies. In order for ice to dry out, sublimation must be faster than deposition. This is fairly common in your freezer. I included the EVP at -15 °C (5 °F) in the list above because it's a typical temperature for a freezer compartment in a refrigerator. Thus, if your ice cubes in your freezer compartment are at equilibrium at -15 °C, then the water vapor pressure is 1.24 Torr. But a freezer compartment is not always at equilibrium due to opening/closing, on/off cycles, and the frost-free design of many freezers. Instead, the water vapor pressure is often less than EVP and your ice cubes keep subliming into oblivion. It's the same with the water in your frozen foods and that's the source of "freezer burn". Although we generally regard freezer burn as bad, "freeze drying" deliberately makes use of this sublimation process.

Back in Chapter 34, we calculated the enthalpy of fusion and of vaporization for 15.0 g of water. Let's repeat that calculation, now for sublimation in a freezer compartment. Here's the problem: how many kJ are required to sublime 15.0 g of ice at -15 °C? You'll need the enthalpy of sublimation at that temperature, which is 51 kJ for one mol. Here's the whole setup.

$$15.0 \text{ g H}_2\text{O} \times \frac{\text{mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{51 \text{ kJ}}{\text{mol H}_2\text{O}} = 42 \text{ kJ}$$

This tells you that 42 kJ are required to sublime 15.0 g of ice at -15 °C.

Although water is the most common example of sublimation, many other compounds also sublime. Here are values for  $\Delta H_{\text{sub}}^{\circ}$  and EVP for some of the compounds mentioned previously.

	$\text{I}_2$	$\text{C}_{10}\text{H}_8$	$\text{C}_6\text{H}_4\text{Cl}_2$	$\text{C}_6\text{H}_5\text{OH}$
$\Delta H_{\text{sub}}^{\circ}$ (25 °C):	62.42 kJ	72.3 kJ	64.8 kJ	68 kJ
EVP (25 °C):	0.3 Torr	0.087 Torr	1.0 Torr	0.3 Torr

In the last Chapter, we interpreted EVP and enthalpy relative to qualitative comparisons of intermolecular forces. Unfortunately, we can't do that with this group of compounds and there are numerous reasons for this. For one thing, comparisons which involve a solid phase are more troublesome because there are more subtleties involved in the energies of solid phase compared to liquid or gas phases. Also, as we get into more complex molecules such as some of those here, our simple comparisons get more complicated; qualitatively ranking these four in a comparison of IFs would be very difficult. Nevertheless, the above numbers give you an idea of the small vapor pressures which can be involved for a typical smelly solid. Just don't smell them too much, since that can have adverse health effects.

Let's do a calculation with one of these.

**Example.** Consider a storage compartment of dimensions 2.0 ft by 4.0 ft by 7.0 ft; this storage compartment has a volume of 1,600 L. Put some naphthalene mothballs inside. How many grams of naphthalene vapor,  $\text{C}_{10}\text{H}_8(g)$ , can be contained in that volume at equilibrium at 25 °C?

This is a  $PVnRT$  problem again, just like the water-vapor-in-the-bottle problem in the last Chapter. You can do this. First, you need  $n$ .  $V$  and  $T$  are given in the problem, while  $P$  is from the above list. Once you have  $n$ , then bring in the molar mass to get grams.

Your final answer should be 0.96 g. (If you can't get this or if you're not sure of how to do this, look back over the vaporization problem in the last Chapter.) That means there is 0.96 g of naphthalene in the gas phase at equilibrium. As fresh air exchanges with the air in the compartment, then some vapor is lost, more solid sublimates to gas, and this continues until the solid is gone. That would make the moths happy.

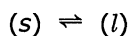
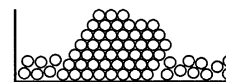
OK, this concludes sublimation/deposition. Now we turn to our final pair of transitions.

### 36.2 Fusion/freezing

Let's start with solid phase at some temperature in some container.



If you increase the temperature of the solid, the individual particles take on more J's. Particles at the surface can break some of the stranglehold of the intermolecular forces and these can collect as liquid phase; this allows for more entropy. This is the melting (or fusion) process, which is endothermic. Liquid phase particles which are in contact with the solid surface can be recaptured back into the solid phase. This is freezing; freezing is exothermic. At some particular temperature, an equilibrium is attained.

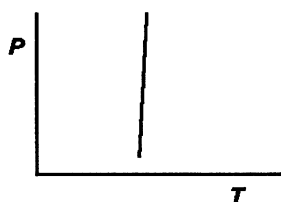
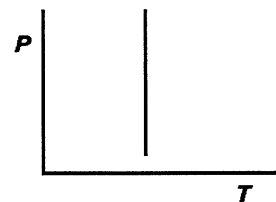


At equilibrium, the speed of melting and the speed of freezing are equal. The enthalpy and entropy of the two phases are in balance. The temperature for this equilibrium is called the melting point (mp) or freezing point (fp). Either term is fine. Over time, as in the case of sublimation/deposition, the dynamic nature of this equilibrium can result in the solid changing its shape.

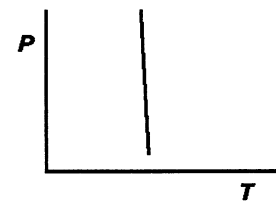
This is all we need for our picture of fusion/freezing. These changes are simpler than the prior phase changes. One big difference between fusion/freezing and the earlier transitions is the effects of pressure. Since the solid phase and the liquid phase already have their particles in contact, increasing  $P$  might scrunch the particles a tad bit closer together but the effect is very small. This is very different from the gas phase which has a huge effect of pressure on volume; as we have seen, that's because most of the

gas volume is nothing. Gas phase is really the only phase that counts much for pressure: any time you have a gas phase component in any system, then pressure can have a really big effect. Any time you have only liquid phase and/or solid phase present in a system, then pressure has zero or very little effect over a moderate range of pressure. (At very high pressures, the effects can become significant.)

As described above for sublimation and deposition, and in the prior Chapter for vaporization and condensation, equilibrium pressures and temperatures are highly dependent on each other. That won't be the case anymore. For fusion/freezing, the pressure at equilibrium has a very small effect on melting point (freezing point). Let me show the graphical consequences. If there were absolutely no effect with pressure, then the temperature of melting (mp) would not vary with  $P$ , and you'd get a straight vertical line for mp as shown at right. To the left of the line (colder, lower  $T$ ), you have solid phase. To the right of the line (warmer, higher  $T$ ), you have liquid phase. Dead smack on the line, you have both in equilibrium.



In reality, since there is a very slight pressure effect, the line is not exactly vertical. It has a slight lean, and the lean can be forward or backward depending on the compound involved. I show the forward lean at left and the backward lean at right. Does it matter? Yes, very much so.



Pictorially, the lean is very slight when the pressure axis covers a moderate range, and it may even be less than what I'm drawing here. Over a very large pressure range, however, the lean will appear greater and there can be some curvature to the line. You may see graphs in other sources which show this. It depends on the scale of the pressure axis in the plot. And sometimes the pressure axis is plotted logarithmically.

Since melting (fusion) has very little dependence on pressure, then we usually don't bother to specify pressure and we usually don't use the "normal" adjective like we did for normal boiling point or normal sublimation point. Melting points (freezing points) are usually given for one atm or close to it, and that's good enough.

The direction of the lean depends on which phase has the higher density at the melting point. Higher pressure favors the phase with higher density. By far, for the vast majority of all substances, the solid phase is denser than the liquid phase at the melting point because the particles are tucked in a bit closer in the solid phase. For these substances, higher pressure favors the solid phase and it will take a bit more thermal energy to melt at higher  $P$ . Thus, mp increases (slightly) with higher  $P$ , and you get a forward lean as shown on the left above.

For very few substances, the liquid phase is denser than the solid phase at the melting point. This is a rare occurrence among all substances, but it does happen. For those, higher pressure favors liquid phase, so it takes less thermal energy to melt at higher  $P$ . Melting point decreases (slightly) with higher  $P$  and you get the backward lean for the mp line as shown on the right above. This behavior is known for some elements (Si, Ga, Ge, Sb and Bi) but it's very rare for compounds. It's weird. It's so rare that, by itself, I wouldn't even bother mentioning it. But I have to bring it up, because there's one very weird compound that's very important. Can you guess it? It's the most common weird compound on Earth.

Water.

Why does this happen to water? As we'll see in Chapter 37, the total intermolecular forces in water are very strong for such a small molecule. In the solid phase, where IFs are the strongest anyway, this imposes a specific positioning of the water molecules in interconnected, zigzag rings. It turns out that these rings are not the most compact arrangement. As the solid melts, the  $H_2O$  molecules in the liquid are no longer restricted to interconnected rings; on average, the molecules can get a bit closer together so the liquid is initially more compact. Being more compact (more dense), the liquid is favored by higher pressure; as a result, less thermal energy (lower mp) is needed to melt at higher  $P$ . Again, this is still not a large effect. It takes  $\sim 130$  atm pressure to lower the melting point of  $H_2O(s)$  to  $-1^\circ C$ .

Although liquid water is denser than solid water at the melting point, it doesn't stay denser. All liquids loosen up and expand slightly with increasing temperature. Their molecules have more energy so they bump around harder and this requires more room.  $H_2O(l)$  increases in density from  $0^\circ C$  to  $4^\circ C$ ,

but then it starts to loosen up. Above 4 °C,  $\text{H}_2\text{O}(l)$  expands slightly like any other liquid so the liquid becomes less compact (less dense) upon further warming.

Interestingly, you yourself have observed water's odd density relationship, every time you have a glass of ice water: ice cubes float. That's weird. It's not supposed to be that way; the solid phase should sink in the liquid phase. At least, that's the way it is for the vast majority of substances. Not for water. Water is weird. But you knew that, right?

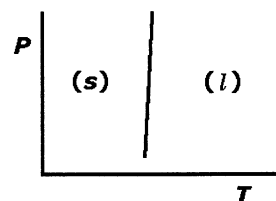
This concludes our discussion of fusion and freezing. We have completed the separate discussions of the various phase transitions and their equilibria. Now, let's bring them all together.

### 36.3 Putting it together

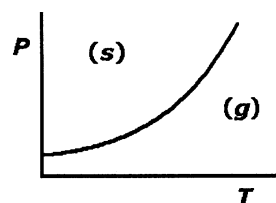
Given all possible transitions, every phase can go either of two ways. A solid phase can sublime to a gas or it can melt to a liquid. A liquid phase can vaporize to a gas or it can freeze to a solid. A gas phase can condense to a liquid or it can deposit to a solid. On the other hand, transitions don't have to happen all the time: under some conditions, the phase can just sit there by itself and do no transition at all. What governs all of these things? These things all lie in the balance of enthalpy and entropy, and that balance depends to a great extent on the conditions of pressure and temperature. Thus, phase behavior is inherently dependent on  $P$  and  $T$  which is reflected in the graphs which I've been showing so far. Up to now, I've been showing the graphs separately but now we need to see how the various parts fit together.

Let's bring back the separate graphs and make a few more points.

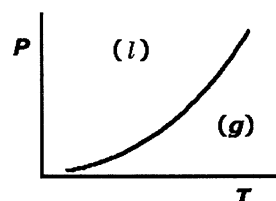
We begin with the last: fusion/freezing. I've repeated it here for the most common cases (those with the forward lean). Any  $P/T$  point on the line represents a condition where both phases are present at equilibrium. To the left of the line we have conditions of pressure and temperature which favor solid phase only. To the right of the line we have conditions of pressure and temperature which favor liquid phase only. (Notice that I haven't been drawing the line all the way down to the horizontal axis. You'll see why as we connect everything here.)



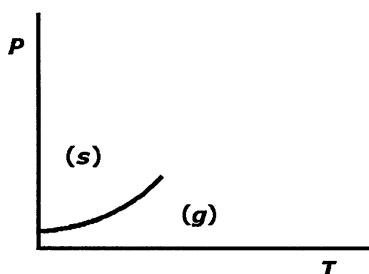
Now we bring back the sublimation/deposition graph. The curve itself represents all  $P/T$  points where both solid and gas phases are present at equilibrium. At higher pressure and/or lower temperature than the curve, the solid phase is favored by itself. This corresponds to the region above and/or to the left of the curve. Below and/or to the right of the curve, the gas phase is favored by itself.



Finally, the vaporization/condensation graph from Chapter 35. At all points on the curve, both liquid and gas phases are present at equilibrium. At higher pressure and/or lower temperature, the liquid phase is favored; this corresponds to all conditions of  $P$  and  $T$  above and/or to the left of the curve. Below and/or to the right of the curve, the gas phase is favored.

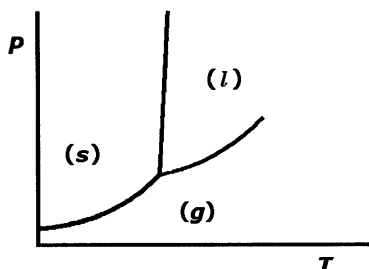
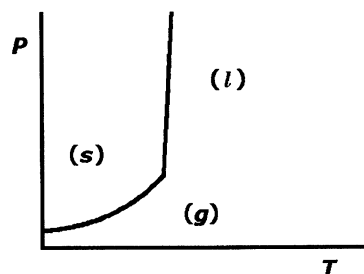


Now we'll connect the separate graphs together into one single diagram. We'll see how they line up with respect to each other.



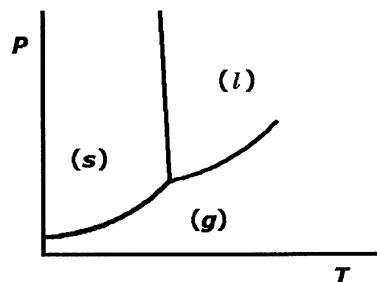
We start with sublimation/deposition since those transitions run down to the lowest temperatures and pressures. I show this at left. At this time, we have two of our three phases in position.

The sublimation/deposition curve ends when it runs into the fusion/freezing curve, which I now add to the diagram at right. This adds the third phase, although we don't have the liquid and gas phases separated yet.



At left, I now add the final equilibrium curve, which is for vaporization/condensation. This completes the general diagram for our coverage here. This type of graph is called a phase diagram.

The phase diagram above is typical for many substances but not for water. The difference lies in the fusion/freezing line which leans backwards for water, as shown at right.



Phase diagrams illustrate the behavior of a pure substance (by itself) over a range of  $P$  and  $T$  conditions. The diagrams show the regions of pressures and temperatures for a single phase to exist by itself or in equilibrium with another phase. Any  $P/T$  point which is not on a curve is a condition for only one phase. Any  $P/T$  point on a curve is an equilibrium condition between two phases. There's also one particular point which occurs at the intersection of all three curves; this is called the triple point. At the triple point, all three phases can coexist at equilibrium.

Phase diagrams provide a pictorial idea as to whether a particular substance will be a solid or a liquid or a gas at typical conditions. "Typical conditions" are what we are most familiar with as we live on the surface of planet Earth; common ranges include 0.8 to 1.1 atm and  $-20$  to  $+40$  °C depending on where you're at. Let's consider the specific condition of one atm and 25 °C. Let's look at three different phase diagrams, representing three different generic substances, as illustrated below.

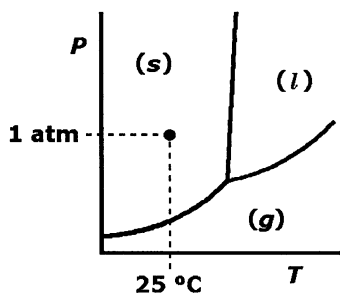


DIAGRAM A

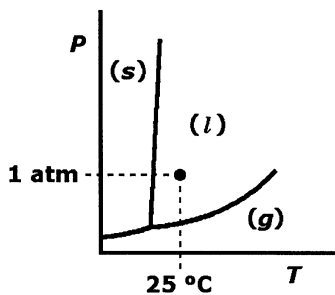


DIAGRAM B

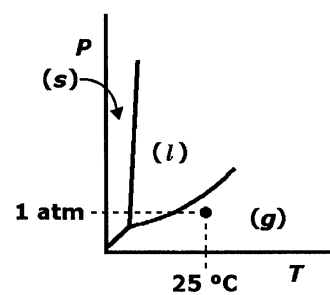


DIAGRAM C

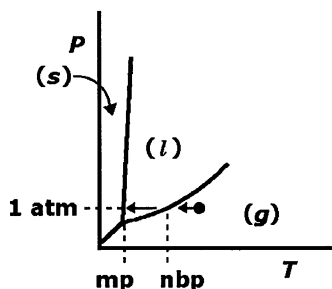
Notice that I have not drawn a full numerical scale to the axes; furthermore, the scales are not intended to be the same in the three Diagrams, and the axes don't go to  $-273$  °C (zero K) or to zero atm. Don't worry about the axes and the scales here because we're going primarily for qualitative aspects. I did put a big dot in each Diagram; the big dot represents the specific  $P$  and  $T$  conditions of one atm (760 Torr) and 25 °C. At the specific conditions represented by the dot, the substance with phase diagram A will be a solid; the substance with phase diagram B will be a liquid; and, the substance with phase diagram C will be a gas.

Let's bring in a few actual substances and see how they fit these general pictures.

- ▶ Elemental iodine,  $I_2$ , is a solid at typical conditions. It would correspond to the general phase diagram A. The triple point for  $I_2$  is  $114\text{ }^\circ\text{C}$  and  $91\text{ Torr}$ ; this is higher temperature and lower pressure than the big dot at  $25\text{ }^\circ\text{C}$  and one atm.
- ▶ Methanol,  $\text{CH}_3\text{OH}$ , is a liquid at typical conditions. It would correspond to the general phase diagram B. The triple point for  $\text{CH}_3\text{OH}$  is  $-98\text{ }^\circ\text{C}$  and  $0.001\text{ Torr}$ ; this is lower temperature and lower pressure than the big dot at  $25\text{ }^\circ\text{C}$  and one atm.
- ▶ Propane,  $\text{C}_3\text{H}_8$ , is a gas at typical conditions. It would correspond to the general phase diagram C. The triple point for  $\text{C}_3\text{H}_8$  is  $-188\text{ }^\circ\text{C}$  and  $1 \times 10^{-6}\text{ Torr}$ ; this is lower temperature and (much) lower pressure than the big dot at  $25\text{ }^\circ\text{C}$  and one atm.

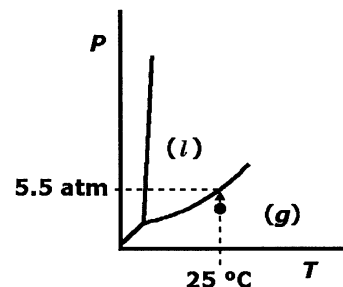
These are just illustrative examples. Again, the different behaviors are a result of how each substance responds to the various  $P/T$  conditions, which ultimately ties back to each compound's enthalpy and entropy properties. Every different compound has a different phase diagram.

We can see from a phase diagram how the phases will respond to changing temperature or pressure. To illustrate, look at Diagram C for propane. If the conditions are  $25\text{ }^\circ\text{C}$  and one atm, it's a gas. Let's consider two scenarios starting from there.



Scenario 1. Let's see what happens if we decrease the temperature while staying at a constant pressure of propane of one atm. This means start at the original big dot and then move directly left, following the horizontal arrows as shown at left. At some temperature, you run into the vaporization/condensation curve which means you have liquid and gas at equilibrium. Since we specified one atm pressure, then this temperature is the normal boiling point; nbp for  $\text{C}_3\text{H}_8$  is  $-62\text{ }^\circ\text{C}$ . If you move further to the left and off the curve, you have only liquid phase. Continuing more to the left, you hit the fusion/freezing curve; now, solid and liquid are in equilibrium; this temperature is the melting (freezing) point, which is  $-187\text{ }^\circ\text{C}$  for propane. Cooling even further beyond that gives only solid phase.

Scenario 2. Now, we change  $P$  while staying at the same temperature,  $25\text{ }^\circ\text{C}$ . Start at the original big dot again. Increase the pressure, which means you go straight up vertically from the dot. As you increase  $P$  above the original one atm, you hit the vaporization/condensation curve; now, you have both liquid and gas phases. This pressure is the EVP at  $25\text{ }^\circ\text{C}$ , which is  $5.5\text{ atm}$  for propane. Increasing  $P$  above  $5.5\text{ atm}$  gives only liquid phase.



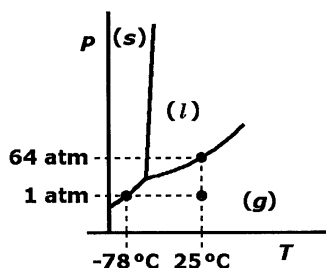
You may be familiar with the latter Scenario. This was mentioned back in Chapter 19.

“ Let's do a combustion example... Think food. Think grilling. Think about getting ready and then finding out that your gas tank is empty. Time for LPG. That's liquified petroleum gas. It's used in all sorts of things, not just grills. Some vehicles use it instead of gasoline. Some tractors, trucks, buses, fork lifts, zambonis and even some cars. LPG is primarily propane,  $\text{C}_3\text{H}_8$ . It's a gas at normal pressure but, at high pressure, some will condense to a liquid. If you pick up a gas tank and jiggle it, you can feel the liquid inside sloshing around but, when it's attached to the grill and you open the burners, the stuff that comes out is all of a sudden back to normal pressure and you get gas phase. That's vaporization again. ”

That description is reflected in the phase diagram, assuming pure propane. Inside the tank, you have liquid phase and gas phase propane in equilibrium at EVP ( $5.5\text{ atm}$  at  $25\text{ }^\circ\text{C}$ ). When you open the valve, propane is released as gas but its pressure drops down to one atm (or whatever the atmospheric pressure is at the time) as it comes out the burners. Back in the tank, the loss of  $\text{C}_3\text{H}_8(g)$  throws off the equilibrium balance. Vaporization is faster than condensation until you close off the tank and equilibrium is restored. For as long as you have liquid propane present, the tank pressure will be EVP; once your liquid phase is gone, you're running on fumes and the pressure drops until you're empty. "Empty" isn't really empty!

It means the pressure inside the tank is the same as outside air pressure. When the pressures are equal, the propane gas inside the tank doesn't have any more push left to it against the surrounding air. It's time for a refill.

The phase diagrams above are fairly general for many substances although there will be variations in detail. Let me illustrate one such variation using  $\text{CO}_2$ . You are familiar with  $\text{CO}_2$  gas and you may be familiar with dry ice as the solid form of  $\text{CO}_2$ ; both of these can be kept at one atm although the solid needs to be very cold ( $-78^\circ\text{C}$ ). Liquid  $\text{CO}_2$ , however, is not stable at one atm at any temperature. The triple point for  $\text{CO}_2$  is  $-57^\circ\text{C}$  and 5.2 atm; the triple point pressure is unusually high for substances which are typically gases. The phase diagram at left illustrates a triple point above one atm pressure. For  $\text{CO}_2$ , if you start at one atm and  $25^\circ\text{C}$  and then decrease  $T$  along the horizontal line, you see that cooling the gas phase below  $25^\circ\text{C}$  will eventually form solid without ever going through a liquid phase. Likewise, warming solid  $\text{CO}_2$  above  $-78^\circ\text{C}$  at one atm pressure will cause it to sublime but not melt. Liquid  $\text{CO}_2$  cannot be kept at one atm, no matter what the temperature may be. On the other hand,  $\text{CO}_2(l)$  can exist at higher pressure, at or above 5.2 atm. For example, at  $25^\circ\text{C}$ , tanks of  $\text{CO}_2$  at equilibrium will have liquid inside with an EVP of 64 atm.



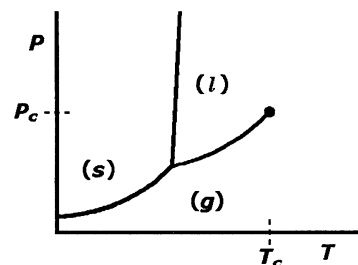
We commonly encounter gas, liquid and solid phases because of the moderate nature of Earth surface conditions. When you get away from those moderate conditions, however, all sorts of strange things can happen. At very high pressures (and low to moderate temperatures), you won't find the gas phase very often. For example, pressures are very high at ocean depths or deep within the Earth. The common gases  $\text{CH}_4$  and  $\text{CO}_2$  are liquids at those conditions. Even the solid phase itself becomes complicated at extreme conditions: at very high pressures, water has 16 (or more!) other forms of ice. Continuing into even greater extremes, elemental hydrogen is believed to become a metal at several million atm pressure; this could have astronomical impact in the cores of large planets. Our phase diagrams here don't cover those extremes, so there are more parts to phase diagrams than what we are covering.

Keep in mind that our life's experiences are based primarily on Earth surface conditions and that other things become possible when we get away from those conditions. Actually, you really don't have to go too extreme in order to get into strange behavior; sometimes, you can get strange just by going critical.

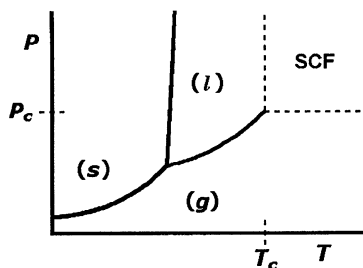
### 36.4 A critical point

There's another point on our phase diagrams which I need to describe. It's part of the vaporization/condensation curve: that curve begins at the triple point and continues out a ways before coming to a complete stop at a specific  $P$  and  $T$  point. The curve stops because the liquid phase and gas phase merge at this point into one phase. We can look at this merger in the following manner.

Start at some  $T$  and  $P$  point which lies on the liquid-gas curve; you will have an equilibrium between the liquid and the gas phases. Now, increase  $T$  and  $P$  along the curve. The primary effect on the liquid is to expand somewhat (decrease concentration) due to increasing temperature. The primary effect on the gas is to greatly reduce volume (increase concentration) due to increasing pressure. The latter is the greater effect: the gas phase volume is contracting much faster than the liquid phase is expanding. At some point of  $T$  and  $P$ , the two phases become the same concentration and they become one phase. That point is called the critical point. The temperature at the critical point is called the critical temperature, designated  $T_c$ ; the pressure is called the critical pressure,  $P_c$ . At the critical point and beyond, we have a fluid with some properties of a liquid and some properties of a gas. Like a liquid, this fluid can dissolve solids and other solutes. Like a gas, this fluid completely fills its container.







This fluid is called a "supercritical fluid" or SCF. ("Supercritical" means beyond critical, meaning beyond the critical point.) It is simply that fluid which exists beyond the critical temperature and critical pressure. Supercritical fluids can take on strange properties. Curiously, water becomes less weird.

We do not typically encounter supercritical fluids with their strange behavior because critical points tend to be much higher than typical conditions. This is especially true for  $P_c$  although  $T_c$  can also run high. Below are data for some of the compounds which we have been discussing.

	CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> OH	H <sub>2</sub> O
$T_c$ :	31 °C	97 °C	240. °C	374 °C
$P_c$ :	73 atm	42 atm	80. atm	218 atm

When water goes supercritical, it loses much of its weirdness as a solvent and it starts to behave like a normal solvent. Supercritical water is only slightly polar and its dissolving properties change dramatically. Many salts are no longer soluble in supercritical water while nonpolar things like oils become soluble. It has been of interest for some time to use some of the properties of supercritical water in various applications, but this is very limited because water becomes extremely corrosive at the high temperature and pressure required. Typical container materials cannot withstand these conditions, so applications for now are fairly limited.

That does not apply to all SCFs, however, and other substances have also been studied for their supercritical properties as a solvent. The best of all so far is CO<sub>2</sub>. In fact, some of what you drink and some of what you wear may be taking a bath in it.

Supercritical CO<sub>2</sub> has very attractive solvent properties for a wide range of applications. Furthermore, its critical temperature is mild and its critical pressure is not too high. It is less toxic and less environmentally harmful than most nonaqueous solvents currently in use throughout the world. CO<sub>2</sub> used in supercritical applications comes from other industrial processes which otherwise would just release it to the environment; thus, loss of CO<sub>2</sub> through supercritical applications is considered environmentally neutral. It certainly has a lot of positive features and these have found more and more applications in recent decades.

One of the primary, large-scale applications of supercritical CO<sub>2</sub> has been for decaffeinating coffee and tea, although other methods are also in use. Supercritical CO<sub>2</sub> is also used in other aspects of the food industry for flavor extraction. It is also receiving tremendous interest from the microelectronics industry for use in chip manufacturing. There are also applications in the pharmaceutical and biomedical industries. Closer to home, supercritical CO<sub>2</sub> is now spreading in use for dry cleaning. Traditional dry cleaning uses C<sub>2</sub>Cl<sub>4</sub>, which also has numerous safety and environmental concerns. You can even smell traces of it on some heavier articles after you bring them home. Newer dry cleaning processes are using supercritical CO<sub>2</sub> and completely eliminating C<sub>2</sub>Cl<sub>4</sub>.

Research continues into even more applications for supercritical CO<sub>2</sub> in particular and other SCFs in general. There's quite a lot going on in this area. These things are part of your world, now and in the future.

## Problems

- True or false.
  - In a phase diagram showing solid, liquid and gas, the solid phase appears at the bottom.
  - Sublimation can occur over various temperature/pressure conditions up to (and including) the triple point.
  - At the melting point, H<sub>2</sub>O(s) is denser than H<sub>2</sub>O(l).
  - The solid, liquid, and gas phases are in equilibrium at the triple point.
  - A supercritical fluid exists at all temperatures greater than the triple point.

2. Consider the sublimation of ice in a freezer compartment at  $-15\text{ }^{\circ}\text{C}$ . For a gas volume of  $20.0\text{ L}$ , how many grams of  $\text{H}_2\text{O}(g)$  are present at equilibrium?
3. Solid  $\text{I}_2$  was placed in a vessel at  $320.\text{ K}$  and allowed to sublime. At equilibrium, the gas phase was found to contain  $0.241\text{ g}$  of  $\text{I}_2(g)$ . The gas volume was  $10.6\text{ L}$ . What is the EVP (in Torr) for  $\text{I}_2(s)$  at this temperature?
4. On a wintry morning, the air temperature is  $14\text{ }^{\circ}\text{F}$  ( $-10.\text{ }^{\circ}\text{C}$ ) and the RH is  $71\%$ . If that air comes into a house and is warmed to  $68\text{ }^{\circ}\text{F}$  ( $20.\text{ }^{\circ}\text{C}$ ) at constant pressure, what is the RH of that air indoors?

5. Consider the phase diagram at right with points labeled A - H.
  - a. Which point corresponds to liquid phase only?
  - b. Which point corresponds to equilibrium conditions for solid and liquid phases (only)?
  - c. Which point corresponds to equilibrium conditions for sublimation and deposition (only)?
  - d. On going from point E to point F, which phase change occurs?

