

## Chapter 35

## PHASES, Part 2

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At this time, we start taking a closer look at the physical processes involved in a phase change. We begin with vaporization and condensation. I will spend this whole Chapter solely on these two transitions. Much of what is here will also apply to other phase transitions in the next Chapter.

### 35.1 Vaporization/condensation

Vaporization and condensation are extremely important in many ways to many things. On Earth, the greatest impact of this lies in the weather: evaporation from bodies of water distributes moisture to all parts of the planet where it can condense and fall as rain (or snow). Rain, snow, streams, rivers, lakes, glaciers and oceans have helped shaped the surface (and below) of this planet over the eons. Biology is heavily influenced by these phase changes also: for example, loss of water via evaporation is a major concern to massive numbers of organisms living on land. The reason is simple: excess dehydration means death. Humans are also subject to this. You constantly lose water right through your skin by transpiration; this can amount to several hundred mL of water (measured as liquid) each day. You constantly exhale water; this can amount to another several hundred mL of water (measured as liquid) daily. You also sweat water for the primary purpose of regulating body temperature. This can be a hundred mL per day (measured as liquid) under resting conditions, but several liters per day for heavy work. Even your comfort level is influenced by the combination of vaporization and condensation. All of these things are part of your world.

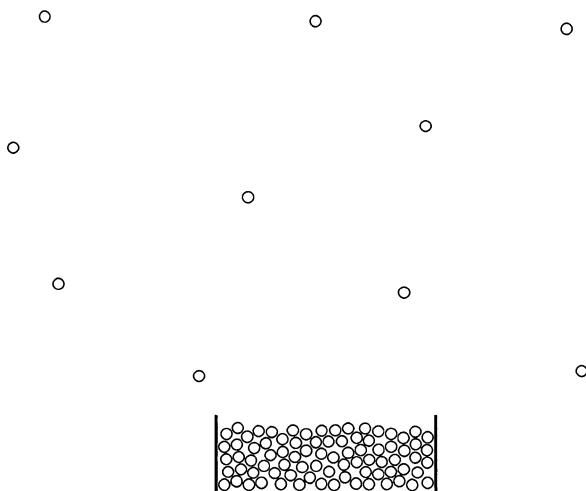
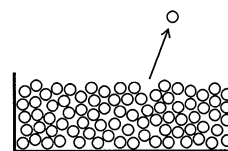
Let's take a closer look at these transitions.

Consider a liquid phase in some container. I show this diagrammatically at right. (The scale in the diagram is wrong: in a real liquid phase sample, there would be massively huge numbers of infinitesimally tiny particles. In addition, the walls of the container would consist of massively huge numbers of infinitesimally tiny particles, but I just drew the walls as lines. I'm keeping the diagram simple; it conveys the necessary information for now.) The particles in the liquid phase cling to each other in loose contact by the attraction of their intermolecular forces. The particles are doing the usual liquid phase things: they move and they bump, a kick here and a kick there, a little nudge, etc. Depending on the temperature, there is some average amount of energy per particle. But that is an average energy; some have more and some have less, and they can trade off their energies among each other by bumping and kicking.



Now, keep your eyeballs on the particles at the top surface.

If a particle at the surface at some point in time happens to possess a sufficiently high energy, sufficient enough to overcome intermolecular forces, then that particle can escape to the gas phase where it will have greater entropy. This is shown at right and it represents the simplest act of vaporization. In reality, for any real sample, very large numbers of particles are escaping at any given time, so it's much busier than this simple picture shows.

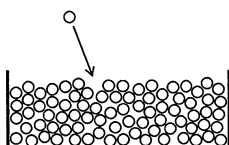


Once in the gas phase, those particles then do the usual gas phase things: they move rapidly, widely and randomly; they diffuse with surrounding air molecules; they collide every now and then; etc.

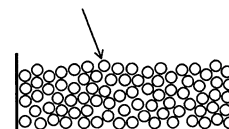
This picture for vaporization applies to the specific case of evaporation. As you know from normal experience, left to time and open to air, a drop or a puddle or water in a cup will evaporate completely. The water molecules in the liquid phase escape to the gas phase and mix with molecules in the air. Eventually, all of the water molecules do this and the liquid phase dries out completely. Boiling is also a vaporization process, but it's different. We'll boil later.

There's a key feature to point out in the description so far with respect to energies. The particles which escape the liquid to the gas phase are the ones with the higher energies. As the particles with higher energy continue to escape, the liquid is left with lesser-energy particles (on average); less energy means less heat, and the remaining liquid cools down. In order to keep the liquid at constant temperature, the surroundings must continually pass heat to the liquid. (Even a drop of water on a table top will pick up heat from the table or from the air.) These energy aspects are part of the endothermic nature of vaporization, and the amount of heat necessary is the enthalpy of vaporization.

Since the particles in the gas phase are moving and colliding randomly, some of those particles can collide back with the surface of the liquid before they wander off too far. There are two possible outcomes to these collisions. In some cases, the gas particles simply bounce off the particles which make up the liquid surface, and they then continue on their way in the gas phase. In other cases, the gas-phase

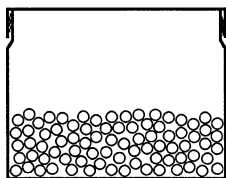


particle can be recaptured by intermolecular forces, now trapping it again within the liquid phase. This is shown at left (on the approach) and at right (after collision and recapture). This represents the simplest act of condensation. During the collision, the higher energy gas particle loses some of its energy to the liquid-phase molecules; as a result, it can no longer



escape the IFs. The former gas phase particle is now a liquid phase particle. As this continues and as more particles condense, the liquid phase gains more energy which would heat the liquid phase. In order to keep constant temperature, some J's must exit to the surroundings. This reflects the exothermic character of condensation.

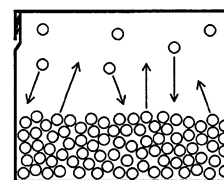
The illustrations so far have dealt with a container of liquid open to air. After evaporating into the gas phase, the particles will constantly be moving and diffusing further away from the liquid surface. This will continue until the liquid eventually dries out. Now, let's put a lid on things.



Place a liquid into a jar and close the jar. What happens?

The usual vaporization occurs, allowing molecules to escape to gas phase. Once there are some molecules in the gas phase, condensation can occur and this becomes more important than in the open system above. In order to understand this importance, we need to consider how fast things vaporize and how fast they condense.

Let's assume the liquid's temperature stays the same and its upper surface area stays the same. Under these conditions, the number of molecules escaping per time remains the same. We can also say that the rate (speed) of vaporization stays constant with time. On the other hand, the rate for condensation changes at first. If we consider the exact moment when the liquid is first placed into the jar, before there are any molecules in the gas phase, the rate of condensation is zero. But that doesn't last long: as soon as any molecules have escaped from the liquid to the gas phase, then some of these can collide back with the liquid surface and condense. As more and more molecules escape to the gas phase over time, their concentration in the gas phase increases. With more molecules in the gas phase, then more and more of them collide back at the surface; this increases the number of molecules condensing per unit time. Thus, the rate of condensation increases as the concentration in the gas phase increases.



Let me emphasize two points:

- vaporization occurs at the same rate throughout;
- the rate of condensation initially increases as more and more molecules are in the gas phase.

This brings us to a very important aspect: balance. As the rate of condensation increases, there will come a point at which the number of molecules condensing per time equals the number of molecules vaporizing per time. At this point, both of these opposing processes occur at equal speeds. The two processes are in balance. At balance, the concentration in the gas phase remains the same. You have equilibrium.

### 35.2 Balance

The above description is only one way of describing the balance of equilibrium. We can also describe the equilibrium as the balance between enthalpy (IFs, which favor liquid) and entropy (which favors gas). Neither wins overall, so neither the liquid phase nor the gas phase wins completely. Both phases are present and both phase changes continue to occur, but they are equally favored and they occur at the same speed. The system is in balance.

The notion of equilibrium is immensely important to phase changes. Furthermore, equilibrium is immensely important to many things in general. We first talked about equilibrium in Chapter 12.

“ As applied to chemical reactions, balance is called equilibrium... Chemical equilibrium will occur whenever opposing forces are operating within a chemical system. There will be a competition. ”

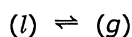
We now apply these notions to phase changes. In the prior two paragraphs, I gave you two essential, key aspects which are very general to many equilibria, not just phase changes. This is really important, so I want to emphasize this now. Pay very close attention.

There are two approaches to describe the balance which is associated with any equilibrium.

1. The first approach is by the speeds (rates) of the opposing processes. At the point of equilibrium, these speeds are equal and in balance. This approach is the kinetic description of equilibrium.
2. The second approach is by enthalpy and entropy. At the point of equilibrium, a system's enthalpy and its entropy are in balance. This approach is the thermodynamic description of equilibrium.

As I said, these two items are really big for all equilibria in general. Write "THE BIG TWO" in the margin next to them.

For our current application of vaporization and condensation, we can represent the equilibrium as follows, which uses the double half-arrow notation as introduced in Chapter 12.



When an equilibrium system has reached its point of balance, then we say that it has reached the "point of equilibrium" or that it is "at equilibrium" or "in equilibrium". There's a catch to the terminology here: you can have a system with opposing processes, but that does not mean that the system is at (or in) equilibrium. "At (or in) equilibrium" specifically refers to being at the point of balance. When you first pour water into a jar and then close it up, the system is not immediately at equilibrium. It can take a few minutes to get there. (Other kinds of equilibria can take years!) Be aware that "at (or in) equilibrium" means at the point of balance and the speeds of the opposing processes are equal.

You are familiar with closed jars or bottles containing water. To your eyeball, they don't look like they're doing anything and one can get the impression that the system is motionless. WRONG! A system at equilibrium is definitely in motion. In a closed jar of water at equilibrium, vaporization still occurs and condensation still occurs but they occur at the same speed. Although change continues to happen, there is no net change overall. At equilibrium, the amount of  $H_2O(l)$  and the amount of  $H_2O(g)$  stay the same. We refer to this motion as dynamic: EQUILIBRIA ARE DYNAMIC. At the point of equilibrium, the system is in motion but the motions are in balance.

Circle or highlight the last six sentences. Remember them. Understand them. These things are also extremely important to ALL equilibria in general, not just phases.

Alright, let's return to our closed jar and now let's bring back some  $PVnRT$  stuff from Chapter 16. As seen in Chapter 16, concentration relates to pressure (at a specific temperature).

$$P = \text{concentration} \times R \times T$$

$$P = \frac{n}{V} \times R \times T$$

Thus, for a given concentration of vapor in the jar, there is a corresponding pressure of that vapor; this pressure is called the vapor pressure. At equilibrium with everything in balance, the vapor has a steady concentration which means that it has a steady pressure; we call this pressure the equilibrium vapor pressure (EVP).

Equilibrium vapor pressure is a very important characteristic of liquid-gas equilibria. Many of these have been measured for many different compounds. For example, water's EVP at 20. °C is 17.5 Torr. If you have a closed jar of pure water at 20. °C, then the pressure of the water vapor inside is 17.5 Torr at equilibrium. If the vapor pressure is not 17.5 Torr, then the system is not at equilibrium. Thus, EVP is a result of being at equilibrium and it is an indicator of being at equilibrium: if the liquid/gas system is at equilibrium, then its vapor pressure must equal EVP; if the system's vapor pressure does not equal EVP, then the system is not at equilibrium.

By the way, for our phase changes here, I have only referred to the one compound which is undergoing that phase change. Usually, of course, we would also have air in the jar, so there are  $N_2$

molecules and  $O_2$  molecules and who knows what else. In general, for typical conditions, the presence of air (or any other gas, for that matter) does not have a major effect on the phase change which we are studying. (For technical measurements, they absolutely must exclude air and other gases.) If air or another gas is indeed present, then the total in the jar is a gas mixture and all the things about gas mixtures from Chapter 16 applies. That includes pressure: the pressure inside the jar is the original air pressure plus the vapor pressure from the evaporated liquid.

Notice when I gave water's EVP just a moment ago that I also specified the temperature. A compound's EVP is very dependent on temperature. You might think that this is due to the usual  $PV=nRT$  relationship, and you'd be partly correct but that tends to be a minor factor. The greater factor has to do with the energy of the liquid phase at different temperatures. Remember from above that vaporization depends on the molecules in the liquid phase having enough energy to overcome the IFs. As you heat a liquid phase, then more and more of the molecules have the required energy. Thus, more and more molecules can escape, giving a higher concentration in the gas phase. Now, combine the effects of higher concentration in the gas phase with the higher temperature of the gas phase.

$$P = \text{concentration} \times R \times T$$

higher                      higher  
↓                                      ↓

Both of these give a higher pressure as a result. Here are some numbers for water.

$T$ :	0. °C	10. °C	20. °C	25 °C	30. °C	40. °C	50. °C
EVP (Torr):	4.59	9.21	17.5	23.8	31.8	55.4	92.6



The general mathematical trend for the variation of EVP with temperature for different compounds is shown at left. Several logarithmic equations are known which can approximate the curve, but we won't go into those here.

Let's bring in some  $PV=nRT$  calculations to the discussion. I'll illustrate this with a simple sample problem. Place a teaspoon or so of liquid water into a 2 L bottle at 20. °C (68 °F) and cap the bottle. Let the system go to equilibrium; at that time, there will be some water vapor and there will be some liquid water remaining. At equilibrium, how many grams of water vapor will be present? Assume the gas volume is 2.0 L.

You may not immediately recognize this as a  $PV=nRT$  problem, but it is. You're given  $V$  and  $T$  directly, although you need kelvins for the latter.  $P$  is from the list above: at equilibrium at 20. °C, the pressure of water vapor is 17.5 Torr.  $R$  is the usual  $R$ . With all of these, we can calculate moles,  $n$ . Then, moles will lead to grams. Let's start by setting this up for  $n$ .

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{\left(\frac{17.5}{760} \text{ atm}\right)(2.0 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(293 \text{ K})}$$

That gives moles; multiply by molar mass (18.02 g/mol) and you get 0.035 g for the final result. This tells us that 0.035 g  $H_2O(g)$  is contained in 2.0 L at equilibrium at 20. °C.

By the way, when you first put the water into the bottle, there was air inside. Let's assume you had 760.0 Torr of dry air inside when you capped the bottle initially. Then, after the water reached equilibrium, the total pressure inside is 760.0 Torr (from air) + 17.5 Torr (from  $H_2O(g)$ ) = 777.5 Torr (total).

### 35.3 A wet and dry topic

$H_2O(g)$  in air is humidity. The most common encounter with humidity lies in weather applications, and these actually use relative humidity, commonly abbreviated as RH. Relative humidity is the humidity relative to equilibrium conditions; in other words, it's the actual vapor pressure relative to EVP at a

specific temperature. Usually, the RH is expressed as a percent. The arithmetic definition for RH is the following.

$$\text{RH} = \frac{\text{actual } P(\text{H}_2\text{O})}{\text{EVP}} \times 100\%$$

Let's say that the air temperature on some day is 20. °C (68 °F) and that the actual vapor pressure of water in that air is 8.4 Torr. We can calculate the RH for these conditions, knowing the EVP (from the prior list, 17.5 Torr).

$$\text{RH} = \frac{8.4 \text{ Torr}}{17.5 \text{ Torr}} \times 100\% = 48\%$$

This tells us that the relative humidity is 48%. By the way, you can use any pressure unit in this equation as long as they're both the same for the numerator and the denominator. It doesn't matter because this is a ratio and the units will cancel. You can also do this problem using atm.

$$\text{RH} = \frac{0.011 \text{ atm}}{0.0230 \text{ atm}} \times 100\% = 48\%$$

You still get the same answer.

RH near 100% is typical of rain or fog conditions. You may hear the weather people refer to 100% RH as "saturated": the air is saturated with moisture. "Saturated" means the system contains the equilibrium amount of water vapor. Since the system is at equilibrium, condensation and vaporization occur at the same speed. "Unsaturated" means the actual vapor pressure is less than EVP; under this condition, more vaporization is possible before reaching EVP. "Supersaturated" means the actual vapor pressure is greater than EVP; under this condition, more condensation is possible before reaching EVP. We can also relate these terms to RH: saturated means RH = 100%; unsaturated means RH < 100%; and, supersaturated means RH > 100%. If the air is supersaturated with H<sub>2</sub>O(g), then you can get rain.

The terms saturated, unsaturated and supersaturated also apply to solution equilibria. We'll see these terms again in Chapter 41. Put a star in the margin next to the prior paragraph.

One of the reasons that RH is so commonly encountered is that it affects drying speeds for a wide variety of operations, including you. The simple act of drying depends on vaporization being faster than condensation. Drying does not occur at equilibrium and, in fact, for fast drying you want to be far from equilibrium. This means that you want the actual vapor pressure to be far below EVP, and that means you want low relative humidity. Overall, drying is faster at lower RH.

But you knew that, didn't you? Or at least your body knew that. Human comfort is very sensitive to RH. This is well known in hot weather but it's also very important in cold weather. Let's take a look at these conditions.

Much of this is about sweat. We first discussed this back in Chapter 18 when we talked about the endothermic nature of vaporization.

“ Nature designed your body to utilize this endothermic phase change. After all, that's why you sweat: it cools you down. Here's what happens. Think of the sweat as the system and your skin as part of the surroundings. Sweat is mostly water. The water on the skin evaporates to gas phase. The evaporation process costs J's and your skin pays those J's. The water molecules take those J's with them as they leave into the air around you. Your skin loses those J's as heat, and your skin cools down. That's Nature's cooling system for humans. ”

The success of this cooling process depends on the speed of drying the sweat by evaporation. Even partial drying by evaporation will provide some cooling. (Drying by a towel isn't the same: there's no endothermic phase change associated with that.) Drying by evaporation will be faster at low RH and slower at high RH. Thus, lower RH gives faster cooling and higher RH gives slower cooling.

While high RH would bother us most in the summer, it's low RH that bothers us most in the winter time. Unless you're in moderate climates year round, you may be aware that air in homes tends to be "drier" in the winter time. Although we sense the air to be "drier" indoors, outside air can be moderate or high relative humidity. How can inside air feel "drier" when outside air is fairly humid?

The answer lies in the variation of EVP with *T*.



- ▶ As the temperature drops below 20. °C, the EVP decreases below 17.5 Torr. The air would be supersaturated if it kept its actual  $P(\text{H}_2\text{O})$  at 17.5 Torr, but usually condensation kicks in so that equilibrium can be maintained. Condensation decreases the amount of water in the gas phase and that decreases  $P(\text{H}_2\text{O})$ . By this process, dew starts to form or rain starts to fall.

Have your bumbershoot handy for the latter.

### 35.4 It's not just about water.

We've been using water so far to illustrate vaporization/condensation and that is for good reason: water is by far the most obvious and most important example of this. On the other hand, water is not the only liquid and now we will consider other compounds for more generality.

Except for the terms humidity and RH, everything above applies to other liquids as well. Diethyl ether,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ , is a liquid at room temperature. It vaporizes and it condenses and it can set up an equilibrium in a closed container and it has an EVP, etc. Methanol (methyl alcohol),  $\text{CH}_3\text{OH}$ , is also a liquid at room temperature. It vaporizes and it condenses and it can set up an equilibrium in a closed container and it has an EVP, etc. Although different liquids have the same qualitative aspects for phase changes, the quantitative factors are different. For example, enthalpies of vaporization are different and values of EVP are different. One of the most important reasons for these differences lies in the intermolecular forces which are involved. Let's see how this arises.

Recall that intermolecular forces favor the liquid phase relative to the gas phase. If the IFs are weak, then there's less to favor the liquid phase and it's easier for liquid phase molecules to escape to the gas phase; under these conditions, there will be a higher concentration and pressure in the gas phase at equilibrium. Conversely, if the IFs are strong, then there's more to favor the liquid phase and it's harder to escape to the gas phase; this will give a lower concentration and pressure of molecules in the gas phase at equilibrium. These are simple notions but they have a massive impact on enthalpies of vaporization and on EVP. We can summarize this as follows.

Weak IFs:	Less energy needed to escape to gas phase More molecules can escape to gas phase	<ul style="list-style-type: none"> <li>➔ lower <math>\Delta H_{\text{vap}}^\circ</math></li> <li>➔ higher concentration in (g)</li> <li>➔ higher EVP</li> </ul>
Strong IFs:	More energy needed to escape to gas phase Fewer molecules can escape to gas phase	<ul style="list-style-type: none"> <li>➔ higher <math>\Delta H_{\text{vap}}^\circ</math></li> <li>➔ lower concentration in (g)</li> <li>➔ lower EVP</li> </ul>

To illustrate these effects, let me compare water to the other two liquids which were just mentioned, diethyl ether and methanol.

We haven't gotten to the specific details of intermolecular forces yet so, for now, I'll just tell you the final result of such a comparison for these three compounds: diethyl ether has the weakest IFs, methanol is in the middle, and water has the strongest IFs.

	diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	methanol, $\text{CH}_3\text{OH}$	water, $\text{H}_2\text{O}$
IFs:	weakest	middle	strongest

Later, in Chapter 37, you will see how to judge the comparative strengths of IFs for different compounds.

The relative consequences for these compounds are the following. Diethyl ether molecules will be the easiest to escape to gas phase; this compound will have the lowest  $\Delta H_{\text{vap}}^\circ$ , the highest concentration in the gas phase, and the highest EVP (at a given temperature). Water molecules will be the hardest to escape to gas phase; water will have the largest  $\Delta H_{\text{vap}}^\circ$  and the lowest EVP. Methanol will be in the middle.

	diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	methanol, $\text{CH}_3\text{OH}$	water, $\text{H}_2\text{O}$
IFs:	weakest	middle	strongest
$\Delta H_{\text{vap}}^\circ$ :	lowest	middle	highest
EVP:	highest	middle	lowest

Actual numbers illustrate these trends.

	diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	methanol, $\text{CH}_3\text{OH}$	water, $\text{H}_2\text{O}$
$\Delta H_{\text{vap}}^\circ$ (25 °C):	27.10 kJ	38.00 kJ	44.00 kJ
EVP (25 °C):	536 Torr	127 Torr	23.8 Torr

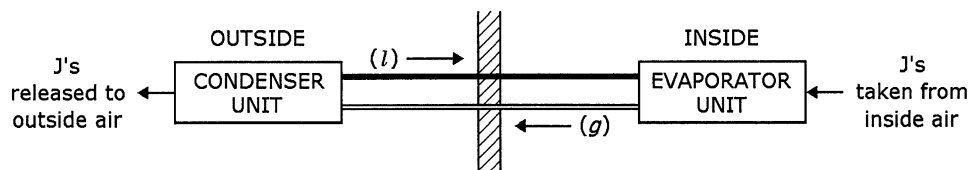
Notice how intermolecular forces can have a large impact on physical properties. We shall see more of this in the following Chapters.

As noted previously, EVP will vary with temperature, and this is true for all liquids. For illustration purposes, the EVP at 0. °C for the three liquids above is 186, 30. and 4.59 Torr, respectively.

While we're on the subject of liquids other than water, let's turn to another application of vaporization and condensation. It's a chilling topic. It's not a part of the natural world but it's very much a part of your world.

This is about air conditioning and refrigeration. That includes your home's AC, your car's AC, your refrigerator, etc. The primary methodology is called vapor-compression, and this works by utilizing vaporization and condensation. In fact, two of the most important parts of the system are called the evaporator and the condenser; the other important parts are the compressor, which makes condensation possible, and the expansion valve, which makes vaporization possible. Let's see how this operation works.

I'll describe home, central air conditioning, although the principles are the same for others. The evaporator is located indoors, typically within the main furnace structure. You don't usually see this part but it's the part that gets cold and your indoor air blows over it. The condenser is outside the home; it releases the heat of the home to the outside air. It's composed of coils and cooling fins which are the part you need to keep clean for efficiency; there's also a fan to help cool the coils.



The compressor is outside the home with the condenser; it involves a motor which turns on and off periodically (as does the condenser fan). Tubing connects the various parts inside and outside the home. A fluid circulates throughout the system, part of the way as liquid and part of the way as gas. There's no air and no moisture in the system (unless they didn't fill it up right). Fluids used in refrigeration are generically called refrigerants. I mentioned some of them back in Section 5.4.

“ There're hundreds of these compounds and the industry uses an R-number to identify them. (R is for refrigerant. These are not their real chemistry names.) Previously, R-12, whose chemical formula is  $\text{CF}_2\text{Cl}_2$ , was one of the most widely used in automobile air conditioners; it was quite hazardous to the ozone layer and it was banned years ago. Many automobile air conditioner designs switched to R-134a, which is  $\text{C}_2\text{H}_2\text{F}_4$ . Many home air conditioners had been using R-22 ( $\text{CHF}_2\text{Cl}$ ), but those systems were being replaced by newer ones which use mixtures of compounds such as R-410A (a mix of  $\text{CH}_2\text{F}_2$  and  $\text{C}_2\text{HF}_5$ ). There are many considerations involved in the design of a refrigeration system and the refrigerant it uses, such as toxicity, flammability, reactivity, environmental impact, boiling point, cost, etc.

By the way, if you want to know how air conditioners work, you can find this later in Chapter 35. ”

Later is now.

The system is a closed loop and we need to start our description somewhere. We'll start outside with gas phase refrigerant entering the compressor within the condenser unit. The gas phase refrigerant is mechanically compressed to a very high pressure; the work done on the gas also raises its temperature. The high-pressure, high-temperature gas passes into the cooling coils with its fins and fan; the temperature drops, the EVP drops, and the gas condenses to a liquid. Since condensation is exothermic, it also loses that heat of condensation via the coils. Now cooled down but still at high pressure, the refrigerant is liquid phase. This goes through the tubing back inside the house to the evaporator unit. There, it passes through an expansion valve into a larger volume. The refrigerant's pressure suddenly drops below its EVP and it vaporizes rapidly in the evaporator. Since vaporization is endothermic, the gas gets very cold and takes J's from the evaporator, which then gets cold and takes J's from the indoor air which is blowing over it. Ultimately, your indoor air loses J's to pay for the enthalpy of vaporization and that is what cools your house. Gas phase refrigerant returns to the compressor outside to repeat the cycle. That's it.

Overall, this process moves joules from the inside air and transfers those J's to the outside air. In essence, vapor-compression units are simply devices for transferring thermal energy from one location to another, using the enthalpies of vaporization and condensation. They work in the opposite direction



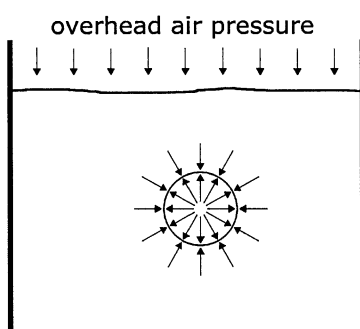
of natural heat flow. In natural heat flow, joules pass from warmer air to cooler air. In refrigeration, joules pass from cooler air to warmer air. Because this direction is opposite the natural flow, you must pay energy for the overall operation. That's in your electric bill.

By the way, your air conditioner doesn't just cool the inside air. It also dries it out by removing some of the humidity in the air. This dehumidification is why the AC/furnace unit inside your home has a pipe or tubing running from the evaporator to a drain. It's also the reason for pavement piddle when your car's AC is running. This is condensation again, following the same EVP and  $T$  principles mentioned earlier.

### 35.5 Coming to a boil

As noted earlier, boiling is also vaporization but it's a different process from evaporation. The difference is quite simple: evaporation involves vaporization at the liquid-gas surface, while boiling involves vaporization below that surface.

Vaporization below the surface gives bubbles and those bubbles are what we call boiling. Each bubble is its own little gas phase sample of that compound. (You can also have bubbles of air in a liquid, but that's a separate issue and it is not a part of this discussion.) Since each bubble is a gas phase sample, each bubble follows  $PVnRT$ . It's the  $P$  which we need to consider.



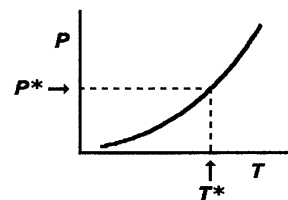
Let's say you have a pan of water boiling on the stove. I show a very simplistic representation of this at left with just one bubble rising through the liquid. The water vapor pressure inside the bubble opposes and equals the surrounding pressure of the liquid water bearing down on it. (The arrows are meant to convey the opposing pressures; the pressures are really in three dimensions.) Where does the surrounding pressure come from? Mostly it comes from the atmospheric pressure which is bearing down on it from above. There is also some hydrostatic pressure due to the water itself, but that is small in a shallow pan. We will ignore that part and we will take the liquid's pressure to be equal to the atmospheric pressure overhead. Given that much, then the pressure inside the bubble equals the overhead atmospheric pressure.

If the water in the pan is boiling smoothly, then the gas bubble and the liquid phase around it are in equilibrium. Since they are in equilibrium, then the pressure inside the bubble equals water's EVP. We now connect this to the atmospheric pressure overhead: the bubble's EVP will equal the surrounding air pressure.

OK, let's start this picture over. We begin with a pan of water, let's say at 20. °C, and we'll heat it on the stove to boil. We'll assume the surrounding air pressure is one atm (760 Torr). At 20. °C, water's EVP is only 17.5 Torr, so a poor bubble of only 17.5 Torr pressure could not possibly survive against a surrounding pressure of 760 Torr. Ergo, no bubble. With more heat, the water temperature rises through 30. °C, then 40. °C, then 50. °C, etc. EVP increases as you go: 31.8 Torr, 55.4 Torr, 92.6 Torr, etc. Still, no bubble could survive against the surrounding pressure. Finally, when the water hits 100. °C where the EVP equals surrounding pressure (760 Torr), then we can start to form bubbles. Now, we can boil.

Boiling water at 100. °C at one atm pressure is common everyday stuff, but you can actually boil water at a wide range of temperatures. Let's say you put water into a container at 20. °C and remove the air using a vacuum pump. The water can then boil until its gas pressure reaches EVP, which is 17.5 Torr. If the vacuum pump continuously removes the water vapor, then the water liquid would continue to boil at 20. °C. On the other hand, you can put water into a system at high pressure, such as 1,000. Torr; then, the water boils at 108 °C.

The temperature of boiling is called the boiling point, typically abbreviated as bp. The boiling point of water is 20. °C at 17.5 Torr, 100. °C at 760. Torr, and 108 °C at 1,000. Torr. Since these pressures are EVPs, then the EVP and  $T$  relationship from earlier is the same as the pressure and bp relationship. We can use the same graph from earlier to show this, as repeated at right but the  $y$ -axis is now labeled  $P$ . For any desired pressure for boiling (such as  $P^*$ ), the curve gives the boiling point ( $T^*$ ). Conversely, for any boiling point ( $T^*$ ), the curve gives the pressure ( $P^*$ ).



For the specific case of one atm (760 Torr), the boiling point is often further specified as the normal boiling point (nbp). Thus, the normal boiling point of water is 100. °C.

For liquids other than water, the same generalities apply for boiling but the numbers will be different. Let's bring back diethyl ether and methanol and compare these to water for their normal boiling points. What trend do you expect? Let's return to the prior comparisons.

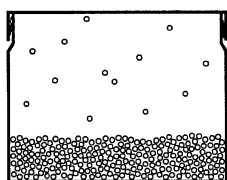
	diethyl ether, C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	methanol, CH <sub>3</sub> OH	water, H <sub>2</sub> O
IFs:	weakest	middle	strongest
$\Delta H_{\text{vap}}^{\circ}$ (25 °C):	27.10 kJ	38.00 kJ	44.00 kJ
EVP (25 °C):	536 Torr	127 Torr	23.8 Torr

If we start heating separate containers of these liquids, which one will boil at the lowest temperature? That will be diethyl ether: it has the weakest IFs, it needs the least energy to vaporize, and it already starts at the highest EVP at 25 °C. After diethyl ether, it's methanol and then water. Here are the numbers.

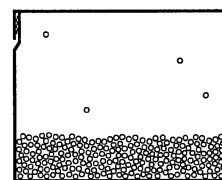
	diethyl ether, C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	methanol, CH <sub>3</sub> OH	water, H <sub>2</sub> O
IFs:	weakest	middle	strongest
$\Delta H_{\text{vap}}^{\circ}$ (25 °C):	27.10 kJ	38.00 kJ	44.00 kJ
EVP (25 °C):	536 Torr	127 Torr	23.8 Torr
normal bp:	35 °C	65 °C	100. °C

This will be general: weaker IFs for a liquid will result in a lower boiling point, while stronger IFs will result in a higher bp.

Let's summarize our trends so far for different compounds.



Weak IFs	Strong IFs
lower $\Delta H_{\text{vap}}^{\circ}$	higher $\Delta H_{\text{vap}}^{\circ}$
higher concentration in (g)	lower concentration in (g)
higher EVP	lower EVP
lower bp	higher bp



With these trends, we see more of the impact of IFs on physical properties. These are very important. Take some time and get used to these relationships. If you need to, go back over the parts above.

There's more to come.

## Problems

- True or false.
  - Air at 80% RH is unsaturated.
  - EVP increases as temperature increases.
  - Evaporation involves vaporization from the surface of a liquid.
  - Stronger intermolecular forces tend to give a greater (more positive)  $\Delta H_{\text{vap}}^{\circ}$ .
  - Boiling cannot occur until a liquid's vapor pressure equals the surrounding pressure.
  - Sweating cools you down because vaporization is exothermic.
- True or false.
  - At higher temperatures, more molecules can escape a liquid phase and go to gas phase.
  - Stronger intermolecular forces tend to give a higher normal boiling point.
  - Drying processes are faster at higher relative humidity.
  - Weaker intermolecular forces give a lower EVP.
  - Boiling points decrease at higher pressures.
  - At dewpoint, the air is saturated with H<sub>2</sub>O(g).

3. Consider air which has a water vapor pressure of 5.6 Torr. What is the relative humidity at 10. °C and at 25 °C?
4. Consider a closed, 50.0 L container of air which has 63.0% RH at 40. °C. The container is then cooled until the contents are at equilibrium at 10. °C, resulting in some condensation.
  - a. How many grams of  $\text{H}_2\text{O}(g)$  were present initially at 40. °C?
  - b. How many grams of  $\text{H}_2\text{O}(g)$  are present at 10. °C?
  - c. How many grams of  $\text{H}_2\text{O}(l)$  are present at 10. °C?
5. Handling elemental mercury is always a safety issue. The liquid phase is often not the primary concern; a greater concern is breathing the very small amount of vapor which results.  $\text{Hg}(l)$  has an equilibrium vapor pressure of  $2.6 \times 10^{-6}$  atm at 25 °C. Consider a room with an air volume of 33,000 L (12 ft  $\times$  12 ft  $\times$  8 ft). How many grams of  $\text{Hg}(g)$  would be contained in that air volume at equilibrium at that temperature?