

13: Phase Equilibrium and Intermolecular Interactions

Foundation

The "phase" of a substance is the particular physical state it is in. The most common phases are solid, liquid, and gas, each easily distinguishable by their significantly different physical properties. A given substance can exist in different phases under different conditions: water can exist as solid ice, liquid, or steam, but water molecules are H_2O regardless of the phase. Furthermore, a substance changes phase without undergoing any chemical transformation: the evaporation of water or the melting of ice occur without decomposition or modification of the water molecules. In describing the differing states of matter changes between them, we will also assume an understanding of the principles of the **Atomic Molecular Theory** and the **Kinetic Molecular Theory**. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

Goals

We have developed a very clear molecular picture of the gas phase, via the Kinetic Molecular Theory. The gas particles (atoms or molecules) are very distant from one another, sufficiently so that there are no interactions between the particles. The path of each particle is independent of the paths of all other particles. We can determine many of the properties of the gas from this description; for example, the pressure can be determined by calculating the average force exerted by collisions of the gas particles with the walls of the container.

To discuss liquids and solids, though, we will be forced to abandon the most fundamental pieces of the Kinetic Molecular Theory of Gases. First, it is clear that the particles in the liquid or solid phases are very much closer together than they are in the gas phase, because the densities of these "condensed" phases are of the order of a thousand times greater than the typical density of a gas. In fact, we should expect that the particles in the liquid or solid phases are essentially in contact with each other constantly. Second, since the particles in liquid or solid are in close contact, it is not reasonable to imagine that the particles do not interact with one another. Our assumption that the gas particles do not interact is based, in part, on the concept that the particles are too far apart to interact. Moreover, particles in a liquid or solid must interact, for without attractions between these particles, random motion would require that the solid or liquid dissipate or fall apart.

In this study, we will pursue a model to describe the differences between condensed phases and gases and to describe the transitions which occur between the solid, liquid, and gas phases. We will find that intermolecular interactions play the most important role in governing phase transitions, and we will pursue an understanding of the variations of these intermolecular interactions for different substances.

Observation 1: Gas-Liquid Phase Transitions

We begin by returning to our observations of **Charles' Law**. Recall that we trap an amount of gas in a cylinder fitted with a piston, and we apply a fixed pressure to the piston. We vary the temperature of the gas, and since the pressure applied to the piston is constant, the piston moves to maintain a constant pressure of the trapped gas. At each temperature, we then measure the volume of the gas. From our previous observations, we know that the volume of the gas is proportional to the absolute temperature in degrees Kelvin. Thus a graph of volume versus absolute temperature is a straight line, which can be extrapolated to zero volume at 0 K.



Figure 13.1: Vapor-Liquid Phase Transition

Consider, then, trying to measure the volume for lower and lower temperatures to follow the graph. To be specific, we take exactly 1.00 mol of butane, C_4H_{10} at 1 atm pressure. As we lower the temperature from 400 K to 300 K, we observe the expected proportional decrease in the volume from 32.8 L to 24.6 L. However, when we reach 272.6 K, the volume of the butane drops very abruptly, falling to about 0.097 L at temperatures just slightly below 272.6 K. This is less than one-half of one percent of the previous volume! The striking change in volume is shown in the graph as a vertical line at 272.6 K.

This dramatic change in physical properties at one temperature is referred to as a **phase transition**. When cooling butane through the temperature 272.6 K, the butane is abruptly converted at that temperature from one phase, gas, to another phase, liquid, with very different physical properties. If we reverse the process, starting with liquid butane at 1 atm pressure and temperature below 272.6 K and then heating, we find that the butane remains entirely liquid for temperatures below 272.6 K and then becomes entirely gas for temperatures above 272.6 K. We refer to the temperature of the phase transition as the **boiling point** temperature. (We will discuss the phases present at the boiling point, rather than above and below that temperature, in another section.)

We now consider how the phase transition depends on a variety of factors. First, we consider capturing 2.00 mol of butane in the cylinder initially, still at 1 atm pressure. The volume of 2.00 mol is twice that of 1.00 mol, by **Avogadro's Hypothesis**. The proportional decrease in the volume of 2.00 mol of gas is shown in Figure 13.2 along with the previous result for 1.00 mol. Note that the phase transition is observed to occur at exactly the same temperature, 272.6 K, even though there is double the mass of butane.



Figure 13.2: Variation of Phase Transition with Pressure

Consider instead then varying the applied pressure. The result for cooling 1.00 mol of butane at a constant 2.00 atm pressure is also shown in Figure 13.2. We observe the now familiar phase transition with a similar dramatic drop in volume. However, in this case, we find that the phase transition occurs at 293.2 K, over 20 K higher than at the lower pressure. We can measure the boiling point temperature of butane as a function of the applied pressure, and this result is plotted in Figure 13.3.



Figure 13.3: Boiling Point versus Pressure

Finally, we consider varying the substance which we trap in the cylinder. In each case, we discover that the boiling point temperature depends on both what the substance is and on the applied pressure, but does not depend on the amount of the substance we trap. In Figure 13.3, we have also plotted the boiling point as a function of the pressure for several substances. It is very clear that the boiling points for different substances can be very different from one another, although the variation of the boiling point with pressure looks similar from one substance to the next.

Observation 2: Vapor pressure of a liquid

Our previous observations indicate that, for a given pressure, there is a phase transition temperature for liquid and gas: below the boiling point, the liquid is the only **stable** phase which exists, and any gas which might exist at that point will spontaneously condense into liquid. Above the boiling point, the gas is the only stable phase.

However, we can also commonly observe that any liquid left in an open container will, under most conditions, eventually evaporate, even if the temperature of the liquid is well below the normal boiling point. For example, we often observe that liquid water evaporates at temperatures well below the boiling point. This observation only seems surprising in light of the discussion above. Why would liquid water spontaneously evaporate if liquid is the more stable phase below the boiling point? We clearly need to further develop our understanding of phase transitions.

The tendency of a liquid to evaporate is referred to as its **volatility**: a more volatile liquid evaporates more readily. To make a quantitative measure of liquid volatility, we slightly modify our previous cylinder-piston apparatus by adding a gauge to measure the pressure of gas inside the cylinder (see Figure 13.4). We begin with liquid water only in the cylinder with an applied pressure of 1 atm at a temperature of 25°C. We now pull back the piston by an arbitrary amount, and then we lock the piston in place, fixing the volume trapped inside the cylinder. We might expect to have created a vacuum in the cavity above the liquid water, and as such we might expect that the pressure inside the cylinder is small or zero.



Figure 13.4: Measuring Vapor Pressure

Although there was initially no gas in the container, we observe that the pressure inside the container rises to a fixed value of 23.8 torr. Clearly, the observation of pressure indicates the presence of gaseous water inside the container, arising from evaporation of some, but not all, of the liquid water. Therefore, some of the liquid water must have evaporated. On the other hand, a look inside the container reveals that there is still liquid water present. Since both a liquid phase and a gas phase are present at the same time, we say that the liquid water and the water vapor must be in **phase equilibrium**. The term **equilibrium** in this case indicates that neither the vapor nor the liquid spontaneously converts into the other phase. Rather, both phases are stable at equilibrium.

Very interestingly, we can repeat this measurement by pulling the piston back to any other arbitrary position before locking it down, and, provided that there is still some liquid water present, the pressure in the container in every case rises to the same fixed value of 23.8 torr. It does not matter what volume we have trapped inside the cylinder, nor does it matter how much liquid water we started with. As long as there is still some liquid water present in the cylinder at equilibrium, the pressure of the vapor above that liquid is 23.8 torr at 25°C.

Note that, in varying either the amount of liquid initially or the fixed volume of the container, the **amount** of liquid water that evaporates must be different in each case. This can be seen from the fact that the volume available for vapor must be different in varying either the volume of the container or the initial volume of the liquid. Since we observe that the pressure of the vapor is the same at a fixed temperature, the differing volumes reveal differing numbers of moles of water vapor. Clearly it is the **pressure** of the vapor, not the amount, which is the most important property in establishing the equilibrium between the liquid and the vapor. We can conclude that, at a given fixed temperature, there is a single specific pressure at which a given liquid and its vapor will be in phase equilibrium. We call this the **vapor pressure** of the liquid.

We can immediately observe some important features of the vapor pressure. First, for a given substance, the vapor pressure varies with the temperature. This can be found by simply increasing the temperature on the closed container in the preceding experiment. In every case, we observe that the equilibrium vapor pressure increases with increases in the temperature.

The vapor pressures of several liquids at several temperatures are shown in Figure 13.5. The vapor pressure for each liquid increases smoothly with the temperature, although the relationship between vapor pressure and temperature is definitely not proportional.



Figure 13.5: Vapor Pressures of Various Liquids

Second, Figure 13.5 clearly illustrates that the vapor pressure depends strongly on what the liquid substance is. These variations reflect the differing **volatilities** of the liquids: those with higher vapor pressures are more volatile. In addition, there is a very interesting correlation between the volatility of a liquid and the boiling point of the liquid. Without exception, the substances with high boiling points have low vapor pressures and vice versa.

Looking more closely at the connection between boiling point and vapor pressure, we can find an important relationship. Looking at Figure 13.5, we discover that the vapor pressure of each liquid is equal to 760 torr (which is equal to 1 atm) at the boiling point for that liquid. How should we interpret this? At an applied pressure of 1 atm, the temperature of the phase transition from liquid to gas is the temperature at which the vapor pressure of the liquid is equal to 1 atm. This statement is actually true regardless of which pressure we consider: if we apply a pressure of 0.9 atm, the boiling point temperature is the temperature at which the liquid has a vapor pressure of 0.9 atm. Stated generally, the liquid undergoes phase transition at the temperature where the vapor pressure equals the applied pressure.

Observation 3: Phase Diagrams

Since the boiling point is the temperature at which the applied pressure equals the vapor pressure, then we can view Figure 13.5 in a different way. Consider the specific case of water, with vapor pressure given in Figure 13.6. To find the boiling point temperature at 1 atm pressure, we need to find the temperature at which the vapor pressure is 1 atm. To do so, we find the point on the graph where the vapor pressure is 1 atm and read off the corresponding temperature, which must be the boiling point. This will work at any given pressure. Viewed this way, for water Figure 13.6 gives us **both** the vapor pressure as a function of the temperature **and** the boiling point temperature as a function of the pressure. They are the same graph.



Figure 13.6: Vapor Pressure of Liquid Water

Recall that, at the boiling point, we observe that both liquid and gas are at equilibrium with one another. This is true at every combination of applied pressure and boiling point temperature. Therefore, for every combination of temperature and pressure on the graph in Figure 13.6, we observe liquid-gas equilibrium.

What happens at temperature/pressure combinations which are not on the line in Figure 13.6? To find out, we first start at a temperature-pressure combination on the graph and elevate the temperature. The vapor pressure of the liquid rises, and if the applied pressure does not also increase, then the vapor pressure will be greater than the applied pressure. We must therefore not be at equilibrium anymore. All of the liquid vaporizes, and there is only gas in the container. Conversely, if we start at a point on the graph and lower the temperature, the vapor pressure is below the applied pressure, and we observe that all of the gas condenses into the liquid.

Now, what if we start at a temperature-pressure combination on the graph and elevate the applied pressure without raising the temperature? The applied pressure will be greater than the vapor pressure, and all of the gas will condense into the liquid. Figure 13.6 thus actually reveals to us what phase or phases are present at each combination of temperature and pressure: along the line,

liquid and gas are in equilibrium; above the line, only liquid is present; below the line, only gas is present. When we label the graph with the phase or phases present in each region as in Figure 13.6 we refer to the graph as a **phase diagram**.

Of course, Figure 13.6 only includes liquid, gas, and liquid-gas equilibrium. We know that, if the temperature is low enough, we expect that the water will freeze into solid. To complete the phase diagram, we need additional observations.

We go back to our apparatus in Figure 13.4 and we establish liquid-gas water phase equilibrium at a temperature of 25°C and 23.8 torr. If we slowly lower the temperature, the vapor pressure decreases slowly as well, as shown in Figure 13.6. If we continue to lower the temperature, though, we observe an interesting transition, as shown in the more detailed Figure 13.7. The very smooth variation in the vapor pressure shows a slight, almost unnoticeable break very near to 0°C. Below this temperature, the pressure continues to vary smoothly, but along a slightly different curve.



Figure 13.7: Water Phase Transitions

To understand what we have observed, we examine the contents of the container. We find that, at temperatures below 0°C, the water in the container is now an equilibrium mixture of water vapor and solid water (ice), and there is no liquid present. The direct transition from solid to gas, without liquid, is called **sublimation**. For pressure-temperature combinations along this new curve below 0°C, then, the curve shows the solid-gas equilibrium conditions. As before, we can interpret this two ways. The solid-gas curve gives the vapor pressure of the solid water as a function of temperature, and also gives the sublimation temperature as a function of applied pressure.

Figure 13.7 is still not a complete phase diagram, because we have not included the combinations of temperature and pressure at which solid and liquid are at equilibrium. As a starting point for these observations, we look more carefully at the conditions near 0°C. Very careful measurements reveal that the solid-gas line and the liquid-gas line intersect in Figure 13.7 where the temperature is 0.01°C. Under these conditions, we observe inside the container that solid, liquid, and gas are all three at equilibrium inside the container. As such, this unique temperature-pressure combination is called the **triple point**. At this point, the liquid and the solid have the same vapor pressure, so all three phases can be at equilibrium. If we raise the applied pressure slightly above the triple point, the vapor must disappear. We can observe that, by very slightly varying the temperature, the solid and liquid remain in equilibrium. We can further observe that the temperature at which the solid and liquid are in equilibrium varies almost imperceptibly as we increase the pressure. If we include the solid-liquid equilibrium conditions on the previous phase diagram, we get Figure 13.8, where the solid-liquid line is very nearly vertical.



Figure 13.8: Phase Diagram of Water

Each substance has its own unique phase diagram, corresponding to the diagram in Figure 13.8 for water.

Observation 4: Dynamic Equilibrium

There are several questions raised by our observations of phase equilibrium and vapor pressure. The first we will consider is why the pressure of a vapor in equilibrium with its liquid does not depend on the volume of the container into which the liquid evaporates, or on the amount of liquid in the container, or on the amount of vapor in the container. Why do we get the same pressure for the same temperature, regardless of other conditions? To address this question, we need to understand the coexistence of vapor and liquid in equilibrium. How is this equilibrium achieved?

To approach these questions, let us look again at the situation in Figure 13.4. We begin with a container with a fixed volume containing some liquid, and equilibrium is achieved at the vapor pressure of the liquid at the fixed temperature given. When we adjust the volume to a larger fixed volume, the pressure adjusts to equilibrium at exactly the same vapor pressure.

Clearly, there are more molecules in the vapor after the volume is increased and equilibrium is reestablished, because the vapor exerts the same pressure in a larger container at the same temperature. Also clearly, more liquid must have evaporated to achieve this equilibrium. A very interesting question to pose here is how the liquid responded to the increase in volume, which presumably only affected the space in which the gas molecules move. How did the liquid "know" to evaporate when the volume was increased? The molecules in the liquid could not detect the increase in volume for the gas, and thus could not possibly be responding to that increase.

The only reasonable conclusion is that the molecules in the liquid were always evaporating, even before the volume of the container was increased. There must be a constant movement of molecules from the liquid phase into the gas phase. Since the

pressure of the gas above the liquid remains constant when the volume is constant, then there must be a constant number of molecules in the gas. If evaporation is constantly occurring, then condensation must also be occurring constantly, and molecules in the gas must constantly be entering the liquid phase. Since the pressure remains constant in a fixed volume, then the number of molecules entering the gas from the liquid must be exactly offset by the number of molecules entering the liquid from the gas.

At equilibrium, therefore, the pressure and temperature inside the container are unchanging, but there is constant movement of molecules between the phases. This is called **dynamic equilibrium**. The situation is "equilibrium" in that the observable properties of the liquid and gas in the container are not changing, but the situation is "dynamic" in that there is constant movement of molecules between phases. The dynamic processes that take place offset each other exactly so that the properties of the liquid and gas do not change.

What happens when we increase the volume of the container to a larger fixed volume? We know that the pressure equilibrates at the same vapor pressure, and that therefore there are more molecules in the vapor phase. How did they get there? It must be the case that when the volume is increased, evaporation initially occurs more rapidly than condensation until equilibrium is achieved. The rate of evaporation must be determined by the number of molecules in the liquid which have sufficient kinetic energy to escape the intermolecular forces in the liquid, and according to the kinetic molecular theory, this number depends only on the temperature, not on the volume. However, the rate of condensation must depend on the frequency of molecules striking the surface of the liquid. According to the Kinetic Molecular Theory, this frequency must decrease when the volume is increased, because the density of molecules in the gas decreases. Therefore, the rate of condensation becomes smaller than the rate of evaporation when the volume is increased, and therefore there is a net flow of molecules from liquid to gas. This continues until the density of molecules in the gas is restored to its original value, at which point the rate of evaporation is matched by the rate of condensation. At this point, this pressure stops increasing and is the same as it was before the volume was increased.

Review and Discussion Questions

In the phase diagram for water in Figure 13.8, start at the point where the temperature is 60°C and the pressure is 400 torr. Slowly increase the temperature with constant pressure until the temperature is 100°C . State what happens physically to the water during this heating process.

In the phase diagram for water in Figure 13.8, start at the point where the temperature is 60°C and the pressure is 400 torr. Slowly lower the pressure at constant temperature until the pressure is 80 torr. State what happens physically to the water during this process.

Explain why Figure 13.6 is both a graph of the boiling point of liquid water as a function of applied pressure and a graph of the vapor pressure of liquid water as a function of temperature.

We observe that, when the applied pressure is less than the vapor pressure of a liquid, all of the liquid will spontaneously evaporate. In terms of dynamic equilibrium, explain why no liquid can be present under these conditions.

Using arguments from the Kinetic Molecular Theory and the concept of dynamic equilibrium, explain why, at a given applied pressure, there can be one and only one temperature, the boiling point, at which a specific liquid and its vapor pressure can be in equilibrium.

Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the amount of liquid present.

Using dynamic equilibrium arguments, explain why the vapor pressure of a liquid is independent of the volume available for the vapor above the liquid.

Using dynamic equilibrium arguments, explain why a substance with weaker intermolecular forces has a greater vapor pressure than one with stronger intermolecular forces.

According to Figure 13.5, the vapor pressure of phenol is much less than the vapor pressure of dimethyl ether. Which of these substances has the greater intermolecular attractions? Which substance has the higher boiling point? Explain the difference in the intermolecular attractions in terms of molecular structure.

The text describes dynamic equilibrium between a liquid and its vapor at the boiling point. Describe the dynamic equilibrium between a liquid and its solid at the melting point. Using this description, explain why the melting point of a solid varies very little as the pressure increases.

Contributors and Attributions

[John S. Hutchinson](#) (Rice University; Chemistry)

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