

8.5: Real Gases

So far in this chapter, most of you have not learned anything that you have not learned in your calculus courses. The math in this chapter is actually pretty easy, but yet, it is common that students find it very hard to apply these mathematical tools to actual problems in the physical sciences. To get you comfortable using math in chemistry we will first learn a little bit about gases and thermodynamics. Having some background will help us use the math in a context that we (chemists) can relate to.

We have already mentioned some thermodynamic variables, but in order to make more connections between chemistry and math we need to introduce some concepts that we need to start discussing real gases. You will talk about these concepts in more depth in CHM 346. An important thermodynamic variable that is used to characterize the state of a system is the internal energy (U). Let's think about a container containing a gas (e.g. O_2). The internal energy of the system is the sum of the following contributions:

- Kinetic energy: The kinetic energy is the energy that the molecules have due to their motions. It is related to their velocity, and as expected, it increases with increasing temperature, as molecules move faster.
- Vibrational and rotational energy: Molecules store energy in their bonds. As we already discussed, atoms vibrate around their equilibrium position, and there is an energy associated with these vibrations. The vibrational energy of a molecule also depends on temperature, and on the number of bonds. Atomic gases (He, Ar, etc) do not have vibrational energy. Molecules also rotate, and there is energy stored in these motions. As in the case of vibrations, atomic gases do not have contributions from rotations. You will learn about vibrational and rotational energy in CHM 345.
- Potential energy: This is the energy due to the interactions between the molecules that make up the gas. Atoms (e.g. Ar) will also interact if brought close enough. The energy of the interactions between the molecules depends obviously on the chemical nature of the molecules. We know that polar molecules will interact more strongly than non-polar molecules, and atoms with more electrons (e.g. Ar) will interact more strongly than atoms of low atomic number (e.g. He). For a given gas, these interactions depend on the distance between the molecules.

For simplicity, we will concentrate on atomic gases, where the only contributions to U are the kinetic energy (which depends on temperature only), and potential energy. You already learned about the simplest model used to describe the behavior of gases: the ideal (or perfect) gas. You learned that there are two assumptions behind the model. First the particles do not have any size, meaning that you can push them together as close as you want. In reality, atoms have a size, and if you try to push them together too hard the electronic clouds will repel each other. The other assumption is that particles do not interact with each other at any distance. In reality, this makes sense only at very low densities, when molecules are very far away from each other. However, as molecules get closer together, they experience attractive forces that in many cases are so strong that result in the formation of a liquid. Of course if we push them too close the forces become repulsive, but there is a range of distances in which attractive forces dominate. This makes sense for polar molecules, but what about atoms (e.g. Ar), that do not have a permanent dipole moment? You probably heard about London dispersive forces, without which we would never be able to liquefy a noble gas. London forces are stronger for atoms containing more electrons, and that is why the boiling point of Xe is much higher than the boiling point of Ne.

With all this in mind, let's think about what happens to an ideal gas in the three situations depicted in Figure 8.5.1. The densities (molecules per unit volume) increase as we increase the pressure applied to the container. Let's assume the three containers are equilibrated at the same temperature, and let's think about how the internal energy compares among the three cases. We do not have any equations yet, so we need to think in terms of the concepts we just discussed. We have two contributions to think about. The kinetic term should be the same in the three containers because the temperature is the same, and that is the only factor that determines the velocity of the molecules. What about the potential energy? The particles do not have a size, so there are no repulsive forces that arise if we try to push them together too close. They do not have any type of attractive interactions either, so an ideal gas does not store any potential energy. We just concluded that the internal energy for an ideal gas equals the kinetic energy, and it is therefore a function of the temperature of the gas, but not its density. Now, we know that ideal gases are simplified representations of real gases, but they do not exist. In which of these three situations is a gas more likely to behave as an ideal gas? Clearly, when the density is low, the molecules are further away, the interactions between them are weaker, and we do not need to worry about potential energy much.

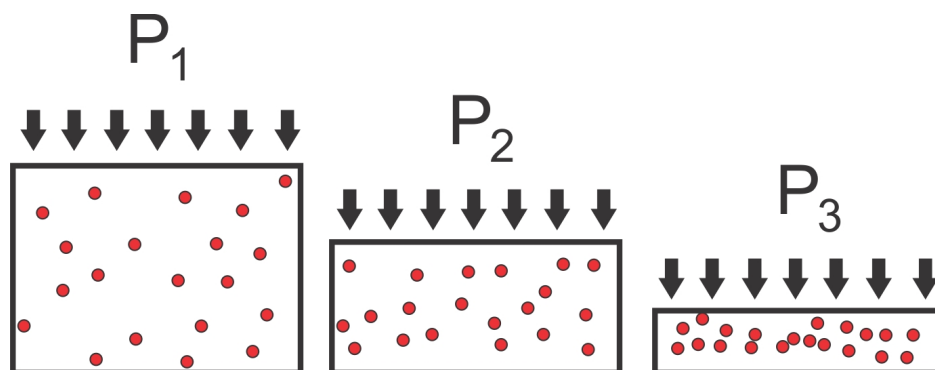


Figure 8.5.1: The internal energy of gases (CC BY-NC-SA; Marcia Levitus)

The van der Waals Model

Let's come back to the equation of state of an ideal gas [8.5.1](#):

$$P = \frac{nRT}{V} \quad (8.5.1)$$

In order to improve our description of gases we need to take into account the two factors that the ideal gas model neglects: the size of the molecules, and the interactions between them. The size of the molecules can be taken into account by assuming that the volume that the molecules have to move around is not really V , but instead $V - nb$, where nb is a measure of the volume that the molecules occupy themselves. In this context b is a measure of the volume of one molecule, so nb takes into account the volume of all molecules present in the gas. This first correction gives:

$$P = \frac{nRT}{V - nb} \quad (8.5.2)$$

which is known as the 'hard spheres' model. note that we have not introduced anything regarding interactions yet, so this model tells us that we can increase the density as much as we want without changing the internal energy until we get to the point where the spheres touch each other. Because they are 'hard', the force required to reduce the volume any further would be infinitely large (not too different from pushing a billiard ball inside another one). Translated into potential energy, this means that the potential energy will jump to infinity when the distance between the center of the particles equals two times their radius. This is better than nothing, but not entirely realistic. In reality molecules are not completely hard, and can be pushed against each other a little bit without an infinite force.

What about interactions? We discussed that at moderate densities, attractive interactions dominate over repulsive interactions. In order to incorporate a correction due to attractive interactions we need to recognize that the pressure of the gas needs to be smaller than the pressure of a gas without attractions (like the hard spheres model). The pressure of a gas is a measure of the collisions of the molecules with the walls of the container. Attractive forces should decrease this frequency, so the resulting pressure should be lower:

$$P = \frac{nRT}{V - nb} - C$$

where C will be a positive term, that takes into account the attractive interactions. What should this term depend on? Clearly on the chemical nature of the molecules, and should be larger for atoms with more electrons (e.g. Xe) than for atoms with less electrons (e.g. He). In addition, it should depend on the density of the gas (n/V), as attractive forces are stronger the closer the molecules are. Van der Waals proposed the following equation that satisfies everything we just said:

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \quad (8.5.3)$$

Check the following examples of van der Waals constants, and see if you understand how the values of a and b make sense in terms of the sizes of the molecules, and what you know about chemical interactions from your general chemistry courses. Pay attention to the units as well.

gas	$a(L^2\text{bar/mol}^2)$	$b(L/\text{mol})$

gas	$a(L^2 bar/mol^2)$	$b(L/mol)$
He	0.035	0.0237
Ar	1.35	0.0320
Kr	2.349	0.0398
H ₂	0.248	0.02661
O ₂	1.378	0.03183
H ₂ O	5.536	0.03049
CO ₂	3.64	0.0427

It is worth stressing that the van der Waals model is still a model, that is, it is not the exact representation of a real gas. It improves many of the deficiencies of the real gas law, but it is still a model.

Coming back to Figure 8.5.1, imagine now that the containers are filled with a van der Waals gas. The three states have different internal energy now, because the density of the molecules is different, and that changes the forces between them. The potential energy is zero if the molecules are too far for any attractive or repulsive force to be significant, or when the attractive and repulsive forces exactly cancel each other. When attractive forces dominate we would need to exert work to separate the molecules, and the potential energy is negative. When repulsive forces dominate the potential energy is positive, and we would need to exert work to push the molecules closer. With all this in mind, in which of the three situations is the potential energy lower? The answer is container number 3. Molecules are closer (but not close enough to touch each other), so attractive forces are stronger than in container number 1. Attractive forces lower that internal energy of the system. These arguments allow us to plot the potential energy for a van der Waals gas as a function of the distance between the center of the molecules:

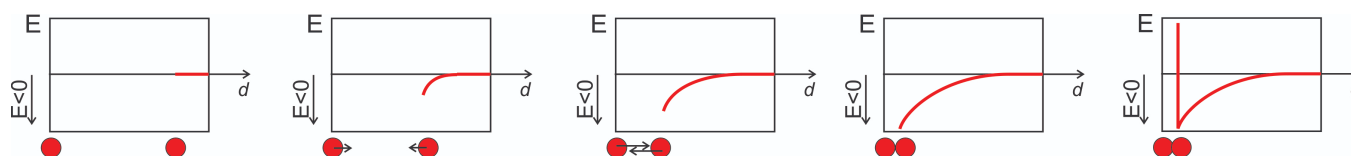


Figure 8.5.2: The potential energy (E) of a van der Waals gas as two atoms or molecules are brought to close proximity (CC BY-NC-SA; Marcia Levitus)

The potential energy is zero when the distance between molecules is much longer than their diameters. If we start decreasing the density they get closer, and the attractive interactions become significant, lowering the internal energy. This continues until they touch each other. Because they are 'hard spheres' they cannot penetrate each other at all, and the potential energy jumps to infinity. This is equivalent to saying that the force required to push them closer together is infinitely large.

We discussed the difference between a real gas and a model of a real gas. How does this plot look like in reality, and how different is it from the van der Waals model? Below are examples for different gases. Notice that 'Ar₂' does not refer to a gas made up of molecules of Ar₂, but instead to the interactions between two Ar atoms. All the gases in this figure, as we know, are monoatomic.

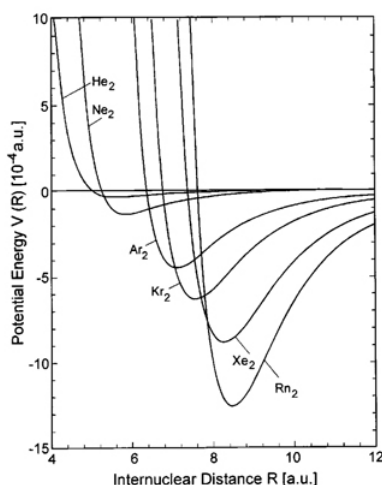


Figure 8.5.3: The potential energy of real gases. (CC BY-NC-SA; Marcia Levitus)

There are a few things worth noting. First, atoms with more electrons (look at a periodic table) show a deeper well. This makes sense because more electrons result in stronger attractive London forces. Also, atoms with more electrons experience these attractive forces at longer distances than atoms with less electrons. In all cases the potential energy increases very sharply when we continue to decrease the distance between the atoms, but the potential energy does not jump to infinity suddenly, as in the case of the van der Waals gas. This means the atoms are not exactly hard spheres. As expected, we can bring two atoms of He much closer than two atoms of Rn before we see these repulsive interactions because atoms of He are much smaller than those of Rn.

Pressure-Volume Isotherms

Scientists started to study the behavior of gases back in the 1600s. As you can imagine, they had very rudimentary laboratory supplies, and their observations were mostly qualitative. One of the earliest quantitative studies in chemistry was performed by Robert Boyle, who noticed that the volume and the pressure of a fixed amount of gas at constant temperature change according to the simple law $P \propto 1/V$, where the symbol “ \propto ” means “proportional to”. This is of course true for an ideal gas, whose equation of state is $P = nRT/V$, but not for a real gas. Boyle’s law predicts that the volume of a gas decreases as the pressure is increased at constant temperature. Mathematically, this curve is called an hyperbola (hyperbolas are graphs where the product xy is a constant), and physically we call these plots isotherms, because they represent the behavior at constant temperature (*iso* means equal in Latin). In other words, the isotherm for an ideal gas is an hyperbola, but the isotherm for a real gas will show deviations from the hyperbolic shape.

We can of course go to the lab and measure the isotherms for any real gas in any range of temperatures we want. We know that whenever the conditions are such that the density of the gas is low, we expect interactions to be negligible, and therefore isotherms should be very close to the hyperbolas that Boyle described in the 1600s. What happens when interactions are significant? Some experimental isotherms for CO_2 are shown in Figure 8.5.4. At higher temperatures (e.g. 50°C), the isotherm is close to the prediction for an ideal gas: we can compress the volume to small volumes and the pressure will increase following Boyle’s law. The isotherms at higher temperatures will be even closer to the hyperbolas predicted by Boyle’s law because interactions become less and less noticeable.

What happens at lower temperatures? Let’s consider the isotherm at 20°C . Imagine you have a container with one mole of CO_2 , and you start reducing its volume at constant temperature. The initial volume is somewhere between 0.5 and 0.6 L (point A in Figure 8.5.4). As you start reducing the volume the pressure starts increasing in approximate agreement with Boyle’s law, but notice that important deviations are observed as you approach point B. When the pressure reaches 60 atm (point C), the behavior of the fluid deviates greatly from that predicted by the laws of ideal gases. You continue reducing the volume of the gas, but the pressure not only does not go up as predicted by Boyle’s law, but it remains constant for a while (between points C and E)! What is going on? How can we reduce the volume of a gas without increasing the pressure? The answer is that we are not dealing with a pure gas anymore: we are liquefying part of it. As we move from C to E, we increase the amount of liquid and reduce the amount of gas, and the pressure of the system remains constant as long as we have gas and liquid in equilibrium. Of course the more liquid we have the less volume the CO_2 occupies.

As we mentioned before, ideal gases are not supposed to form liquids because in principle, the molecules that make up the gas do not have any size and do not experience any interactions with the other molecules in the container. To form a liquid, molecules need to experience strong attractive forces, or otherwise the motions they experience due to their thermal energy would not allow them to stay close enough. Liquefying a gas, therefore, is a clear experimental evidence of non-ideal behavior and the existence of attractive interactions among molecules.

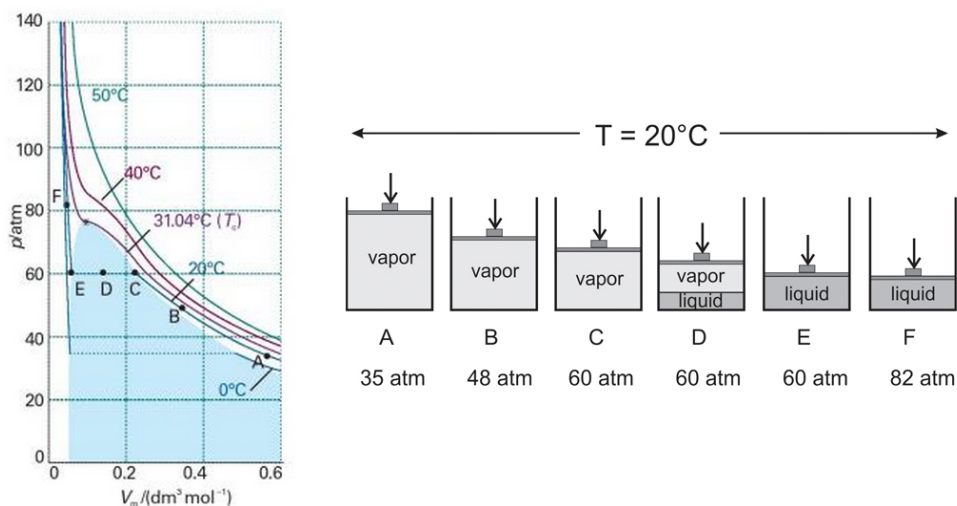


Figure 8.5.4: CO₂ isotherms. (CC BY-NC-SA; Marcia Levitus)

Coming back to Figure 8.5.4, any point in the horizontal line CDE represents a state where liquid and gas coexist. We call the gas “vapor” in these circumstances, but the distinction is more semantic than physical. When we reach point E, all the CO₂ molecules are part of the liquid. We can continue to reduce the volume, but the pressure of the container will go up much more dramatically than before because we would need to exert a considerable amount of force to push the molecules of liquid closer together. In more technical terms, liquids are much less compressible than gases (see the definition of compressibility in page). The area highlighted in light blue in Figure 8.5.4 represents the conditions under which CO₂ can exist in equilibrium between the liquid and vapor phases. For example, if we perform the experiment at 0° C, we would start seeing the first drops of liquid when the pressure of the container reaches ≈ 35 atm. The pressure will remain constant as we continue to reduce the volume and we form more and more liquid. When no CO₂ remains in the vapor phase, reducing the volume even further would require that we increase the pressure of the container dramatically, as we would be compressing a liquid, not a gas.

Notice that the length of the horizontal line that represents the co-existence of liquid and gas decreases as we increase the temperature. If we were to perform the experiment at 30° C (not shown), we would see that the volume at which we see the first drop of liquid is not too different from the volume at which we stop seeing CO₂ in the gas phase. Liquefying all the gas would require a small change in volume, which means that at that particular temperature and pressure, the volume that the gas occupies is not too different from the volume the liquid occupies. Pretty strange if you think about it...a mole of an ideal gas occupies 22.4L at room temperature, and a mole of liquid water occupies only 18 mL, almost a thousand times less. If we think in terms of densities, the density of water at room temperature is about 1 g/mL, or 0.056 mol/mL. The density of an ideal gas at room temperature is $n/V = P/RT \approx 4 \times 10^{-5}$ mol/L, again, around a thousand times less. Yet, at 30° C, and around 80 atm, the density of CO₂ in the liquid state is almost the same as the density of CO₂ in the gas phase. If we put CO₂ in a high pressure cell, and increase P to 80 atm, it would be hard for us to say whether the CO₂ is liquid or gas. At much lower pressures, distinguishing between liquid and gas becomes much more evident, as we are used to from our daily experience.

Critical Behavior

There is a particular isotherm where the CDE line of figure [c2v:fig:isotherms] reduces to a point. In the case of CO₂, this isotherm is the one we measure at 31.04° C, and it is so unique and important that it has a special name: the ‘critical isotherm’. At temperatures below the critical isotherm, we see that the gas condenses to form liquid, and that the pressure of the system remains constant as we convert more and more gas into liquid. The lower the temperature, the more different the densities of the vapor and the liquid are. This is very intuitive for us, because it is what we are used to seeing with the liquid we know best: water. In the case of water, we would need to increase the pressure to 218 atm and work at 374 °C to lose our ability to distinguish between liquid water and vapor. The conditions on earth are so far away from the critical point, that we can clearly distinguish liquid water from

vapor from their densities. Coming back to CO_2 , as we increase the temperature at high pressures (more than 60 atm), the liquid and the vapor states of the fluid become more and more similar. Right below the critical temperature we can hardly distinguish what is liquid and what is vapor, and at exactly the critical temperature, that distinction is lost. Above the critical temperature we never see a separation of phases, we just see a fluid that becomes denser as we reduce the volume of the container. Notice that the critical point is an inflection point in the critical isotherm. This happens at a particular molar volume (for CO_2 $V_c = 0.094 \text{ L/mol}$) and at a particular pressure (for CO_2 $P_c = 72.9 \text{ atm}$), which we call the critical molar volume and critical pressure of the fluid. If we want to liquefy CO_2 , we need to do it at temperatures below its critical temperature (31.04°C). At temperatures above this value the fluid will always be a gas, although it could be a very dense gas! Chemists call this state ‘supercritical fluid’ just to differentiate it from a low-density gas such as CO_2 at 1 atm. Again, to give you an idea, one mole of CO_2 occupies about 25L at 1 atm and 40°C , and we call it a gas without thinking twice. From figure [c2v:fig:isotherms], at 80 atm and 40°C one mole of CO_2 occupies about 0.15L, about 170 times less than the gas we are used to seeing at 1 atm. This is a very dense fluid, but technically it is not a liquid because we are above the critical temperature. Instead, we use the term supercritical fluid. As it turns out, supercritical CO_2 is much more than a curiosity. It is used as a solvent for many industrial processes, including decaffeinating coffee and dry cleaning.

From our discussion above, it is clear that ideal gases do not display critical behavior. Again, ideal gases do not exist, so when we say that ideal gases do not display critical behavior we are just saying that 1) gases show critical behavior at conditions of temperature, pressure and molar volume that are very far from the conditions where the simple equation $PV = nRT$ describes the behavior of the gas and that 2) if we want to describe a gas close to the critical point we need an equation of state that is consistent with critical behavior. If we plot the isotherms of an ideal gas ($P = nRT/V$) we will obtain hyperbolas at any temperature. Again, this works well with gases at very low densities, but because the model does not include interactions, it cannot possibly describe the isotherms at or around the critical point.

Is the hard spheres model of Equation 8.5.2 consistent with the existence of the critical point? To answer this question, we could plot many isotherms according to this equation and see if the model gives one isotherm that has an inflection point as the one shown in Figure 8.5.4. Once again, keep in mind that the figure contains the data we measure experimentally, which is what CO_2 is actually doing in nature. Equations of state by definition are models that are meant to describe the system as close as possible, but they are by definition simplifications of the real behavior. Coming back to the model of hard spheres, you can plot as many isotherms as you want, but you will see that none of them show an inflection point. This is pretty obvious from the equation, as the isotherms are basically the same we would get with the ideal gas equation, but just shifted in the x -axis by the quantity b . Physically speaking, it is not surprising because the hard spheres model does not contain any parameter that accounts for the attractive interactions between molecules, and that is what we need to describe critical behavior.

We know that the van der Waals equation is the simplest equation that introduces a term to account for attractive forces (Equation 8.5.3), so it is likely that his equation might be consistent with critical behavior. Let’s discuss what we mean by this in more detail. Again, van der Waals gases do not exist in nature. They are a theoretical construction where we think about molecules as hard spheres with kinetic energy that interact with each other so that the average interaction between two randomly oriented molecules is inversely proportional to the inverse of the sixth power of the distance between them. If we could create a gas whose molecules followed these exact physical laws, the gas would behave exactly as the van der Waals equation predicts. So, now we wonder: would such a gas show an isotherm with an inflection point like the one shown for the case of real CO_2 ? The answer is yes, and the critical constants (P_c , T_c and V_c) depend on the values of the van der Waals parameters, a and b .

Now, the fact that the van der Waals model predicts critical behavior does not mean at all that it describes the whole isotherm well. If you plot the van der Waals equation at different temperatures you will see that this model does not predict the “flat” $P - V$ part of the curve, where the liquid and the gas coexist. This is not surprising, as the treatment of the attractive interactions in the van der Waals model is too simple to describe the liquid state. In fact, you will see that the van der Waals equation predicts that the derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ is positive in certain regions of the isotherm, which of course does not make any physical sense. Compressing the gas will never lower the pressure as the van der Waals gas predicts, so we can clearly see how the model fails when attractive forces are important and complex. In any case, it is pretty impressive to see how such a simple equation predicts such complex behavior as the critical point.

This page titled 8.5: Real Gases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Marcia Levitus via source content that was edited to the style and standards of the LibreTexts platform.