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CHM103: Introductory Physical Chemistry

Summary

Many people usually talk about physical chemistry as if it was a group of isolated subjects - Thermodynamics, Kinetics, Statistical Mechanics, Quantum Mechanics and sometimes macromolecules, solids, surfaces and dynamic electrochemistry. I prefer the view that all of it is connected by a central question. In my view, the central question in physical chemistry is what happens to a system when **energy** flows into or out of it.

When we talk about different fields of physical chemistry we're just asking different questions about the **disposition of the energy**. For example, our first topic will be **thermodynamics**. The basic question of thermodynamics is "If you put energy into some system, what can happen and what can't happen?" A couple of the limits of the questions that thermodynamics can address are that it deals only with **macroscopic systems**, and we can only ask **what happens** to a system we add energy to, **not *how*** these things happen. Along the way to answering basic thermodynamic questions we have to establish answers to narrower questions like "If we have two substances, which is stabler?" or "If we have two states, which is stabler?"

But the purpose of answering these questions is so that we can say what happens when we put energy into or take it out of a system.

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Our second subject will be **classical kinetics**. In classical kinetics, the critical question is "For a given system in a given state, **how fast** will a reaction occur?" Questions that we'll ask along the way will include, "If I increase the energy what happens to the speed of the reaction?",

"How many steps occur in going from reactant to product, and what are they?", and "Is there a way to change the nature of the steps so that the reaction goes faster?"

In Chemistry 310 we will begin with our third subject, which will be **quantum mechanics**. The question here is what happens to a **molecule** when you put energy into it. Does it react or does it not? Does it vibrate? Do its electrons move differently? Along the way, we have to answer questions like "How do electrons move?" "How much energy does it take to move an electron?" "Can they move any way they want?" "Is one molecule stabler than another?

Why?" But again, all this is so we know what happens when we put energy into a molecule.

Our fourth subject, which we will touch on only briefly, is **Statistical Mechanics**. This subject is a tool to take results of quantum or classical mechanics and apply them to bulk matter. The first stage in studying this subject is to derive the results of thermodynamics from the quantum mechanics of individual molecules. Why? Because thermodynamics doesn't tell you anything about the microscopic details of what goes on in a system when you add energy, just what can and can't happen. A theory of bulk matter derived from models of individual molecules can tell you much more, like how a change occurs. So we are developing tools that will allow us to ask questions about **how things happen** when we put energy into a molecule or solid or gas.

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In other words, we're developing tools that allow us to ask mechanistic questions.

This is the topic of our final subjects, the **kinetic theory of gases**, and **chemical dynamics**. For different systems and to differing degrees of sophistication, they ask the question, "When energy is put into a system, what happens between the beginning and the end of the resulting process?" Does the energy stay put until reaction occurs or does it move all around the molecule? How much energy does it actually take for the reaction to occur? How fast will energy leave a molecule?

So we see that in all these areas of physical chemistry, energy is a common thread.

A number of you are here as BMB majors, and many of you will be either curious or skeptical about the relevance of this material for your studies and research. Let me briefly attempt to address this issue. This is somewhat easier from the biochemistry point of view, since many biochemistry questions are answered either by studying the rates or energetics of biological processes, and therefore a deeper understanding of kinetics and thermodynamics is directly relevant to your work. A deeper understanding is important if you wish to treat energetics or kinetics quantitatively because the way these subjects are treated in general chemistry does not allow you to account for the intrinsic complexity of biological systems.

Many of you are in the molecular biology end of things, and do not study quantitative energetics or kinetics. In this case the main relevance of the course is in developing a strong qualitative understanding of the parameters that drive the processes that you are interested in, and that determine how quickly they can occur. For example, understanding entropic effects on DNA

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transcription requires a subtle understanding of the nature of entropy and of the factors that increase or decrease entropy. Understanding the appropriate temperature ranges for various processes depends on understanding why and how heat can be effective in driving a process.

The approach that I prefer to take to this is to focus on very basic and fundamental principles, because a deep understanding of these can be applied to any system. I am happy to talk to any of you about thermodynamics and kinetics and the way that it relates to the systems you are most interested in.

Let's begin our discussion of **thermodynamics**. In thermodynamics, we put energy into a macroscopic system, and try to figure out what can and can't happen. At this point in your chemical educations, you should have a qualitative idea of the meaning of **energy** and **system**, but we will have to make these ideas more precise. Let's begin by talking about the **state of a system**. We must begin by defining our terms. A **system** is the part of the universe you are interested in. Everything else is the **surroundings.** As an example, I do my experiments by shining light on molecules suspended in crystals of rare gases. I might define as my system the rare gas crystal, the molecules I am studying, and the photons, or particles of light, and as the surroundings the substrate the crystal rests on, the refrigerator which cools the rare gas to the low temperature necessary to freeze it, the chemistry building the experiment sits in, the state the building is in, and for sake of completeness, the rest of the universe, both known and unknown. A biochemical example of this could define a system as a mitochondrion, and the surroundings the rest of the cell, or it could be an enzyme plus the ATP supplying its energy as the system, or alternatively the

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system could be the enzyme, with the ATP as part of the surroundings. Choice of system and surroundings depends on the nature of the calculation we wish to do, and the specific question we are asking about the processes we are studying.

In order to distinguish the system from the surroundings we must have a **boundary**. In the example above, one of the boundaries would be the interface between the substrate and the rare gas crystal. Different types of systems are defined by the nature of the boundary separating the system from the surroundings. An **isolated system** has a boundary that prevents any interaction between the system and the surroundings. In particular this means no transfer of energy, and no transfer of matter. An **open system** has a boundary that allows matter to be transferred. A **closed system** has a boundary that allows no transfer of matter. Q: WHAT IS THE DIFFERENCE BETWEEN A CLOSED SYSTEM AND AN ISOLATED SYSTEM? If heat transfer between the system and the surroundings is prevented, we have an **adiabatic system**. Two more types of systems are homogenous systems and heterogeneous systems. A **homogenous system** has uniform properties throughout. A **heterogeneous system** will have more than one phase. Q: WHAT DOES THE DISTINCTION BETWEEN HOMOGENEOUS AND HETEROGENEOUS SYSTEMS HAVE TO DO WITH BOUNDARIES? Q: CAN YOU THINK OF A SITUATION IN WHICH A SYSTEM HAS NO INTERNAL BOUNDARIES, YET IS NOT HOMOGENEOUS? (Non-equilibrium) Note that the choice of a boundary can be defined by a natural feature of a system, such as a cell wall, or the wall of a thermos. However, the boundary choice can also be hypothetical, and chosen simply for simplicity in calculations.

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If we add energy to our system, it will presumably make some change in the system, so we need to be able to **describe our system** quantitatively. We do this by specifying **measurable properties** of the system, like density, pressure, volume, temperature and mass. We divide all of these properties into two groups, extensive properties and intensive properties. **Extensive properties** are ones that depend on the size of the system. **Intensive properties** are ones that are not dependent on the size of the system. Temperature, pressure and density are intensive properties. As an example, let's consider a container with a gaseous sample inside. We can cut this sample into two parts by inserting a barrier. The temperature and pressure in both halves will be same as original temperature and pressure. WHAT IS THE VOLUME IN EACH HALF? IS VOLUME INTENSIVE OR EXTENSIVE? WHAT ABOUT MASS?

As always the **amount of substance** in a system is given by the number of moles of each of the components of the system. If an extensive property is divided by the number of moles in the system, an intensive property is obtained. For example, volume V, is an extensive property. V/n, called molar volume and symbolized by $\bar{V}$ or V_m, is an intensive property. IN THIS EXAMPLE, IS VOLUME EXTENSIVE OR INTENSIVE? IS MOLE NUMBER EXTENSIVE OR INTENSIVE? WHAT GENERALIZATION MIGHT WE MAKE ABOUT THE RATIO OF TWO EXTENSIVE QUANTITIES? CAN WE THINK OF OTHER EXAMPLES?

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Lecture 2

We'll continue by asking the question "What is the state of a system, and how do we measure it?" To do this we need to talk about equilibrium first. A limitation of thermodynamics is that it deals only with **states in equilibrium**. Q: WHAT IS A STATE OF EQUILIBRIUM? CAN SOMEONE STATE THAT WITH AN EQUATION? This means that we will limit our descriptions of systems to systems in equilibrium. A system that is at equilibrium is said to be in a **definite state**. This means that each of its properties is not changing with respect to time. This is exactly the same as our mathematical description of equilibrium. The measurable properties of a system are called **state variables**.

What I'm going to say next is very important. **When a system is in equilibrium, its properties depend only on the values of its state variables, and not on the history of the system.** In other words, it is important only where you are and not how you got there, and not where you were before.

A very practical question that we might ask is "How many state variables need to be specified to completely define the state of a system?" We've mentioned five state variables already but the potential number of measurable properties depends only on the ingenuity of the experimentalist. ASK FOR LIST OF MEASURABLES (GROUPS). How many of this potential multitude of measurables is necessary to **uniquely** define a system? In thermodynamics, this usually turns out to be quite a small number. For the simplest systems, (ones with only one component and which have a charge of zero) one extensive property and two intensive properties are enough. It

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is important to understand that this means that once these three properties are fixed, the values of all other measurable properties of the system are completely determined. As systems grow more complicated more properties are necessary to uniquely define the system.

Let's talk about two of our state variables, temperature, and pressure. **Pressure** is defined as **force per unit area**. This implies that there are two different ways to obtain a large pressure – one is to have a large force exerted on a given area, and the other is to have a smaller force exerted on a small area. This latter is the reason that someone can step on your foot with flat heeled shoes and cause only moderate pain, but the same person stepping on your foot with a spike heel will easily break a bone.

The simplest measurements of pressure are made with either a manometer, or a barometer. A similar principle is used in both instruments. A **manometer** is a U shaped tube half filled with mercury or some other low vapor pressure liquid, and then evacuated on one side. [Draw] If both sides are evacuated, then the only force is due to the weight of the mercury on each side, which is equal, since the mercury can flow until the forces equalize. If gas is added to one side, it exerts a force that moves the mercury on the gas side down, and on the vacuum side up. The mercury stops moving when the pressure due to the difference in heights of the mercury columns equals the pressure exerted by the gas. Therefore, **the pressure exerted by the gas is proportional to the difference in heights of the two mercury columns**. To simplify matters, the pressure can be defined in terms of the difference in heights of mercury columns in a manometer. The oldest

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pressure unit still found in texts is the mm of mercury. However, there's a problem with using heights of mercury columns as units of pressure. Q: CAN ANYONE TELL ME

WHAT THE PROBLEM IS? Because of this, the mm of mercury (mm Hg) has been replaced by the Torr, which is exactly equal to the mm of mercury at 25□C.

Our preferred pressure units will be neither mm Hg or Torr, but SI units. The **basic units in the SI system** are the kilogram, abbreviated Kg, for mass; the meter, abbreviated m, for length; the second, abbreviated s, for time; the ampere, abbreviated A, for electrical current; the Kelvin, abbreviated K, for temperature; the candela, abbreviated cd, for luminous intensity, and the mole, abbreviated mol, for amount of substance. **All other units are derived from these basic units**. The SI unit of force is the Newton, N, 1 kg m s^{-2}. Since p = f/area, the SI unit of pressure is N/m^2 and is called the Pascal, Pa. 1 Atm = 101,325 Pa. It is useful to have an SI unit of pressure closer to 1 atm so another common pressure unit is 1 Bar = 10^5 Pa.

We now turn to **temperature**, the most abstract of the state variables. The question we'll now try to address is "What is temperature and how do we measure it?" It's actually easier to answer the first question by turning to measurement first. The measurement of temperature is called thermometry. A basic law of thermodynamics underlies thermometry. It is called the **Zeroth Law of Thermodynamics**. It concerns thermal equilibrium. We define **thermal equilibrium** this way. Suppose we bring two objects (for example, a thermometer and hot water) into contact in such a way that heat can flow between them. Some observable physical property will change due to the heat flow (such as the height of the fluid in the thermometer). If we wait

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long enough, the physical properties stop changing. Then we say that the two objects have reached a state of thermal equilibrium.

The **Zeroth law of thermodynamics** says suppose you have three objects, A, B, and C. If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then A is also in thermal equilibrium with C. Let's look at how we can use the zeroth law of thermodynamics to establish a temperature scale.

First, we observe some object like an alcohol filled tube. We notice that when this tube is in contact with a hot object, the alcohol expands, and when it is in contact with a cold object it contracts. Adding or removing heat changes the height of the alcohol, so we propose that the height of the fluid changes due to a variable which we will call temperature, which is somehow related to heat flow (we will refine this definition of temperature). We need to invent this variable because there is no other measurable variable that can always account for the changes in property of matter that occur when heat flows into or out of a system.

Now we put the tube in boiling water, and mark the height of the alcohol when thermal equilibrium is achieved. We say that the height of the alcohol is representative of the temperature of boiling water. Now say we have another hot object, say a chunk of metal. We place the tube on this piece of metal and let it come to thermal equilibrium. If the height of the alcohol at thermal equilibrium is the same as that when it is in boiling water, then the zeroth law tells us that we can say that this property called temperature is the same for both.

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But what is temperature itself? Dictionaries would define it as the measure of hotness or coldness in an object, which is a frustratingly circular definition, since in this case the definition of temperature is tied to the measurement of temperature. A macroscopic definition might be "a macroscopic equilibrium property of matter that predicts the direction of heat flow", since we know that the direction of heat flow is from hotter to colder." On a molecular basis, we can define temperature as a variable proportional to the average internal kinetic energy in an macroscopic sample at equilibrium.

Note the necessity of the equilibrium condition. Temperatures (and in fact, other state variables) are not defined for systems that are not in equilibrium. An interesting example of a nonequilibrium system that illustrates the difficulty in defining temperatures for such systems is called a supersonic free jet. This is a device invented in the 1960's to allow experiments to be conducted on gas phase systems at temperatures below 10K. It works by expanding a gas from a reservoir containing gases at high pressures (20 atm or greater) through a pinhole into a vacuum. As the gas shoots out of the pinhole, the random motions that constitute its temperature are converted into directed flow, cooling the gas. If such a gas consists of atoms, like He gas, the system achieves equilibrium and the temperature is well defined. However if the gas contains molecules, as in a mixture of He and benzene, then there are different classes of motion, translation, rotation and vibration, each of which contributes to the temperature. It turns out that the rate of cooling for each of these motions is different, with translation fastest and vibration slowest. As a result, when cooling stops, the amounts of translational, rotational and vibrational motion will each correspond to a different temperature, with the translational temperature the lowest and the

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vibrational temperature the highest. The fact that different motions of the gas yield different temperatures makes it impossible to assign an unambiguous temperature to the gas.

You should all be familiar with the most common temperature scales, Fahrenheit, Celsius, and Kelvin. The Kelvin scale has two other important names. One is the **ideal gas scale**. The name comes from the fact that most gases, if used as fluids for thermometers, give very similar heights for the same temperatures, unlike most liquids. If the gases used are at low pressures, then the heights are identical. Under conditions where gases show identical behaviors, they are called **ideal gases**.

The other name is the **thermodynamic temperature scale**. It is called this because the Kelvin scale can be derived from considerations about a thermodynamic state function called the entropy. The only correct temperature scale for use in most thermodynamic calculations is the Kelvin scale.

We now turn to **Equations of State**. In discussing Equations of State we'll be asking the question, "Are state variables independent, or is there a relationship between them?" So far we've talked about several state variables. For pure gases, pressure, volume, and temperature are all properties of a system. Generally we can vary both pressure and volume independently. In other words, for a given system with constant mass, you can simultaneously set it to any p and any V. Each property of a system that can be varied **independently** is called a **degree of freedom**. Now suppose you place this system in thermal equilibrium with another system. You will now find that for each pressure there is only one possible volume and vice versa. Now only one of the two

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variables can be varied independently. Thus when we take our gas and subject it to a thermal equilibrium, the number of independent variables is reduced by one.

Another way of saying that the system is in a state of thermal equilibrium is to say that we are holding the temperature constant. Q. WHY IS THIS EQUIVALENT? When we hold the temperature constant, we find that for every p there is only one V. Similarly we find that if we hold the volume constant, you will find only one p for every T, and if we hold the p constant there will be only one T for every V. We can express these statements mathematically as

$$\Box(p, V) = T$$

$$\Box(p, T) = V \text{ and}$$

$$\Box(V, T) = p,$$

where $\Box$, $\Box$, and $\Box$ are different functions of the respective variables. The first equation simply says that there is some function of p and V that yields the temperature T, and so on. These equations, which relate the values of state variables, are called **equations of state**. All gases can be described by such equations, although the exact equation depends on the identity of the gas.

You are all familiar with at least one equation of state, **the ideal gas law**, which holds for most gases under conditions of low pressure and moderate temperatures. The ideal gas law is

$$pV = nRT,$$

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where R is the gas constant, with a value of 8.314 J K^{-1} mol^{-1}. The value of R in several other units is given in your book, the other useful value being R = 0.08206 L atm mol^{-1} K^{-1}. You can see that the ideal gas law satisfies each of our above equations, since we can write, pV/nR = T, nRT/p = V, etc.

The effect of **an equation of state** is that it **allows us to reduce the number of state variables we need to use to describe a system**. Even though four or more state variables can be found to describe a pure gas, when we know the equation of state, knowing only three is enough to set the values of the others.

We can draw two major conclusions from this discussion. First, Equations of State are useful because they allow us to relate different state variables and limit the number that we need to know. Second, if we apply a constraint to our system, like holding a variable constant, it restricts the number of ways that the state variables can vary.

I said earlier that for the simplest systems very few variables are required to describe the system. A logical question to ask at this point is how the situation changes when we consider a more complex system. A relatively simple example of a more complex system is a **mixture of non-reacting gases**. If we are going to describe mixtures of gases, we need more variables to describe the system, particularly variables that describe the composition of the mixture. The most typical variables that are used to describe composition are p_i, the **partial pressures**, which are the pressures exerted by the individual components in a gaseous mixture, and n_i, the number of moles

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of the various components. The description of mixtures can be simplified for ideal gases by Dalton's law of partial pressures, which you were first introduced to in General Chem.

It says that for a component *i*, $p_i = \frac{n_i RT}{V}$. In other words, the pressure exerted by a gas in a mixture is the same that the sample would exert if it were the only gas in the container. A logical implication of Dalton's law is that the total pressure is related to the partial pressures by

$$p = p_1 + p_2 + p_3 + \ldots ,$$

where p_n indicates the partial pressure of the n^{th} component of the mixture. If we combine these equations we get

$$p = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \ldots + \frac{RT}{V} \sum n_i = \frac{nRT}{V} ,$$

where n is the total number of moles of gas in the mixture. So we see that for a *mixture* of ideal gases the ideal gas law still holds, as long as n represents the total number of gaseous moles. We can use this result to rewrite our equation for partial pressure, $p_i = \frac{n^i RT}{V}$, by noting that

$$\frac{RT}{V} = p$$

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, and substituting to obtain

$$\frac{V}{n} = \frac{RT}{p}$$

$$p = \frac{n_i p_i}{n}$$

The quantity n_1/n is extremely useful and is given the special name of **mole fraction, symbolized by X_i.** From the definition of the mole fraction we can see that $\sum X_i = 1$. It turns out that for many non-ideal mixtures, the mole fraction is the description of the composition that we will find most useful. For these same non-ideal mixtures, Dalton's law will not hold. This means that we need a more general definition of partial pressure. The general definition is

$$p_i = X_i p,$$

where p_i and X_i are the partial pressure and mole fraction of the *i*th component of the mixture. The generality of the definition is due to the fact that there are no assumptions of ideality in the definition of the mole fraction.

Note that whether we are using partial pressures, moles or mole fractions to describe our composition, that we need to add an additional n-1 variables to describe systems containing n components. WHY IS IT N-1 INSTEAD OF N?

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Lectures 3 and 4

Last time we talked about equations of state, and as one example, discussed the ideal gas equation of state. In general chemistry, we tend to limit our discussions to simple systems such as ideal gases. However, one of the real strengths of thermodynamics is that it can, with relative simplicity, make predictions about real chemical systems. Therefore, our questions for today have to do with non-ideal systems, how they differ from ideal systems and how these differences can be expressed mathematically.

When we talked last time about using gases as a fluid for thermometry, we pointed out that **when the pressure was low and the temperature was high all gases behaved identically**. We called gases under these conditions ideal gases. Under these same conditions all gases will obey the ideal gas law. However, **under the great majority of conditions a gas will not follow the ideal gas law**. There is evidence for non-ideality all around us. One way to see this is that the ideal gas law predicts that as we lower temperature, a substance will remain a gas all the way until a volume of zero is obtained. It is our common experience that this does not happen but that at some sufficiently low temperature the substance will liquefy. This is a dramatic example of real gas behavior, but non-ideal behavior occurs over conditions far away from the boiling point as well.

A useful measure of non-ideal behavior is called the **compressibility factor, Z**. This is defined as pV_m/RT. This is a useful quantity because it clearly indicates ideal behavior, since for all ideal gases pV_m/RT will be one. For real gases the compressibility factor will not be constant

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at one but will change as the pressure and temperature change. If, at a given temperature and pressure, the gas is easier to compress than an ideal gas, the compressibility factor will be less than one, and if it is harder to compress than an ideal gas its compressibility factor will be greater than one. A typical plot of Z vs. p for a real gas looks like this.

Note that at very high pressures, say 400 atm and above, a typical real gas will have a compressibility factor greater than one, i.e. at this point it is harder to compress than an ideal gas. As pressure is reduced the compressibility factor decreases until at pressures around 200 atm it drops below one, i.e., is easier to compress than an ideal gas. When the pressure gets very low, Z approaches the ideal gas value of 1.

The way that Z depends on pressure tells us something of the **intermolecular forces** between our molecules and the scale of distance at which they act. Real gases are harder to compress than ideal gases at high pressures. Q: WHAT KIND OF FORCES WOULD MAKE IT HARDER TO COMPRESS A GAS? WHAT HAPPENS TO THE DISTANCES BETWEEN MOLECULES AS WE INCREASE PRESSURE? SO WHEN THE PRESSURE IS HIGHEST WHAT CAN WE SAY ABOUT THE DISTANCES

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BETWEEN THE MOLECULES IN OUR GAS? Therefore we conclude that when distances between molecules are short, repulsive forces dominate between molecules.

WHAT TYPES OF FORCES MAKE IT EASIER TO COMPRESS A GAS? WHEN PRESSURES ARE INTERMEDIATE WHAT CAN WE SAY ABOUT THE DISTANCES BETWEEN OUR MOLECULES? Therefore we can conclude that at intermediate distances attractive forces dominate. To continue this line of reasoning, we see that at low pressures and therefore long distances, there is no deviation from ideality and therefore, neither attractive nor repulsive forces are strong enough to make a difference. We see from this analysis that just by looking at something as simple as the pVT behavior of a gas we can learn something about its intermolecular forces.

The plot of compressibility versus pressure depends on the temperature. If we plot Z vs. p at several temperatures we see that each has a different shape, as below. A curve like these in which some property is studied at constant temperature is called an **isotherm**.

There is one temperature called the **Boyle temperature**, where Z = 1 over a wide range of pressures, and therefore the behavior of the gas is most nearly ideal. This happens because at the Boyle temperature the attractive and repulsive forces are balanced and cancel each other.

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When we get to **real gases**, it becomes much harder to understand all of the interrelations between the state variables. For ideal gases, this is pretty easy, because our ideal gas law is a single simple equation that gives the relation between p, V_m and T under all conditions. However, even for this simple equation, the relationship between these variables is impossible to reduce to an equation with one independent variable. One way to represent this information economically is graphically. Unfortunately, it's nearly impossible to comprehend a graph that simultaneously shows the relationship between all three variables. So we tend to **hold one variable constant, and look at the interaction of the other two**. This is a common and important procedure in physical chemistry, where we often deal with very complex systems with large numbers of variables. In order to comprehend the relationships in these complex systems we tend to deal with them two at a time, but holding all other known variables constant. The analysis is then repeated for all other independent variables. However, it's important in these analyses to be intensely aware of the variables being held constant, or incorrect conclusions will be drawn from the individual graphs.

We've already identified graphs where the temperature is held constant as isotherms. If pressure is held constant we call the equation or graph an **isobar**, and if we hold volume constant, it is called an **isochore**. Each of these graphs which hold one variable constant are essentially slices through a four dimensional diagram which represents the full relationship between the three variables.

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One of these graphs, the slice that looks at p as a function of T, is an isochore, and is simply the **phase diagram** that you learned about in general chemistry. It has regions

corresponding to gas, liquid, and solid phases, and lines at which the two phases are in equilibrium. There are two noteworthy points, the **triple point**, at which all three phases are in equilibrium, and the **critical point**. The critical point is significant because **at temperatures above the critical point it is no longer possible to condense a gas**. At the critical point itself, matter has strange properties that are not yet completely understood. One of them is an anomalous tendency to scatter light, called critical opalescence. At the critical point, there is a unique set of critical properties, the critical temperature, T_c, the critical pressure, p_c, and the

critical volume $\bar{V}_c$. In other words, just as there is only one triple point for a pure substance, there is only one critical point.

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A second slice, a series of isotherms for which temperature is held constant and we vary volume and pressure, may be less familiar to you. Consider an isotherm at a relatively low temperature. As we decrease the volume the pressure increases slowly until we reach a plateau at which the compression can continue without the pressure increasing. The beginning of the plateau is the point at which the gas starts condensing. Note that the beginning of condensation is physically marked by the appearance of an observable phase boundary. Condensation continues with continued compression until all the gas has been converted to liquid. At this point any further compression results in a sharp increase in pressure. At the critical temperature, the p-V isotherm does not have a line indicating condensation, rather, there is an inflection point in the curve. At temperatures above the critical temperature, the curve varies smoothly, with no discontinuities and no inflection points.

Gases at temperatures and pressures beyond the critical point are called supercritical fluids. Originally of interest purely for reasons of scientific curiosity, they are an area of active investigation both in applied and basic chemical research. Applications range from use of supercritical CO_2 as an environmentally friendly dry cleaning fluid, to use of supercritical CO_2 as a non-toxic decaffeinating agent for coffee beans.

The graphs of real gas behavior give us qualitative information about the way that real gas properties change under various conditions, but it is also necessary to have more quantitative

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information about the states of real gases. We will introduce two equations of states for real gases, an empirical one called the virial equation of state, and a theoretical one called the van der Waals equation.

The empirical approach is based on the compression factor, $Z = pV_m/RT$. Remember that this factor has a low-pressure limit of one, but deviates at higher pressure. This behavior allows us to write the compression factor as an infinite series expansion in $1/V$,

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots$$

Since this equation relates p, V_m and T, it is an equation of state for real gases. Alternatively one may write

$$\frac{pV}{RT} = 1 + B'p + C'p^2 + \ldots$$

where the constants B and B' and C and C' are related by the equations

$$B' = \frac{B}{RT} \quad \text{and} \quad C' = \frac{(C - B^2)}{(RT)^2} \quad .$$

These expansions are different forms of what is called the **Virial Equation of State**. The coefficients B, C, etc. are called **Virial Coefficients**. The virial equation is an empirical equation

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of state. It is obtained by taking an empirical isotherm, and varying the values of B, C until the equation comes as close as possible to reproducing the experimental isotherm. The virial equation is used for all p-V-T calculations that require a high degree of accuracy. Virial coefficients for some gases may be found in your book, and many others can be found in the literature or in various handbooks such as the CRC, Lange's Handbook of Chemistry or the multi-volume International Critical Tables.

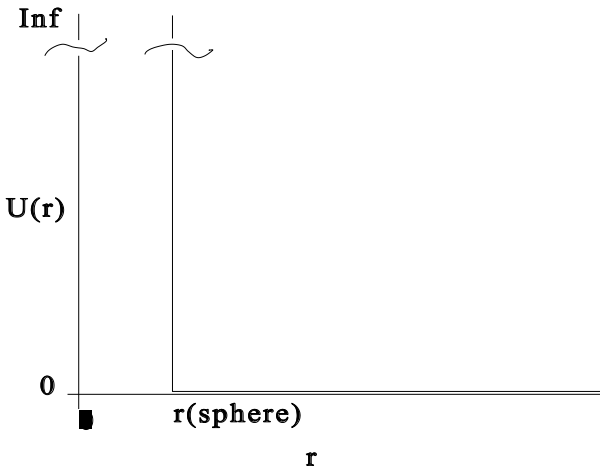
Remember that we get a different graph of Z vs. p for each temperature. Thus for each different temperature, it is necessary to obtain a different set of virial coefficients. An interesting case of this is that there is always a temperature at which the second virial coefficient, B or B', is zero. This is the Boyle temperature we mentioned earlier, the temperature at which a gas most closely resembles an ideal gas. Each gas will have a different Boyle temperature.

The virial equation is an empirical equation of state. It tells us only what the behavior of a gas is at a certain temperature, but gives us no insight into why this behavior is observed. It would be useful to find a theoretical equation of state which is valid for real gases, and which yields insights into both the nature of gases in general and the nature of the specific gases under study. Let’s try to do this by modifying the ideal gas law to account for molecular interactions.

As we mentioned in our discussion of the pressure dependence of Z, there are two broad types of interactions, attractive and repulsive. The simplest model for the repulsive interaction is the **hard sphere model**. A hard sphere is a particle with no attractive force, and a repulsive force

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that is zero outside of the radius of the sphere, and infinite at the radius of the sphere (think of a billiard ball as a model of this). If a gas of hard spheres is compressed, it



takes up a volume proportional to its mole number. Therefore a gas of hard spheres has less free volume for the motions of its component particles. This suggests that we replace the molar

volume in the ideal gas law with the term $V - b$, where b is proportional to the volume taken up by a mole of gas particles.

Now let's add attractive forces, and consider their effect on pressure. The pressure a gas exerts depends both on the frequency of collisions in a gas and on the force of these collisions.

Let's consider the effect of density, $1/V$, on both of these factors. We know that over a wide range of distances attractive forces get stronger as particles get closer, which is the same as saying that their density increases. The effect of these attractive forces is to decrease the pressure of the gas,

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since the attractive forces decrease both the frequency and the force of collisions with the wall of the container. The correction term is therefore negative. If we want to figure out the actual dependence on the density, we should once again turn to a potential energy function. It turns out that for neutral molecules, the potential energy of attraction is proportional

to $1/r^6$, where r is the distance between molecules. Notice that $\square 1/V\square^2$ also has dimensions of $1/r^6$, which suggests that the attractive portion will be proportional to the density squared and will have the form $-a/V_m^2$, where a is a proportionality constant. Taken together, the correction terms yield the Van der Waals equation,

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

The constants b and a are different for each gas (and must be determined for each gas. Thus the van der Waals equation, while based on theoretical arguments, is more properly termed a semiempirical equation). The equation matches experiment over a wider range of p, V_m and T than the ideal gas law, a partial vindication of its theoretical insights. However, isotherms of the equation yield wavy lines called van der Waals loops at pressures and volumes where condensation occurs. While this may not seem to be very realistic, remember that the ideal gas law has no condensation behavior at all, so the van der Waals equation is a serious step forward. It is important to note that the van der Waals equation is not the only theoretical equation of state that has been proposed for real gases. Two others are the Berthelot and Dieterici equations of state. The Berthelot equation of state is

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$$p = \frac{RT}{V - b} - \frac{a}{TV^2}$$

while the Dieterici equation is

$$p = \frac{RTe^{-a/RTV}}{V - b}.$$

Note that the qualitative meaning of the parameters a and b are the same for these two equations as in the van der Waals equation. Of the three equations the Dieterici equation performs the best, but still tends to give good results only for gases with low polarity.

I'd like to take a bit of time here to cover some math that we'll need in the next chapters. We'll begin by covering the basics of partial differentiation. Partial derivatives are tools you use to determine slopes and rates of change of observables that depend on more than one variable. Essentially all they amount to is taking a derivative of a multivariate function one variable at a time. Suppose you have a function f(x, y) which depends on two variables, like

$$f = x^2 + 2xy^2 + y^2.$$

Since the function is a function of two variables we have two different first derivatives, with respect to the independent variables x and y, which are symbolized by $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$. These

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are read as the derivative of f with respect to x at constant y and the derivative of f with respect to y at constant x. The descriptions actually tell us exactly how to take partial derivatives. We merely treat all variables except the one we are interested in as constants, and then take the derivative. So to take $\frac{\partial f}{\partial x}$, we treat all the y's in our function as constants and take the derivative with respect to x as we normally would. Let's take the derivative of our function with respect to x term by term. [Ask for each term] This yields $\frac{\partial f}{\partial x} = 2x+2y$. Now let's take the derivative with respect to y. [Ask for terms] This yields $\frac{\partial f}{\partial y} = 4xy+2y$. So once again, to take partials you merely treat all variables except the one you are differentiating as constants.

Examples - 1) $w = e^{x^2 y^3 z}$. What are $\frac{\partial^3 w}{\partial x^2 \partial y}$, $\frac{\partial^3 w}{\partial y^2 \partial z}$, and $\frac{\partial^3 w}{\partial z^2 \partial x}$?

2) Let $p(V_m, T) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$. What is $\left(\frac{\partial p}{\partial T}\right)_{V_m}$? [$R/(V_m-b)$] What is $\left(\frac{\partial p}{\partial V_m}\right)_T$?

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$[-RT/(V_m - b)^2 + 2a/V_m^3]$.

What if we wanted to calculate $(\partial T/\partial p)_{Vm}$? One way would be to rewrite our van der Waals equations so that T is a function of p, but that would be tedious. Fortunately there is a rule of partial derivatives called the **inverter**, which says that $\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$. This means that

$(\partial T/\partial p)_{Vm} = 1/(\partial p/\partial T)_{Vm} = (V_m - b)/R$.

Another new thing about partial derivatives is that we can take four different second derivatives. Two of them, $\partial^2 z/\partial x^2$ and $\partial^2 z/\partial y^2$, are similar to second derivatives you've seen before. However, we now have two mixed partial second derivatives, $\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)$ *and* $\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)$. The meaning of the first is that you first take the partial with respect to y, and then second with respect to x, while in the second you take the partial with respect to x first and the partial with respect to y second. A result about these mixed partial derivatives that we will use frequently is

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$$\frac{\partial^2 z}{\partial x\,\partial y} = \frac{\partial^2 z}{\partial y\,\partial x}$$

that the two mixed partials are equal, i.e., $\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)$. We can illustrate this for the van

$$\left(\frac{\partial^2 p}{\partial T\,\partial V_m}\right) \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V_m\,\partial T}\right)$$

der Waals equation, by evaluating the partials $\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V_m}\right)$ and $\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)$. We have already taken

$$\left(\frac{\partial p}{\partial V_m}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$$

the two first derivatives, getting $\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)_{V_m} = \frac{R}{V_m - b}$ and $\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)_T = \frac{R}{(V_m - b)^2}$. To take the

$$\left(\frac{\partial^2 p}{\partial T\,\partial V_m}\right) \quad \text{and} \quad \left(\frac{\partial p}{\partial V_m}\right)_T$$

second derivative$\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V_m}\right)$ we take the partial derivative with respect to T of $\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)_T$ getting

$$\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V_m}\right) = \frac{\partial}{\partial T}\left(\frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}\right) = \frac{-R}{(V_m - b)^2}.$$

$$\left(\frac{\partial^2 p}{\partial V_m\,\partial T}\right)$$

Similarly, to take the second derivative $\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)$ we take the partial derivative with

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respect to V_m of $\left(\frac{\partial p}{\partial T}\right)_{V_m}$, getting

$$\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)_{V_m} = \frac{\partial}{\partial V_m}\left(\frac{R}{V_m - b}\right) = -\frac{R}{(V_m - b)^2}.$$

As the rule predicts, the mixed partials are equal.

Another result that is extremely useful is the **chain rule for partial differentiation**. You should all be familiar with the chain rule from your calculus course. It says that if you have a function z = f(y), where y = y(x), then $\frac{dz}{dy}\frac{dy}{dx} = \frac{dz}{dx}$. Notice that the dy's in this expression cancel *dx* to give dz/dx. For partial differentials the chain rule is stated as follows. Suppose you have a function $z = z(y_1, y_2)$ where $y_1 = f_1(x_1, x_2)$ and $y_2 = f_2(x_1, x_2)$. Then

$$\left(\frac{\partial z}{\partial x_1}\right)_{x_2} = \left(\frac{\partial z}{\partial y_1}\right)_{y_2}\left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial z}{\partial y_2}\right)_{y_1}\left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}.$$

Notice that once again, the y terms sort of cancel. For compound functions, this is useful just as the chain rule was, but the main advantage of the chain rule in our course is that it allows us to rewrite one partial derivative in terms of others.

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One of the goals of equilibrium thermodynamics is to be able to predict what will happen, not just for ideal systems but for real systems. As such, we need to develop a series of measurable quantities that are useful in describing a wide range of systems, real and ideal, solid, liquid and gas. Two particularly useful quantities, which are defined in terms of partial

derivatives, are the cubic expansion coefficient, $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and the isothermal

compressibility, $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$. [ASK FOR INTERPRETATION IN WORDS.] These are convenient

because they are easy parameters to measure, describe real, not just ideal, characteristics of materials and are commonly tabulated. Later in the course one of our goals will be to express thermodynamic quantities that we are interested in in terms of these two partials and other quantities that are commonly tabulated.

One last manipulation of partials for today. There is a neat rule called the cyclic rule. Suppose you have a partial, $\left(\frac{\partial x}{\partial y}\right)_z$. Then you can write $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$. Let's use this

$\left(\frac{\partial x}{\partial p}\right)$

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to evaluate the partial derivative $\left(\frac{\partial T}{\partial V}\right)_p$. According to the cyclic rule,

$$\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V = -1.$$ We can rewrite this as

$$\left(\frac{\partial T}{\partial V}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T}$$

From our definition above, $(\partial V/\partial p)_T = -V\kappa$ and $(\partial T/\partial V)_p = 1/(V\alpha)$, so as our final answer we get

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{\alpha}{\kappa V}.$$

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