Concept Development Studies in Chemistry

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C O N N E X I O N S

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Chapter 1

Preface to Concept Development Studies in Chemistry[1]

1.1 Why Concept Development Studies?

The body of knowledge called Science consists primarily of models and concepts, based on observations and deduced from careful reasoning. Viewed in this way, Science is a creative human endeavor. The models, concepts, and theories we use to describe nature are accomplishments equal in creativity to any artistic, musical, or literary work.

Unfortunately, textbooks in Chemistry traditionally present these models and concepts essentially as established facts, stripped of the clever experiments and logical analyses which give them their human essence. As a consequence, students are typically trained to memorize and apply these models, rather than to analyze and understand them. As a result, creative, analytical students are inclined to feel that they cannot "do" Chemistry, that they cannot understand the concepts, or that Chemistry is dull and uninteresting.

This collection of **Concept Development Studies in Chemistry** is presented to redirect the focus of learning. In each concept development study, a major chemical concept is developed and refined by analysis of experimental observations and careful reasoning. Each study begins with the definition of an initial **Foundation** of assumed knowledge, followed by a statement of questions which arise from the Foundation. Analysis of these questions is presented as a series of **observations** and logical deductions, followed by further questions. This detailed process is followed until the conceptual development of a model provides a reasonable answer to the stated questions.

Concept Development Studies in Chemistry is written with two benefits to the reader in mind. First, by analyzing each concept development through critical reasoning, you will gain a much deeper understanding of a significant concept. In addition to knowing how to work with a model, you will have both an understanding of why the model is believable and an appreciation of the essential beauty of the model. Second, the reasoning required to understand these concept development studies will enhance your development of critical, analytical thinking, a skill which is most important to success in Science. As a note, these studies are not intended to be historical developments, although the experiments presented are the ones which led to the concepts discussed. Only a small amount of historical information has been included for perspective.

1.2 How to Study the Concept Development Studies

You should study each concept development study, not by memorization, but by carefully thinking about the experiments and the logical development of the concepts and models. Each study is short, and is meant to be read slowly and meticulously. Each sentence contains substance to be studied and understood. You

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[1] This content is available online at <http://cnx.org/content/m12616/1.5/>.

should, at each step in the analysis, challenge yourself as to whether you can reproduce the reasoning leading to the next conclusion. One good way to do this is to outline the concept development study, making sure you understand how each piece of the argument contributes to the development of a concept or model.

It is very important to understand that scientific models and theories are almost never "proven," unlike mathematical theorems. Rather, they are logically developed and deduced to provide simple explanations of observed phenomenon. As such, you will discover many times in these concept development studies when a conclusion is not logically required by an observation and a line of reasoning. Instead, we may arrive at a model which is the simplest explanation of a set of observations, even if it is not the only one. Scientists most commonly abide by the principle of **Occam's razor**, one statement of which might be that the explanation which requires the least assumptions is the best one.

One very important way to challenge your understanding is to study in a group in which you take turns explaining the development of the model. The ability to explain a concept is a much stronger indicator of your understanding than the ability to solve a problem using the concept. Use the questions at the end of the concept development studies to practice your skill at explaining technical arguments clearly and concisely.

1.3 Acknowledgments

My own thinking in writing Concept Development Studies in Chemistry has been strongly influenced by three books: *The Historical Development of Chemical Concepts*, by Roman Mierzecki; *The History of Chemistry*, by John Hudson; *Chemical Principles*, by Richard Dickerson, Harry Gray, and Gilbert Haight.

I am deeply appreciative of the contributions of Joanna Fair, Karen Aiani Stevens, Kevin Ausman, and Karin Wright in reviewing and criticizing early drafts of the manuscript for this text. I am also indebted to Susan Wiediger, not just for her technical expertise and her knowledge of the educational literature, but also for her commitment to the concept behind this book and this approach to teaching. I appreciate the hard work of Jeffrey Silverman to convert these documents for use in the Connexions Project[2] at Rice University[3] .

Concept Development Studies in Chemistry would not have been written were it not for the encouragement of my wife Paula, who reminded me at the most difficult of times that writing it was the right thing to do. I will be forever grateful.

JSH

> VISION IMPAIRED ACCESS: Thanks to the translation efforts of Rice University's Disability Support Services[4] , this collection is now available in a Braille-printable version. Please click here[5] to download a .zip file containing all the necessary .dxb and image files.

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[2] http://cnx.org

[3] http://www.rice.edu

[4] http://www.dss.rice.edu/

[5] See the file at <http://cnx.org/content/m12616/latest/ConceptDevStudiesBraille.zip>

Chapter 2

The Atomic Molecular Theory[1]

2.1 Foundation

There are over 18 million known substances in our world. We will begin by assuming that all materials are made from **elements**, materials which cannot be decomposed into simpler substances. We will assume that we have identified all of these elements, and that there a very small number of them. All other pure substances, which we call **compounds**, are made up from these elements and can be decomposed into these elements. For example, metallic iron and gaseous oxygen are both elements and cannot be reduced into simpler substances, but iron rust, or ferrous oxide, is a compound which can be reduced to elemental iron and oxygen. The elements are not transmutable: one element cannot be converted into another. Finally, we will assume that we have demonstrated the **Law of Conservation of Mass**.

Law 2.1: Law of Conservation of Mass
The total mass of all products of a chemical reaction is equal to the total mass of all reactants of that reaction.

These statements are summaries of many observations, which required a tremendous amount of experimentation to achieve and even more creative thinking to systematize as we have written them here. By making these assumptions, we can proceed directly with the experiments which led to the development of the atomic-molecular theory.

2.2 Goals

The statements above, though correct, are actually more vague than they might first appear. For example, exactly what do we mean when we say that all materials are made from elements? Why is it that the elements cannot be decomposed? What does it mean to combine elements into a compound? We want to understand more about the nature of elements and compounds so we can describe the processes by which elements combine to form compounds, by which compounds are decomposed into elements, and by which compounds are converted from one to another during chemical reactions.

One possibility for answering these questions is to assume that a compound is formed when indestructible elements are simply mixed together, as for example, if we imagine stirring together a mixture of sugar and sand. Neither the sand nor the sugar is decomposed in the process. And the mixture can be decomposed back into the original components. In this case, though, the resultant mixture exhibits the properties of **both** components: for example, the mixture would taste sweet, owing to the sugar component, but gritty, characteristic of the sand component.

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[1] This content is available online at <http://cnx.org/content/m12432/1.6/>.

In contrast, the compound we call iron rust bears little resemblance to elemental iron: iron rust does not exhibit elemental iron's color, density, hardness, magnetism, etc. Since the properties of the elements are not maintained by the compound, then the compound must not be a simple mixture of the elements.

We could, of course, jump directly to the answers to these questions by stating that the elements themselves are comprised of atoms: indivisible, identical particles distinctive of that element. Then a compound is formed by combining the atoms of the composite elements. Certainly, the Law of Conservation of Mass would be easily explained by the existence of immutable atoms of fixed mass.

However, if we do decide to jump to conclusions and assume the existence of atoms without further evidence (as did the leading chemists of the seventeenth and eighteenth centuries), it does not lead us anywhere. What happens to iron when, after prolonged heating in air, it converts to iron rust? Why is it that the resultant combination of iron and air does not maintain the properties of either, as we would expect if the atoms of each are mixed together? An atomic view of nature would not yet provide any understanding of how the air and the iron have interacted or combined to form the new compound, and we can't make any predictions about how much iron will produce how much iron rust. There is no basis for making any statements about the properties of these atoms. We need further observations.

2.3 Observation 1: Mass relationships during chemical reactions

The Law of Conservation of Mass, by itself alone, does not require an atomic view of the elements. Mass could be conserved even if matter were not atomic. The importance of the Law of Conservation of Mass is that it reveals that we can usefully measure the masses of the elements which are contained in a fixed mass of a compound. As an example, we can decompose copper carbonate into its constituent elements, copper, oxygen, and carbon, weighing each and taking the ratios of these masses. The result is that every sample of copper carbonate is 51.5% copper, 38.8% oxygen, and 9.7% carbon. Stated differently, the masses of copper, oxygen, and carbon are in the ratio of 5.3 : 4 : 1, for every measurement of every sample of copper carbonate. Similarly, lead sulfide is 86.7% lead and 13.3% sulfur, so that the mass ratio for lead to sulfur in lead sulfide is always 6.5 : 1. Every sample of copper carbonate and every sample of lead sulfide will produce these elemental proportions, regardless of how much material we decompose or where the material came from. These results are examples of a general principle known as the **Law of Definite Proportions**.

> **Law 2.2:** Law of Definite Proportions
> When two or more elements combine to form a compound, their masses in that compound are in a fixed and definite ratio.

These data help justify an atomic view of matter. We can simply argue that, for example, lead sulfide is formed by taking one lead atom and combining it with one sulfur atom. If this were true, then we also must conclude that the ratio of the mass of a lead **atom** to that of a sulfur **atom** is the same as the 6.5 : 1 lead to sulfur mass ratio we found for the bulk lead sulfide. This atomic explanation looks like the definitive answer to the question of what it means to combine two elements to make a compound, and it should even permit prediction of what quantity of lead sulfide will be produced by a given amount of lead. For example, 6.5g of lead will produce exactly 7.5g of lead sulfide, 50g of lead will produce 57.7g of lead sulfide, etc.

There is a problem, however. We can illustrate with three compounds formed from hydrogen, oxygen, and nitrogen. The three mass proportion measurements are given in the following table (Table 2.1: Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds). First we examine nitric oxide, to find that the mass proportion is 8 : 7 oxygen to nitrogen. If this is one nitrogen atom combined with one oxygen atom, we would expect that the mass of an oxygen atom is 8/7=1.14 times that of a nitrogen atom. Second we examine ammonia, which is a combination of nitrogen and hydrogen with the mass proportion of 7 : 1.5 nitrogen to hydrogen. If this is one nitrogen combined with one hydrogen, we would expect that a nitrogen atom mass is 4.67 times that of a hydrogen atom mass. These two expectations predict a relationship between the mass of an oxygen atom and the mass of a hydrogen atom. If the mass of an oxygen atom is 1.14 times the mass of a nitrogen atom and if the mass of a nitrogen atom is 4.67 times the mass of a hydrogen atom, then we must conclude that an oxygen atom has a mass which is $1.14 \times 4.67 = 5.34$ times that of a hydrogen atom.

But there is a problem with this calculation. The third line of the following table (Table 2.1: Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds) shows that the compound formed from hydrogen and oxygen is water, which is found to have mass proportion 8:1 oxygen to hydrogen. Our expectation should then be that an oxygen atom mass is 8.0 times a hydrogen atom mass. Thus the three measurements in the following table (Table 2.1: Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds) appear to lead to contradictory expectations of atomic mass ratios. How are we to reconcile these results?

Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds

Compound	**Total Mass**	**Mass of Hydrogen**	**Mass of Nitrogen**	**Mass of Oxygen**	**"Expected" Relative Atomic Mass of Hydrogen**	**"Expected" Relative Atomic Mass of Nitrogen**	**"Expected" Relative Atomic Mass of Oxygen**
Nitric Oxide	15.0 g	-	7.0 g	8.0 g	-	7.0	8.0
Ammonia	8.5 g	1.5 g	7.0 g	-	1.5	7.0	-
Water	9.0 g	1.0 g	-	8.0 g	1.0	-	8.0

Table 2.1

One possibility is that we were mistaken in assuming that there are atoms of the elements which combine to form the different compounds. If so, then we would not be surprised to see variations in relative masses of materials which combine.

Another possibility is that we have erred in our reasoning. Looking back, we see that we have to assume how many atoms of each type are contained in each compound to find the relative masses of the atoms. In each of the above examples, we assumed the ratio of atoms to be 1:1 in each compound. If there are atoms of the elements, then this assumption must be wrong, since it gives relative atomic masses which differ from compound to compound. How could we find the correct atomic ratios? It would help if we knew the ratio of the atomic masses: for example, if we knew that the oxygen to hydrogen mass ratio were 8:1, then we could conclude that the atomic ratio in water would be 1 oxygen and 1 hydrogen. Our reasoning seems to circular: to know the atomic masses, we must know the **formula** of the compound (the numbers of atoms of each type), but to know the formula we must know the masses.

Which of these possibilities is correct? Without further observations, we cannot say for certain whether matter is composed of atoms or not.

2.4 Observation 2: Multiple Mass Ratios

Significant insight into the above problem is found by studying different compounds formed from the same elements. For example, there are actually three oxides of nitrogen, that is, compounds composed only of nitrogen and oxygen. For now, we will call them oxide A, oxide B, and oxide C. Oxide A has oxygen to nitrogen mass ratio $2.28 : 1$. Oxide B has oxygen to nitrogen mass ratio $1.14 : 1$, and oxide C has oxygen to nitrogen mass ratio $0.57 : 1$.

The fact that there are three mass ratios might seem to contradict the Law of Definite Proportions, which on the surface seems to say that there should be just one ratio. However, each mass combination gives rise to a completely unique chemical compound with very different chemical properties. For example, oxide A is very toxic, whereas oxide C is used as an anesthesia. It is also true that the mass ratio is not arbitrary or continuously variable: we cannot pick just any combination of masses in combining oxygen and nitrogen, rather we must obey one of only three. So there is no contradiction: we simply need to be careful with the

Law of Definite Proportions to say **that each unique compound** has a definite mass ratio of combining elements.

These new mass ratio numbers are highly suggestive in the following way. Notice that, in each case, we took the ratio of oxygen mass to a nitrogen mass of 1, and that the resultant ratios have a very simple relationship:

$$\begin{aligned} 2.28 : 1.14 : 0.57 &= 2 : 1 : 0.5 \\ &= 4 : 2 : 1 \end{aligned} \tag{2.1}$$

The masses of oxygen appearing in these compounds are in simple whole number ratios when we take a fixed amount of nitrogen. The appearance of these simple whole numbers is very significant. These integers imply that the compounds contain a multiple of a fixed unit of mass of oxygen. The simplest explanation for this fixed unit of mass is that oxygen is **particulate**. We call the fixed unit of mass an **atom**. We now assume that the compounds have been formed from combinations of atoms with fixed masses, and that different compounds have differing numbers of atoms. The mass ratios make it clear that oxide B contains twice as many oxygen atoms (per nitrogen atom) as does oxide C and half as many oxygen atoms (per nitrogen atom) as does oxide A. The simple mass ratios must be the result of the simple ratios in which atoms combine into molecules. If, for example, oxide C has the molecular formula NO, then oxide B has the formula NO_2, and oxide A has the formula NO_4. There are other possibilities: if oxide B has molecular formula NO, then oxide A has formula NO_2, and oxide C has formula N_2O. Or if oxide A has formula NO, then oxide B has formula N_2O and oxide C has formula N_4O. These three possibilities are listed in the following table (Table 2.2: Possible Molecular Formulae for Nitrogen Oxides).

Possible Molecular Formulae for Nitrogen Oxides

Assuming that:	**Oxide C is** NO	**Oxide B is** NO	**Oxide A is** NO
Oxide A is	NO_4	NO_2	NO
Oxide B is	NO_2	NO	N_2O
Oxide C is	NO	N_2O	N_4O

Table 2.2

We don't have a way (from these data) to know which of these sets of molecular formulae are right. But we can assert that either one of them or one analogous to them is right.

Similar data are found for any set of compounds formed from common elements. For example, there are two oxides of carbon, one with oxygen to carbon mass ratio 1.33:1 and the other with mass ratio 2.66:1. The second oxide must have twice as many oxygen atoms, per carbon atom, as does the first. The general statement of this observation is the **Law of Multiple Proportions**.

Law 2.3: Law of Multiple Proportions

When two elements combine to form more than one compound, the mass of element A which combines in the first compound with a given amount of element B has a simple whole number ratio with the mass of element A which combines in the second compound with the same given mass of element B.

This sounds confusing, but an example clarifies this statement. Consider the carbon oxides, and let carbon be element B and oxygen be element A. Take a fixed given mass of carbon (element B), say 1 gram. The mass of oxygen which combines with 1 gram of carbon to form the first oxide is 1.33 grams. The mass of oxygen which combines with 1 gram of carbon to form the second oxide is 2.66. These masses are in ratio $2.66 : 1.33 = 2 : 1$, a simple whole number ratio.

In explaining our observations of the Law of Multiple Proportions for the carbon oxides and the nitrogen oxides, we have concluded that the simple mass ratio arises from the simple ratio of atoms contained in the individual molecules. Thus, we have established the following postulates of the **Atomic Molecular Theory**.

Rule 2.1: Atomic Molecular Theory

- the elements are comprised of identical atoms
- all atoms of a single element have the same characteristic mass
- these number and masses of these atoms do not change during a chemical transformation
- compounds consist of identical molecules formed of atoms combined in simple whole number ratios

2.5 Review and Discussion Questions

Exercise 2.1
Assume that matter does not consist of atoms. Show by example how this assumption leads to hypothetical predictions which contradict the Law of Multiple Proportions. Do these hypothetical examples contradict the Law of Definite Proportions? Are both observations required for confirmation of the atomic theory?

Exercise 2.2
Two compounds, A and B, are formed entirely from hydrogen and carbon. Compound A is 80.0% carbon by mass, and 20.0% hydrogen, whereas Compound B is 83.3% carbon by mass and 16.7% hydrogen. Demonstrate that these two compounds obey the Law of Multiple Proportions. Explain why these results strongly indicate that the elements carbon and hydrogen are composed of atoms.

Exercise 2.3
In many chemical reactions, mass does not appear to be a conserved quantity. For example, when a tin can rusts, the resultant rusty tin can has a greater mass than before rusting. When a candle burns, the remaining candle has invariably less mass than before it was burned. Provide an explanation of these observations, and describe an experiment which would demonstrate that mass is actually conserved in these chemical reactions.

Exercise 2.4
The following question was posed on an exam:

> *An unknown non-metal element (Q) forms two gaseous fluorides of unknown molecular formula. A 3.2 g sample of Q reacts with fluorine to form 10.8 g of the unknown fluoride A. A 6.4 g sample of Q reacts with fluorine to form 29.2 g of unknown fluoride B. Using these data only, demonstrate by calculation and explanation that these unknown compounds obey the Law of Multiple Proportions.*

A student responded with the following answer:

> *The Law of Multiple Proportions states that when two elements form two or more compounds, the ratios of the masses of the elements between the two compounds are in a simple whole number ratio. So, looking at the data above, we see that the ratio of the mass of element Q in compound A to the mass of element Q in compound B is* $3.2 : 6.4 = 1 : 2$, *which is a simple whole number ratio. This demonstrates that these compounds obey the Law of Multiple Proportions.*

Assess the accuracy of the students answer. In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

Chapter 3

Relative Atomic Masses and Empirical Formulae[1]

3.1 Foundation

We begin by assuming the central postulates of the **Atomic-Molecular Theory**. These are: the elements are comprised of identical atoms; all atoms of a single element have the same characteristic mass; the number and masses of these atoms do not change during a chemical transformation; compounds consist of identical molecules formed of atoms combined in simple whole number ratios. We also assume a knowledge of the observed natural laws on which this theory is based: the **Law of Conservation of Mass**, the **Law of Definite Proportions**, and the **Law of Multiple Proportions**.

3.2 Goals

We have concluded that atoms combine in simple ratios to form molecules. However, we don't know what those ratios are. In other words, we have not yet determined any molecular formulae. In the second table of Concept Development Study #1 (Table 2.2: Possible Molecular Formulae for Nitrogen Oxides), we found that the mass ratios for nitrogen oxide compounds were consistent with many different molecular formulae. A glance back at the nitrogen oxide data shows that the oxide B could be NO, NO_2, N_2O, or any other simple ratio.

Each of these formulae correspond to different possible relative atomic weights for nitrogen and oxygen. Since oxide B has oxygen to nitrogen ratio 1.14 : 1, then the relative masses of oxygen to nitrogen could be 1.14:1 or 2.28:1 or 0.57:1 or many other simple possibilities. If we knew the relative masses of oxygen and nitrogen atoms, we could determine the molecular formula of oxide B. On the other hand, if we knew the molecular formula of oxide B, we could determine the relative masses of oxygen and nitrogen atoms. If we solve one problem, we solve both. Our problem then is that we need a simple way to "count" atoms, at least in relative numbers.

3.3 Observation 1: Volume Relationships in Chemical Reactions

Although mass is conserved, most chemical and physical properties are not conserved during a reaction. Volume is one of those properties which is not conserved, particularly when the reaction involves gases as reactants or products. For example, hydrogen and oxygen react explosively to form water vapor. If we take 1 liter of oxygen gas and 2 liters of hydrogen gas, by careful analysis we could find that the reaction of these

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[1] This content is available online at <http://cnx.org/content/m12431/1.7/>.

two volumes is complete, with no left over hydrogen and oxygen, and that 2 liters of water vapor are formed. Note that the total volume is not conserved: 3 liters of oxygen and hydrogen become 2 liters of water vapor. (All of the volumes are measured at the same temperature and pressure.)

More notable is the fact that the ratios of the volumes involved are simple whole number ratios: 1 liter of oxygen : 2 liters of hydrogen : 2 liters of water. This result proves to be general for reactions involving gases. For example, 1 liter of nitrogen gas reacts with 3 liters of hydrogen gas to form 2 liters of ammonia gas. 1 liter of hydrogen gas combines with 1 liter of chlorine gas to form 2 liters of hydrogen chloride gas. These observations can be generalized into the **Law of Combining Volumes**.

Law 3.1: Law of Combining Volumes
When gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios.

These simple integer ratios are striking, particularly when viewed in the light of our conclusions from the Law of Multiple Proportions. Atoms combine in simple whole number ratios, and evidently, volumes of gases also combine in simple whole number ratios. Why would this be? One simple explanation of this similarity would be that the volume ratio and the ratio of atoms and molecules in the reaction are the same. In the case of the hydrogen and oxygen, this would say that the ratio of volumes (1 liter of oxygen : 2 liters of hydrogen : 2 liters of water) is the same as the ratio of atoms and molecules (1 atom of oxygen: 2 atoms of hydrogen: 2 molecules of water). For this to be true, equal volumes of gas would have to contain equal numbers of gas particles (atoms or molecules), independent of the type of gas. If true, this means that the volume of a gas must be a direct measure of the number of particles (atoms or molecules) in the gas. This would allow us to "count" the number of gas particles and determine molecular formulae.

There seem to be big problems with this conclusion, however. Look back at the data for forming hydrogen chloride: 1 liter of hydrogen plus 1 liter of chlorine yields 2 liters of hydrogen chloride. If our thinking is true, then this is equivalent to saying that 1 hydrogen atom plus 1 chlorine atom makes 2 hydrogen chloride molecules. But how could that be possible? How could we make 2 identical molecules from a single chlorine atom and a single hydrogen atom? This would require us to divide each hydrogen and chlorine atom, violating the postulates of the atomic-molecular theory.

Another problem appears when we weigh the gases: 1 liter of oxygen gas weighs more than 1 liter of water vapor. If we assume that these volumes contain equal numbers of particles, then we must conclude that 1 oxygen particle weighs more than 1 water particle. But how could that be possible? It would seem that a water molecule, which contains at least one oxygen atom, should weigh more than a single oxygen particle.

These are serious objections to the idea that equal volumes of gas contain equal numbers of particles. Our postulate appears to have contradicted common sense and experimental observation. However, the simple ratios of the Law of Combining Volumes are also equally compelling. Why should volumes react in simple whole number ratios if they do not represent equal numbers of particles? Consider the opposite viewpoint: if equal volumes of gas do not contain equal numbers of particles, then equal numbers of particles must be contained in unequal volumes not related by integers. Now when we combine particles in simple whole number ratios to form molecules, the volumes of gases required would produce decidedly non-whole number ratios. The Law of Combining Volumes should not be contradicted lightly.

There is only one logical way out. We will accept our deduction from the Law of Combining Volumes that **equal volumes of gas contain equal numbers of particles**, a conclusion known as **Avogadro's Hypothesis**. How do we account for the fact that 1 liter of hydrogen plus 1 liter of chlorine yields 2 liters of hydrogen chloride? There is only one way for a single hydrogen particle to produce 2 identical hydrogen chloride molecules: each hydrogen particle must contain more than one atom. In fact, each hydrogen particle (or molecule) must contain an even number of hydrogen atoms. Similarly, a chlorine molecule must contain an even number of chlorine atoms.

More explicitly, we observe that

$$\text{1 liter of hydrogen} + \text{1 liter of chlorine} \rightarrow \text{2 liters of hydrogen chloride} \tag{3.1}$$

Assuming that each liter volume contains an equal number of particles, then we can interpret this observation as

$$1\, H_2 \,\text{molecule} + 1\, Cl_2 \,\text{molecule} \rightarrow 2\, HCl \,\text{molecules} \tag{3.2}$$

(Alternatively, there could be any fixed even number of atoms in each hydrogen molecule and in each chlorine molecule. We will assume the simplest possibility and see if that produces any contradictions.)

This is a wonderful result, for it correctly accounts for the Law of Combining Volumes and eliminates our concerns about creating new atoms. Most importantly, we now know the molecular formula of hydrogen chloride. We have, in effect, found a way of "counting" the atoms in the reaction by measuring the volume of gases which react.

This method works to tell us the molecular formula of many compounds. For example,

$$2 \text{ liters of hydrogen} + 1 \text{ liter of oxygen} \rightarrow 2 \text{ liters of water} \tag{3.3}$$

This requires that oxygen particles contain an even number of oxygen atoms. Now we can interpret this equation as saying that

$$2\, H_2 \,\text{molecules} + 1\, O_2 \,\text{molecule} \rightarrow 2\, H_2O \,\text{molecules} \tag{3.4}$$

Now that we know the molecular formula of water, we can draw a definite conclusion about the relative masses of the hydrogen and oxygen atoms. Recall from the Table (Table 2.1: Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds) that the mass ratio in water is 8:1 oxygen to hydrogen. Since there are two hydrogen atoms for every oxygen atom in water, then the mass ratio requires that a single oxygen atom weigh 16 times the mass of a hydrogen atom.

To determine a mass scale for atoms, we simply need to choose a standard. For example, for our purposes here, we will say that a hydrogen atom has a mass of 1 on the atomic mass scale. Then an oxygen atom has a mass of 16 on this scale.

Our conclusions account for the apparent problems with the masses of reacting gases, specifically, that oxygen gas weighs more than water vapor. This seemed to be nonsensical: given that water contains oxygen, it would seem that water should weigh more than oxygen. However, this is now simply understood: a water molecule, containing only a single oxygen atom, has a mass of 18, whereas an oxygen molecule, containing two oxygen atoms, has a mass of 32.

3.4 Determination of Atomic Weights for Gaseous Elements

Now that we can count atoms and molecules to determine molecular formulae, we need to determine relative atomic weights for all atoms. We can then use these to determine molecular formulae for any compound from the mass ratios of the elements in the compound.

We begin by examining data on reactions involving the Law of Combining Volumes. Going back to the nitrogen oxide data given here (Table 2.2: Possible Molecular Formulae for Nitrogen Oxides), we recall that there are three compounds formed from nitrogen and oxygen. Now we measure the volumes which combine in forming each. We find that 2 liters of oxide B can be decomposed into 1 liter of nitrogen and 1 liter of oxygen. From the reasoning above, then a nitrogen particle must contain an even number of nitrogen atoms. We assume for now that nitrogen is N_2. We have already concluded that oxygen is O_2. Therefore, the molecular formula for oxide B is NO, and we call it nitric oxide. Since we have already determined that the oxygen to nitrogen mass ratio is $1.14 : 1$, then, if we assign oxygen a mass of 16, as above, nitrogen has a mass of 14. (That is $\frac{16}{1.14} = 14$.) 2 liters of oxide A is formed from 2 liters of oxygen and 1 liter of nitrogen. Therefore, oxide A is NO_2, which we call nitrogen dioxide. Note that we predict an oxygen to nitrogen mass ratio of $\frac{32}{14} = 2.28 : 1$, in agreement with the data. Oxide C is N_2O, called nitrous oxide, and predicted to have a mass ratio of $\frac{16}{28} = 0.57 : 1$, again in agreement with the data. We have now resolved the ambiguity in the molecular formulae.

What if nitrogen were actually N_4? Then the first oxide would be N_2O, the second would be N_2O_2, and the third would be N_4O. Furthermore, the mass of a nitrogen atom would be 7. Why don't we assume this? Simply because in doing so, we will always find that the minimum relative mass of nitrogen in any molecule is 14. Although this might be two nitrogen atoms, there is no reason to believe that it is. Therefore, a single nitrogen atom weighs 14, and nitrogen gas particles are N_2.

3.5 Determination of Atomic Weights for Non-Gaseous Elements

We can proceed with this type of measurement, deduction, and prediction for any compound which is a gas and which is made up of elements which are gases. But this will not help us with the atomic masses of non-gaseous elements, nor will it permit us to determine the molecular formulae for compounds which contain these elements.

Consider carbon, an important example. There are two oxides of carbon. Oxide A has oxygen to carbon mass ratio 1.33 : 1 and oxide B has mass ratio 2.66 : 1. Measurement of reacting volumes shows that we find that 1 liter of oxide A is produced from 0.5 liters of oxygen. Hence, each molecule of oxide A contains only half as many oxygen atoms as does an oxygen molecule. Oxide A thus contains one oxygen atom. But how many carbon atoms does it contain? We can't determine this yet because the elemental carbon is solid, not gas. This means that we also cannot determine what the mass of a carbon atom is.

But we can try a different approach: we weigh 1 liter of oxide A and 1 liter of oxygen gas. The result we find is that oxide A weighs 0.875 times per liter as much as oxygen gas. Since we have assumed that a fixed volume of gas contains a fixed number of particles, then 1 liter of oxide A contains just as many particles as 1 liter of oxygen gas. Therefore, each **particle** of oxide A weighs 0.875 times as much as a particle of oxygen gas (that is, an O_2 molecule). Since an O_2 molecule weighs 32 on our atomic mass scale, then a particle of oxide A weighs $0.875 \times 32 = 28$. Now we know the molecular weight of oxide A.

Furthermore, we have already determined from the combining volumes that oxide A contains a single oxygen atom, of mass 16. Therefore, the mass of carbon in oxide A is 12. However, at this point, we do not know whether this is one carbon atom of mass 12, two atoms of mass 6, eight atoms of mass 1.5, or one of many other possibilities.

To make further progress, we make additional measurements on other carbon containing gas compounds. 1 liter of oxide B of carbon is formed from 1 liter of oxygen. Therefore, each oxide B molecule contains two oxygen atoms. 1 liter of oxide B weighs 1.375 times as much as 1 liter of oxygen. Therefore, one oxide B molecule has mass $1.375 \times 32 = 44$. Since there are two oxygen atoms in a molecule of oxide B, the mass of oxygen in oxide B is 32. Therefore, the mass of carbon in oxide B is 12, the same as in oxide A.

We can repeat this process for many such gaseous compounds containing carbon atoms. In each case, we find that the mass of carbon in each molecule is either 12 or a multiple of 12. We never find, for examples, 6 or 18, which would be possible if each carbon atom had mass 6. The simplest conclusion is that a carbon atom has mass 12. Once we know the atomic mass of carbon, we can conclude that the molecular formula of oxide A is CO, and that of oxide B is CO_2.

Therefore, the atomic masses of non-gaseous elements can be determined by mass and volume measurements on gaseous compounds containing these elements. This procedure is fairly general, and most atomic masses can be determined in this way.

3.6 Moles, Molecular Formulae and Stoichiometric Calculations

We began with a circular dilemma: we could determine molecular formulae provided that we knew atomic masses, but that we could only determine atomic masses from a knowledge of molecular formulae. Since we now have a method for determining all atomic masses, we have resolved this dilemma and we can determine the molecular formula for any compound for which we have percent composition by mass.

As a simple example, we consider a compound which is found to be 40.0% carbon, 53.3% oxygen, and 6.7% hydrogen by mass. Recall from the Law of Definite Proportions that these mass ratios are independent of the sample, so we can take any convenient sample to do our analysis. Assuming that we have 100.0g of the compound, we must have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. If we could count or otherwise determine the number of atoms of each element represented by these masses, we would have the molecular formula. However, this would not only be extremely difficult to do but also unnecessary.

From our determination of atomic masses, we can note that 1 atom of carbon has a mass which is 12.0 times the mass of a hydrogen atom. Therefore, the mass of N atoms of carbon is also 12.0 times the mass of N atoms of hydrogen atoms, no matter what N is. If we consider this carefully, we discover that 12.0g of carbon contains exactly the same number of atoms as does 1.0g of hydrogen. Similarly, we note that 1 atom of oxygen has a mass which is $\frac{16.0}{12.0}$ times the mass of a carbon atom. Therefore, the mass of N atoms of oxygen is $\frac{16.0}{12.0}$ times the mass of N atoms of carbon. Again, we can conclude that 16.0g of oxygen contains exactly the same number of atoms as 12.0g of carbon, which in turn is the same number of atoms as 1.0g of hydrogen. Without knowing (or necessarily even caring) what the number is, we can say that it is the same number for all three elements.

For convenience, then, we **define** the number of atoms in 12.0g of carbon to be 1 **mole** of atoms. Note that 1 mole is a specific number of particles, just like 1 dozen is a specific number, independent of what objects we are counting. The advantage to defining the mole in this way is that it is easy to determine the number of moles of a substance we have, and knowing the number of moles is equivalent to counting the number of atoms (or molecules) in a sample. For example, 24.0g of carbon contains 2.0 moles of atoms, 30.0g of carbon contains 2.5 moles of atoms, and in general, x grams of carbon contains $\frac{x}{12.0}$ moles of atoms. Also, we recall that 16.0g of oxygen contains exactly as many atoms as does 12.0g of carbon, and therefore 16.0g of oxygen contains exactly 1.0 mole of oxygen atoms. Thus, 32.0g of oxygen contains 2.0 moles of oxygen atoms, 40.0g of oxygen contains 2.5 moles, and x grams of oxygen contains $\frac{x}{16.0}$ moles of oxygen atoms. Even more generally, then, if we have m grams of an element whose atomic mass is M, the number of moles of atoms, n, is

$$n = \frac{m}{M} \tag{3.5}$$

Now we can determine the relative numbers of atoms of carbon, oxygen, and hydrogen in our unknown compound above. In a 100.0g sample, we have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. The number of moles of atoms in each element is thus

$$\begin{aligned} n_C &= \frac{40.0g}{12.0\frac{g}{\text{mol}}} \\ &= 3.33\text{moles} \end{aligned} \tag{3.6}$$

$$\begin{aligned} n_O &= \frac{53.3g}{16.0\frac{g}{\text{mol}}} \\ &= 3.33\text{moles} \end{aligned} \tag{3.7}$$

$$\begin{aligned} n_H &= \frac{6.7g}{1.0\frac{g}{\text{mol}}} \\ &= 6.67\text{moles} \end{aligned} \tag{3.8}$$

We note that the numbers of moles of atoms of the elements are in the simple ratio $n_C : n_O : n_H = 1 : 1 : 2$. Since the number of particles in 1 mole is the same for all elements, then it must also be true that the number of atoms of the elements are in the simple ratio $1 : 1 : 2$. Therefore, the molecular formula of the compound must be COH_2.

Or is it? On further reflection, we must realize that the simple ratio $1 : 1 : 2$ need not represent the exact numbers of atoms of each type in a molecule of the compound, since it is indeed only a ratio. Thus the molecular formula could just as easily be $C_2O_2H_4$ or $C_3O_3H_6$. Since the formula COH_2 is based on empirical mass ratio data, we refer to this as the **empirical formula** of the compound. To determine the **molecular formula**, we need to determine the relative mass of a molecule of the compound, i.e. the molecular mass. One way to do so is based on the Law of Combining Volumes, Avogadro's Hypothesis, and the **Ideal Gas**

Law. To illustrate, however, if we were to find that the relative mass of one molecule of the compound is 60.0, we could conclude that the molecular formula is $C_2O_2H_4$.

3.7 Review and Discussion Questions

Exercise 3.1
State the Law of Combining Volumes and provide an example of your own construction which demonstrates this law.

Exercise 3.2
Explain how the Law of Combining Volumes, combined with the Atomic-Molecular Theory, leads directly to Avogadro's Hypothesis that equal volumes of gas at equal temperatures and pressure contain equal numbers of particles.

Exercise 3.3
Use Avogadro's Hypothesis to demonstrate that oxygen gas molecules cannot be monatomic.

Exercise 3.4
The density of water vapor at room temperature and atmospheric pressure is $0.737\frac{g}{L}$. Compound A is 80.0% carbon by mass, and 20.0% hydrogen. Compound B is 83.3% carbon by mass and 16.7% hydrogen. The density of gaseous Compound A is $1.227\frac{g}{L}$, and the density of Compound B is $2.948\frac{g}{L}$. Show how these data can be used to determine the molar masses of Compounds A and B, assuming that water has molecular mass 18.

Exercise 3.5
From the results above (Exercise 3.4), determine the mass of carbon in a molecule of Compound A and in a molecule of Compound B. Explain how these results indicate that a carbon atom has atomic mass 12.

Exercise 3.6
Explain the utility of calculating the number of moles in a sample of a substance.

Exercise 3.7
Explain how we can conclude that 28g of nitrogen gas (N_2) contains exactly as many molecules as 32g of oxygen gas (O_2), even though we cannot possibly count this number.

Chapter 4

The Structure of an Atom[1]

4.1 Foundation

We begin as a starting point with the atomic molecular theory. We thus assume that most of the common elements have been identified, and that each element is characterized as consisting of identical, indestructible atoms. We also assume that the atomic weights of the elements are all known, and that, as a consequence, it is possible via mass composition measurements to determine the molecular formula for any compound of interest. In addition, we will assume that it has been shown by electrochemical experiments that atoms contain equal numbers of positively and negatively charged particles, called protons and electrons respectively. Finally, we assume an understanding of the Periodic Table. In particular, we assume that the elements can be grouped according to their common chemical and physical properties, and that these chemical and physical properties are periodic functions of the atomic number.

4.2 Goals

The atomic molecular theory is extremely useful in explaining what it means to form a compound from its component elements. That is, a compound consists of identical molecules, each comprised of the atoms of the component elements in a simple whole number ratio. However, our knowledge of these atoms is very limited. The only property we know at this point is the relative mass of each atom. Consequently, we cannot answer a wide range of new questions. We need a model which accounts for the periodicity of chemical and physical properties as expressed in the Periodic Table. Why are elements which are very dissimilar in atomic mass nevertheless very similar in properties? Why do these common properties recur periodically?

We would like to understand what determines the number of atoms of each type which combine to form stable compounds. Why are some combinations found and other combinations not observed? Why do some elements with very dissimilar atomic masses (for example, iodine and chlorine) form very similar chemical compounds? Why do other elements with very similar atomic masses (for example, oxygen and nitrogen) form very dissimilar compounds? In general, what forces hold atoms together in forming a molecule?

Answering these questions requires knowledge of the structure of the atom, including how the structures of atoms of different elements are different. Our model should tell us how these structural differences result in the different bonding properties of the different atoms.

4.3 Observation 1: Scattering of α particles by atoms

We have assumed that atoms contain positive and negative charges and the number of these charges is equal in any given atom. However, we do not know what that number is, nor do we know how those charges are

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[1] This content is available online at <http://cnx.org/content/m12433/1.2/>.

arranged inside the atom. To determine the location of the charges in the atom, we perform a "scattering" experiment. The idea is straightforward: since we cannot "see" the atomic structure, then we instead "throw" things at the atom and watch the way in which these objects are deflected by the atom. Working backwards, we can then deduce what the structure of the atom must be.

The atoms we choose to shoot at are gold, in the form of a very thin gold foil of thickness about 10^{-4}cm. The objects we "throw" are actually α particles, which are positively charged and fairly massive, emitted by radioactive polonium nuclei. The α particles are directed in a very precise narrow line perpendicular to and in the direction of the gold foil. We then look for α particles at various angles about the gold foil, looking both for particles which have been deflected as they pass through the foil or which have been reflected as they bounce off of the foil. The scattering experiment is illustrated here (Figure 4.1: α particle Scattering from Gold Foil).

α particle Scattering from Gold Foil

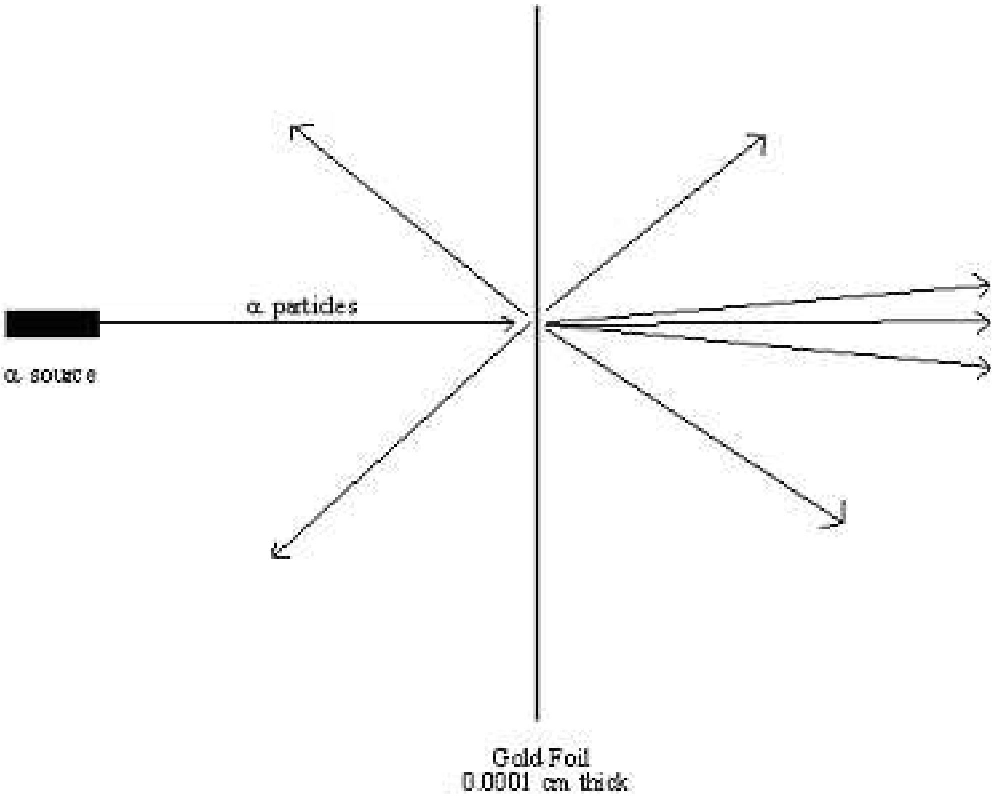

Figure 4.1

The result of the experiment is initially counter-intuitive. Most of the α particles pass through the gold foil undeflected, as if there had been nothing in their path! A smaller number of the particles are deflected sharply as they pass through the foil, and a very small fraction of the α particles are reflected backwards off of the gold foil. How can we simultaneously account for the lack of any deflection for most of the α particles and for the deflection through large angles of a very small number of particles?

First, since the majority of the positively charged α particles pass through the gold foil undeflected, we can conclude that most of the volume of each gold atom is empty space, containing nothing which might deflect an α particle. Second, since a few of the positively charged α particles are deflected very sharply, then they must encounter a positively charged massive particle inside the atom. We therefore conclude that all of the positive charge and most of the mass of an atom is contained in a **nucleus**. The nucleus must be very small, very massive, and positively charged if it is to account for the sharp deflections. A detailed calculation based assuming this model reveals that the nucleus must be about 100,000 times smaller than the size of the atom itself. The electrons, already known to be contained in the atom, must be outside of the nucleus, since the nucleus is positively charged. They must move in the remaining space of the much larger volume of the atom. Moreover, in total, the electrons comprise less than 0.05% of the total mass of an atom.

This model accounts for observation of both undeflected passage most of α particles and sharp deflection of a few. Most α particles pass through the vast empty space of the atom, which is occupied only by electron. Even the occasional encounter with one of the electrons has no effect on an α particle's path, since each α particle is much more massive than an electron. However, the nucleus is both massive and positively charged, but it is also small. The rare encounter of an α particle with the nucleus will result in very large deflections; a head-on collision with a gold atom nucleus will send an α particle directly back to its source.

4.4 Observation 2: X-ray emission

Although we can now conclude that an atom has a nuclear structure, with positive charge concentrated in a very small nucleus and a number of electrons moving about the nucleus in a much larger volume, we do not have any information on how many electrons there are in an atom of any given element or whether this number depends on the type of atom. Does a gold atom have the same number of electrons as a silver atom? All we can conclude from the data given is that the number of positive charges in the nucleus must exactly equal the number of electrons moving outside the nucleus, since each atom is neutral. Our next difficulty is that we do not know what these numbers are.

The relevant observation seems unrelated to the previous observations. In this case, we examine the frequency of x-rays emitted by atoms which have been energized in an electrical arc. Each type of atom (each element) emits a few characteristic frequencies of x-rays, which differ from one atom to the next. The lowest x-ray frequency emitted by each element is found to increase with increasing position in the periodic table.

Most amazingly, there is an unexpected relationship between the frequency and the relative mass of each atom. Let's rank order the elements by atomic mass, and assign an integer to each according to its ranking in order by mass. In the Periodic Table, this rank order number also corresponds to the element's position in the Periodic Table. For example, Hydrogen is assigned 1, Helium is assigned 2, etc. If we now plot the lowest frequency versus the position number in the periodic table, we find that the frequency increases directly as a simple function of the ranking number. This is shown here (Figure 4.2: X-ray Frequencies Versus Atomic Number), where we have plotted the square root of the x-ray frequency as a function of the ranking number. After a single correction, there is a simple straight-line relationship between these numbers. (The single correction is that the rankings of Argon and Potassium must be reversed. These elements have very similar atomic masses. Although Argon atoms are slightly more massive than Potassium atoms, the Periodic Law requires that we place Argon before Potassium, since Argon is a member of the inert gas group and Potassium is a member of the alkali metal group. By switching their order to correspond to the Periodic Table, we can maintain the beautiful relationship shown here (Figure 4.2: X-ray Frequencies Versus Atomic Number).)

X-ray Frequencies Versus Atomic Number

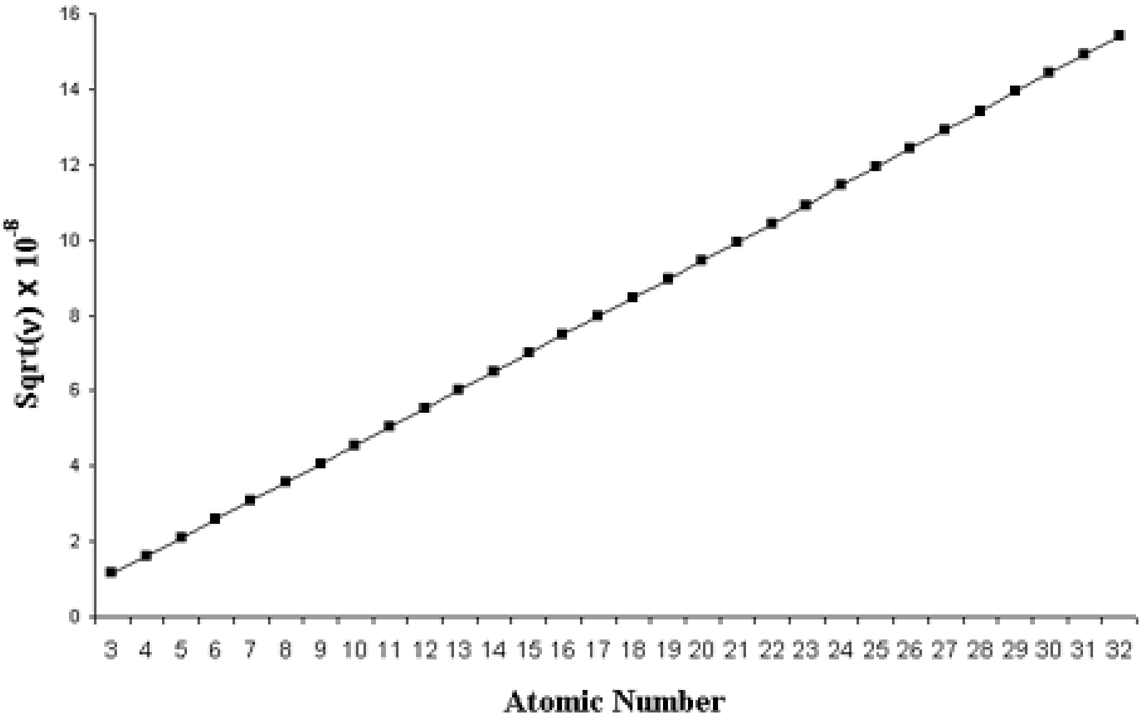

Figure 4.2

Why is this simple relationship a surprise? The integer ranking of an element by mass would not seem to be a physical property. We simply assigned these numbers in a listing of the elements which we constructed. However, we have discovered that there is a simple quantitative relationship between a real physical quantity (the x-ray frequency) and the ranking number we assigned. Moreover, there are no "breaks" in the straight line shown here (Figure 4.2: X-ray Frequencies Versus Atomic Number), meaning that all of the elements in our mass list must be accounted for. Both observations reveal that the ranking number of each atom must also be a real physical quantity itself, directly related to a structural property of each atom. We now call the ranking number the **atomic number**, since it is a number which uniquely characterizes each atom.

Furthermore, we know that each atom must possess an integer number of positive charges. Since the x-ray data demonstrates a physical property, the atomic number, which is also an integer, the simplest conclusion is that the atomic number from the x-ray data is the number of positive charges in the nucleus. Since each atom is neutral, the atomic number must also equal the number of electrons in a neutral atom.

We now know a great deal about the structure of an atom. We know that the atom has a nuclear structure, we know that the positive charges and mass of the atom are concentrated in the nucleus, and we know how many protons and electrons each atom has. However, we do not yet know anything about the positioning and movement of the electrons in the vast space surrounding the nucleus.

4.5 Observation 3: Ionization energies of the atoms

Each electron must move about the nucleus in an electrical field generated by the positive charge of the nucleus and the negative charges of the other electrons. Coulomb's law determines the potential energy of attraction of each electron to the nucleus:

$$V\left(r\right)=\frac{\left(\left(Z\right)e\right)\left(-e\right)}{r} \tag{4.1}$$

where $\left(Z\right)e$ is the charge on the nucleus with atomic number Z and $-e$ is the charge on the electron, and r is the distance from the electron to the nucleus. The potential energy of an electron in an atom is negative. This is because we take the potential energy of the electron when removed to great distance from the atom (very large r) to be zero, since the electron and the nucleus do not interact at large distance. In order to remove an electron from an atom, we have to raise the potential energy from its negative value to zero. According to Coulomb's law, we expect electrons closer to the nucleus to have a lower potential energy and thus to require more energy to remove from the atom.

We can directly measure how much energy is required to remove an electron from an atom. Without concerning ourselves with how this measurement is made, we simply measure the minimum amount of energy required to carry out the following "ionization reaction":

$$A(\mathrm{g})\rightarrow A^{+}(\mathrm{g})+e^{-}(\mathrm{g}) \tag{4.2}$$

Here, A is an atom in the gas phase, and A^{+} is the same atom with one electron e^{-}removed and is thus an ion. The minimum energy required to perform the ionization is called the **ionization energy**. The values of the ionization energy for each atom in Groups I through VIII of the periodic table are shown as a function of the atomic number here (Figure 4.3).

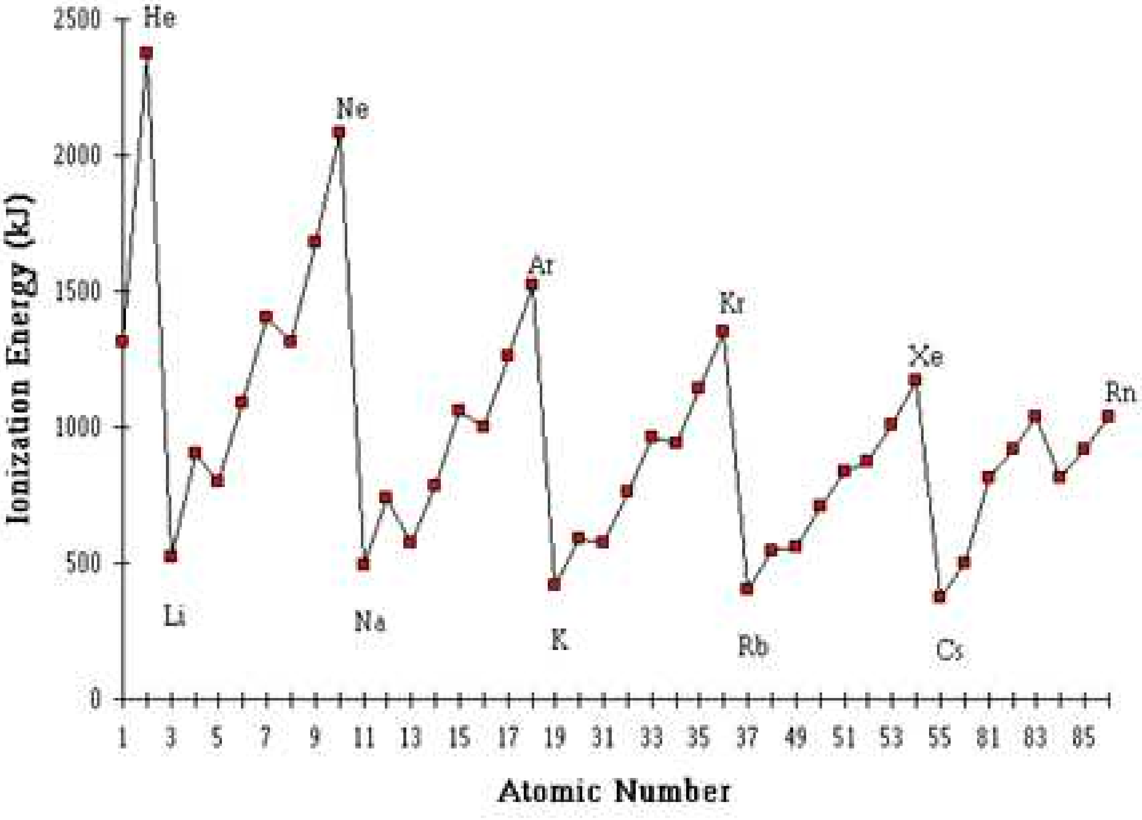

Figure 4.3

This figure is very reminiscent of the Periodic Law, which states that chemical and physical properties of the elements are periodic functions of the atomic number. Notice that the elements with the largest ionization energies (in other words, the most tightly bound electrons) are the inert gases. By contrast, the alkali metals are the elements with the smallest ionization energies. In a single period of the periodic table, between each alkali metal atom and the next inert gas atom, the ionization energy rises fairly steadily, falling dramatically from the inert gas to the following alkali metal at the start of the next period.

We need a model which accounts for these variations in the ionization energy. A reasonable assumption from Coulomb's law is that these variations are due to variations in the nuclear charge (atomic number) and in the distance of the electrons from the nucleus. To begin, we can make a very crude approximation that the ionization energy is just the negative of this attractive potential energy given by Coulomb's law. This is crude because we have ignored the kinetic energy and because each electron may not have fixed value of r.

Nevertheless, this approximation gives a way to analyze this figure (Figure 4.3). For example, from Coulomb's law it seems to make sense that the ionization energy should increase with increasing atomic number. It is easier to remove an electron from Lithium than from Neon because the nuclear charge in Lithium is much smaller than in Neon. But this cannot be the whole picture, because this argument would imply that Sodium atoms should have greater ionization energy than Neon atoms, when in fact Sodium atoms have a very much lower ionization energy. Similarly, although the ionization energy rises as we go from Sodium to Argon, the ionization energy of Argon is still less than that of Neon, even though the nuclear charge in an Argon atom is much greater than the nuclear charge in a Neon atom. What have we omitted from our analysis?

The answer is that we must consider also the distance of the electrons from the nucleus. Since it requires much less energy to ionize a Sodium atom than to ionize a Neon atom even though Sodium's nuclear charge is greater, it must be that the electron which we remove from a Sodium atom is much farther from the nucleus than the electron in the Neon atom. We can make the same comparison of the electrons removed during ionization of Neon and Argon atoms: the Argon electron must be farther from the nucleus than the Neon electron.

On the other hand, since the ionization energy fairly smoothly increases as we move from Lithium to Neon in the second period of elements, this reveals that the electrons are increasingly attracted to the nucleus for greater nuclear charge and suggests that the electrons' distance from the nucleus might not be varying too greatly over the course of a single period of the table.

If we follow this reasoning, we can even estimate how far an electron might typically be from the nucleus by using our crude approximation that the ionization energy is equal to the negative of the Coulomb potential and solving for r for each atom. This gives an estimate of distance of the electron from the nucleus:

$$r_{\text{shell}} = -\frac{((Z)\,e)\,(-e)}{\text{ionization energy}} \tag{4.3}$$

Values of r_{shell} calculated in this way are shown for the first 20 elements here (Figure 4.4). Also shown for comparison is the ionization energy for these elements. Notice that the approximate distance of the electrons from the nucleus increases in steps exactly coinciding with the increases and dips in the ionization energy.

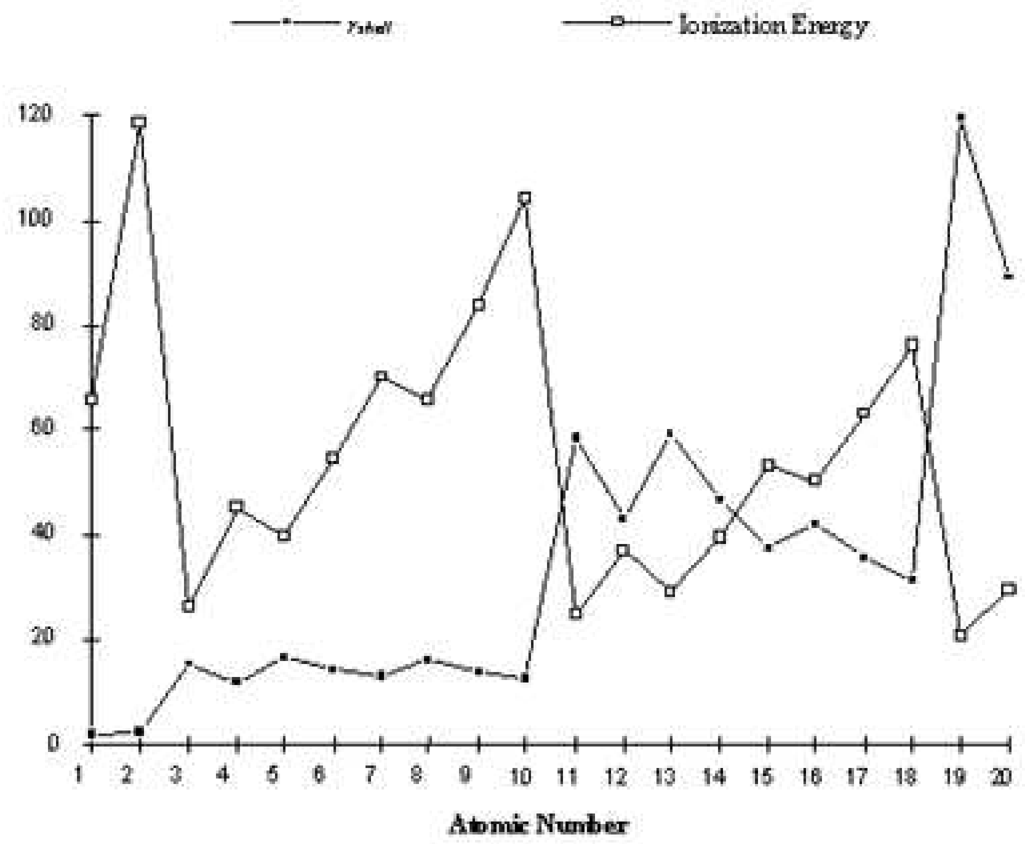

Figure 4.4

Although these distances we have calculated do not have a precise physical meaning, this figure (Figure 4.4) suggests a significant conclusion. The electrons in the elements are arranged into "shells" of increasingly greater distance from the nucleus. Hydrogen and Helium, with one and two electrons, have ionization energies consistent with electrons at similar and close distance from the nucleus. Then the second row elements lithium through neon have virtually identical sizes, though larger than that for the first two elements. The third row elements, sodium argon, have an approximate electron-nuclear distance which fluctuates a bit but is consistently larger than the second row elements.

Because the sizes of the atoms appear to grow in steps which correspond exactly to the periods of the Periodic Table, it seems that the electrons in the atoms are grouped into sets which are differing distances away from the nucleus. The first two electrons, as in Helium, are close to the nucleus, whereas additional electrons, as in Lithium to Neon, are farther from the nucleus than the first two. The suggests that, for atoms Lithium to Neon, the first two electrons are in an inner "shell", and the remaining electrons are in an outer "shell."

We can refine this shell model for the electrons in an atom with further analysis of ionization energies. We can remove any number of electrons in sequence, forming ions with greater charge. We have been examining the first ionization energy,IE_1, but each successively removed electron has successively greater ionization energy:

First ionization energy IE_1:

$$A(g) \rightarrow A^{+}(g) + e^{-}(g) \tag{4.4}$$

Second ionization energy IE_2:

$$A^{+}(g) \rightarrow A^{2+}(g) + e^{-}(g) \tag{4.5}$$

Third ionization energy IE_3:

$$A^{2+} \rightarrow A^{3+}(g) + e^{-}(g) \tag{4.6}$$

The sequential ionization energies for the elements in the second row of the periodic table are shown here (Table 4.1: Successive Ionization Energies (kJ/mol)).

Successive Ionization Energies (kJ/mol)

	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
IE_1	496	738	578	787	1012	1000	1251	1520
IE_2	4562	1451	1817	1577	1903	2251	2297	2665
IE_3	6912	7733	2745	3231	2912	3361	3822	3931
IE_4	9543	10540	11575	4356	4956	4564	5158	5770
IE_5	13353	13630	14830	16091	6273	7013	6542	7238
IE_6	16610	17995	18376	19784	22233	8495	9458	8781
IE_7	20114	21703	23293	23783	25397	27106	11020	11995

Table 4.1

Note that the second ionization energy is always greater than the first, and the third is always greater than the second, etc. This makes sense, since an electron should be more strongly attracted to a positively charged atom than to a neutral atom.

However, the data in the table (Table 4.1: Successive Ionization Energies (kJ/mol)) show a surprising feature. In most cases, the ionization energy increases a fairly large amount for successive ionizations. But for each atom, there is one much larger increase in ionization in the sequence. In Na for example, IE_2 is nearly 10 times greater than IE_1. Similarly, IE_3 is five times greater than IE_2 for Mg, although IE_2 is less than twice IE_1. The data for Na through S all show a single large step in addition to the smaller increases in IE.

Looking closely and counting electrons, we see that this unusually large increase always occurs for the ionization where we have already removed all of the outer shell electrons and are now removing an electron from the inner shell. This occurs uniformly across the second row elements, indicating that our shell model is in fact a very accurate predictor of the higher ionization energies. We can now tell how many electrons there are in the outer shell of each atom: it is equal to the number of electrons since the last inert gas.

We can conclude that an inner shell is "filled" once we have the number of electrons equal to the number in an inert gas atom. The subsequent electrons are added to a new outer shell. This is commonly referred to as the **valence shell** of the atom.

However, we do not know why only a limited number of electrons can reside in each shell. There is no obvious reason at this point why all the electrons in an atom do not reside in the shell closest to the nucleus. Similarly, there is no reason given for why the number of electrons in an inert gas atom exactly fills the outer shell, without room for even a single additional electron. These questions must be addressed further.

4.6 Review and Discussion Questions

Exercise 4.1

Explain how the scattering of α particles from gold foil reveals that an atom contains a massive, positively charged nucleus whose size is much smaller than that of the atom.

Exercise 4.2

Explain the significance of the relationship between the frequency of x-ray emission from each atom and the atomic ranking of that atom in the periodic table.

Exercise 4.3

Provide experimental evidence which reveals that the electrons in an atom are grouped into a valence shell and inner shell electrons.

Exercise 4.4

State and explain the evidence which reveals that the outer shell of each inert gas atom is full.

Exercise 4.5

Why does the ionization energy for each successive ionization increase for every atom? Why is the increase from IE_4 to IE_5 in Si much larger than any of the other increases for Si?

Chapter 5

Quantum Energy Levels In Atoms[1]

5.1 Foundation

The atomic molecular theory provides us a particulate understanding of matter. Each element is characterized as consisting of identical, indestructible atoms with atomic weights which have been determined. Compounds consist of identical molecules, each made up from a specific number of atoms of each of the component elements. We also know that atoms have a nuclear structure, meaning that all of the positive charge and virtually all of the mass of the atom are concentrated in a nucleus which is a very small fraction of the volume of the atom. Finally, we know that the electrons in the atom are arranged in "shells" about the nucleus, with each shell farther from the nucleus that the previous. The electrons in outer shells are more weakly attached to the atom than the electrons in the inner shells, and only a limited number of electrons can fit in each shell.

5.2 Goals

The shell model of the atom is a good start in understanding the differences in the chemical properties of the atoms of different elements. For example, we can understand the periodicity of chemical and physical properties from our model, since elements in the same group have the same number of electrons in the valence shell.

However, there are many details missing from our description. Other than a very crude calculation of "distance" of the shells from the nucleus, we have no description of what the differences are between the electrons in different shells. What precisely is a "shell?"

Most importantly, the arrangement of elements into groups and the periodicity of chemical properties both depend on the concept that a shell is "filled" by a certain number of electrons. Looking at the number of elements in each period, the number of electrons which fills a shell depends on which shell is being filled. In some cases, a shell is filled by eight electrons, in others, it appears to be 18 electrons. What determines how many electrons can "fit" in a shell? Why is there a limit at all?

Finally, a closer look at the ionization energies here (Figure 4.3) reveals that our shell model must be incomplete. Our model implies that the elements of the second period from Lithium to Neon have their valence electrons in the second shell. With increasing nuclear charge, the ionization energy of these atoms should increase from Lithium to Neon. As a general trend, this is true, but there are variations. Note that the ionization energy of Oxygen atoms is less than that of Nitrogen atoms. We need to pursue additional detail in our model of the structure of the atom.

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[1] This content is available online at <http://cnx.org/content/m12451/1.2/>.

5.3 Observation 1: The Spectrum of Hydrogen

To begin, we need to know a little about light. All forms of electromagnetic radiation travel as an oscillating wave, with an electric field component perpendicular to a magnetic field component. As a wave, the radiation can be characterized by its "wavelength", symbolized as λ, which is the distance between adjacent peaks in the wave. Different wavelengths correspond to different forms of electromagnetic radiation. For example, microwave radiation has wavelength in the range of 10^{-2} to 10^{-3} meters, whereas x-ray radiation has wavelength in the range 10^{-9} to 10^{-10} meters. Radiation which is visible to the human eye has wavelength in the very narrow range from 3.8×10^{-7} to 7.8×10^{-7} meters.

Radiation can also be characterized by the frequency of the electromagnetic wave, which is the number of peaks in the wave which pass a point in space per second. Frequency is symbolized by ν. The speed which light travels in a vacuum in the same for all forms of electromagnetic radiation, $c = 2.997 \times 10^8 \frac{m}{s}$. As such, we can relate the frequency of light to the wavelength of light by the equation

$$\lambda\,(m) \times \nu\,\left(s^{-1}\right) = c\left(\frac{m}{s}\right) \tag{5.1}$$

The longer the wavelength λ, the lower the frequency ν. This makes sense when we remember that light travels at a fixed speed. When the wavelength is longer, fewer peaks will pass a point in space in a second. From this equation, there is a specific relationship between frequency and wavelength, and either or both can be used to characterize the properties of radiation.

With this background in hand, we can use our understanding of light to pursue more data about the energies of electrons in atoms. Ionization energies tell us how much energy is required to remove an electron from an atom, but do not tell what happens if an electron changes its energy in an atom. To analyze this, we need a means to measure the energies gained or lost by an atom. One way to do so is to analyze the "spectrum" of an atom, which is the set of frequencies of light emitted by the atom. Since hydrogen is the simplest atom, we analyze the hydrogen spectrum first. We find that, if we pass a current of electricity through a sample of hydrogen gas, light is emitted. Careful analysis shows that, although some of this light is emitted by H_2 molecules, some of the light is also emitted by H atoms. Since light is a form of energy, then these H atoms must release energy supplied to them by the electrons in the current.

Most importantly, if we pass the light emitted by the hydrogen gas sample through a prism, we can separate the colors as in a rainbow, each with a characteristic frequency. The resultant image of separated colors is called the **spectrum** of hydrogen. We find in this experiment that there are only four frequencies (four colors) of light in the emission that are visible. The most intense of the lines in the spectrum is bright red, but there are blue and violet lines. It turns out that there are also many other frequencies of light emitted which are invisible to the human eye.

Careful observation and analysis reveals that every frequency in the hydrogen atom spectrum can be predicted by a very simple formula, called the Rydberg equation:

$$\nu = R \times \left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{5.2}$$

where R is the Rydberg constant ($3.29 \times 10^{15} s^{-1}$). n and m are integers (1,2,3,...). Each choice of n and m predicts a single observed frequency in the hydrogen atom spectrum.

The atoms of all elements emit radiation when energized in an electric current, and as do all molecules of all compounds. However, we find that the specific frequencies of light emitted are characteristic of each atom or molecule. In other words, the spectrum of each element is unique to each element or compound. As a result, the spectrum of each substance can be used to identify that substance. (Note that the Rydberg equation tells us only the spectrum of hydrogen.)

Our interest is in the fact that the radiation emitted by an atom tells us about the amounts of energy which can be released by an atom. For a hydrogen atom, for example, these changes in energy must correspond to the amounts of energy which the electrons inside the atom can gain or lose.

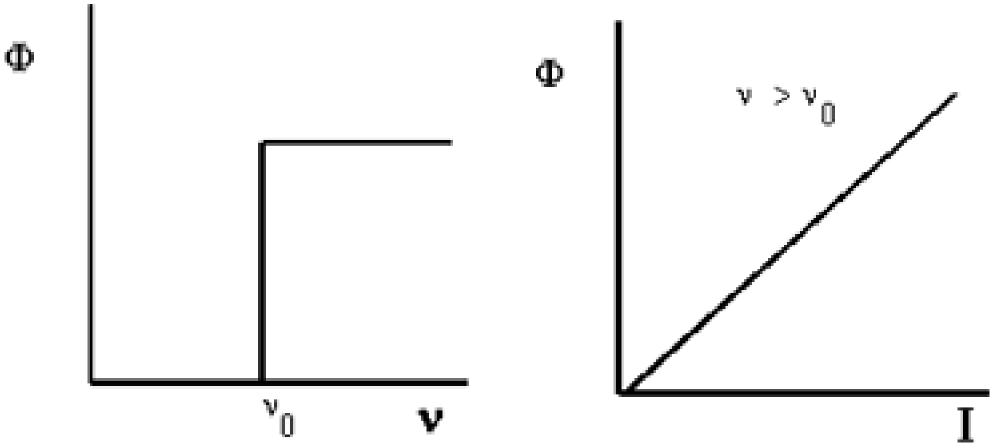
At this point, we need to relate the frequency of radiation emitted by an atom to the amount of energy lost by the electron in the atom. We thus examine some observations about the energy of radiation.

5.4 Observation 2: The Photoelectric Effect

When a light source is directed at a metal surface, it is found under many circumstances that electrons are ejected from the surface. This phenomenon is called the "photoelectric effect." These electrons can be collected to produce a usable electric current. (This effect has a variety of common practical applications, for example, in "electric eye" devices.) It is reasonable to expect that a certain amount of energy is required to liberate an electron from a metal surface, since the electron is attracted to the positively charged nuclei in the metal. Thus, in order for the electron to escape, the light must supply sufficient energy to the electron to overcome this attraction.

The following experimental observations are found when studying the photoelectric effect. First, in order for the effect to be observed, the light must be of at least a minimum frequency which we call the **threshold frequency**, ν_0. This frequency is a characteristic for a given metal. That is, it is the same value for each sample of that metal, but it varies from one metal to the next. For low frequency light, photoelectrons are not observed in any number, no matter how intense the light source is. For light with frequency above ν_0, the number of photoelectrons emitted by the metal (measured by the photoelectric current, Φ) increases directly with the intensity of the light. These results are shown in Figure 5.1 (The Photoelectric Effect).

The Photoelectric Effect

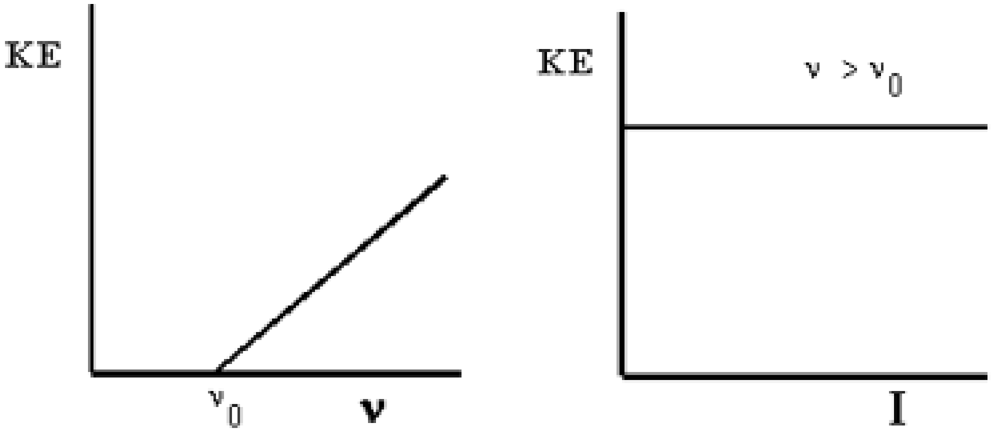


(a) (b)

Figure 5.1: Φ is the photoelectric current, ν is the frequency of incident light, and I is the intensity of incident light. (a) For photoelectrons to be emitted, the light frequency must be greater than a threshold value. (b) If the frequency is high enough, the number of photoelectrons increases directly with the light intensity.

Second, we can measure the energies of the electrons emitted by the metal. For a given metal, all photoelectrons have the same kinetic energy for a fixed frequency of light above ν_0. This fixed kinetic energy is independent of the intensity of the light source. As the frequency of the light is increased, the kinetic energy of the emitted electrons increases proportionally. These results are shown in Figure 5.2 (More Photoelectric Effect).

More Photoelectric Effect



(a) (b)

Figure 5.2: KE is the photoelectron kinetic energy, ν is the frequency of incident light, and I is the intensity of incident light. (a) If the frequency is high enough, the energy of the electrons increases directly with the frequency. (b) However, the energy of the photolectrons does not depend on the light intensity.

Are these results surprising? To the physicists at the end of the nineteenth century, the answer was yes, very surprising indeed. They expected that the energy of the light source should be determined by its intensity. Hence, the energy required to eject a photoelectron should be supplied by light of high intensity, no matter how low the frequency of the radiation. Thus, there should be no threshold frequency, below which no electrons are emitted. Moreover, the kinetic energy of the electrons should increase with intensity, not with light frequency. These predictions are not observed, so the results are counter to physical intuition.

We can account for these results in a straightforward but perhaps non-obvious manner. (Einstein provided the explanation in 1905.) Since the kinetic energy of the emitted photoelectrons increases proportionally with increases in the frequency of the light above the threshold frequency, we can conclude from conservation of total energy that the energy supplied by the light to the ejected electron must be proportional to its frequency: $E \propto \nu$. This does not immediately account for the existence of the threshold frequency, though, since it would still seem to be the case that even low frequency light would possess high energy if the intensity were sufficient. By this reasoning, high intensity, low frequency light should therefore produce as many photoelectrons as are produced by low intensity, high frequency light. But this is not observed.

This is a very challenging puzzle, and an analogy helps to reveal the subtle answer. Imagine trying to knock pieces out of a wall by throwing objects at it. We discover that, no matter how many ping pong balls we throw, we cannot knock out a piece of the wall. On the other hand, only a single bowling ball is required to accomplish the task. The results of this "experiment" are similar to the observations of the photoelectric effect: very little high frequency light can accomplish what an enormous amount of low frequency light cannot. The key to understanding our imaginary experiment is knowing that, although there are many more ping-pong balls than bowling balls, it is only the impact of each individual particle with the wall which determines what happens.

Reasoning from this analogy, we must conclude that the energy of the light is supplied in "bundles" or "packets" of constant energy, which we will call **photons**. We have already concluded that the light supplies energy to the electron which is proportional to the light frequency. Now we can say that the energy of each photon is proportional to the frequency of the light. The intensity of the light is proportional to the number of these packets. This now accounts for the threshold frequency in a straightforward way. For a photon to dislodge a photoelectron, it must have sufficient energy, by itself, to supply to the electron to overcome its attraction to the metal. Although increasing the intensity of the light does increase the total energy of the light, it does not increase the energy of an individual photon. Therefore, if the frequency of the light is too low, the photon energy is too low to eject an electron. Referring back to the analogy, we can say that a single bowling bowl can accomplish what many ping-pong balls cannot, and a single high frequency photon can accomplish what many low frequency photons cannot.

The important conclusion for our purposes is that **light energy is quantized into packets of energy**. The amount of energy in each photon is given by Einstein's equation,

$$E = h\nu \tag{5.3}$$

where h is a constant called Planck's constant.

5.5 Quantized Energy Levels in Hydrogen Atoms

We can combine the observation of the hydrogen atom spectrum with our deduction that light energy is quantized into packets to reach an important conclusion. Each frequency of light in the spectrum corresponds to a particular energy of light and, therefore, to a particular energy **loss** by a hydrogen atom, since this light energy is quantized into packets. Furthermore, since only certain frequencies are observed, then only certain energy losses are possible. This is only reasonable if the energy of each hydrogen atom is restricted to certain specific values. If the hydrogen atom could possess any energy, then it could lose any amount of energy and emit a photon of any energy and frequency. But this is not observed. Therefore, the energy of the electron in a hydrogen atom must be restricted to certain **energy levels**.

The Hydrogen atom spectrum also tells us what these energy levels are. Recall that the frequencies of radiation emitted by Hydrogen atoms are given by the Rydberg equation (5.2). Each choice of the positive integers n and m predicts a single observed frequency in the hydrogen atom spectrum.

Each emitted frequency must correspond to an energy $h\nu$ by Einstein's equation (5.3). This photon energy must be the **difference** between two energy levels for a hydrogen electron, since that is the amount of energy released by the electron moving from one level to the other. If the energies of the two levels are E_m and E_n, then we can write that

$$h\nu = E_m - E_n \tag{5.4}$$

By comparing this to the Rydberg equation, each energy level must be given by the formula

$$E_n = (-h)\, R \frac{1}{n^2} \tag{5.5}$$

We can draw two conclusions. First, the electron in a hydrogen atom can exist only with certain energies, corresponding to motion in what we now call a state or an **orbital**. Second, the energy of a state can be characterized by an integer **quantum number**, n = 1, 2, 3, ... which determines its energy.

These conclusions are reinforced by similar observations of spectra produced by passing a current through other elements. Only specific frequencies are observed for each atom, although only the hydrogen frequencies obey the Rydberg formula.

We conclude that the energies of electrons in atoms are "quantized," that is, restricted to certain values. We now need to relate this quantization of energy to the existence of shells, as developed in a previous study (Chapter 4).

5.6 Observation 3: Photoelectron Spectroscopy of Multi-Electron Atoms

The ionization energy of an atom tells us the energy of the electron or electrons which are at highest energy in the atom and are thus easiest to remove from the atom. To further analyze the energies of the electrons more tightly bound to the nucleus, we introduce a new experiment. The photoelectric effect can be applied to ionize atoms in a gas, in a process often called **photoionization**. We shine light on an atom and measure the minimum frequency of light, corresponding to a minimum energy, which will ionize an electron from an atom. When the frequency of light is too low, the photons in that light do not have enough energy to ionize electrons from an atom. As we increase the frequency of the light, we find a threshold at which electrons begin to ionize. Above this threshold, the energy $h\nu$ of the light of frequency ν is greater than the energy required to ionize the atom, and the excess energy is retained by the ionized electron as kinetic energy.

In photoelectron spectroscopy, we measure the kinetic energy of the electrons which are ionized by light. This provides a means of measuring the ionization energy of the electrons. By conservation of energy, the energy of the light is equal to the ionization energy IE plus the kinetic energy KE of the ionized electron:

$$h\nu = \mathrm{IE} + \mathrm{KE} \tag{5.6}$$

Thus, if we use a known frequency ν and measure KE, we can determine IE. The more tightly bound an electron is to the atom, the higher the ionization energy and the smaller the kinetic energy of the ionized electron. If an atom has more than one electron and these electrons have different energies, then for a given frequency of light, we can expect electrons to be ejected with different kinetic energies. The higher kinetic energies correspond to the weakly bound outer electrons, and the lower kinetic energies correspond to the tightly bound inner electrons.

The ionization energies for the first twenty elements are given in Table 5.1. We note that there is a single ionization energy for hydrogen and helium. This is consistent with the shell model of these atoms since, in both of these atoms, the electron or electrons are in the innermost shell. The energies of these electrons correspond to the $n = 1$ energy level of the hydrogen atom. In lithium and beryllium, there are two ionization energies. Again, this is consistent with the shell model, since now there are electrons in both of the first two shells. Note also that the ionization energy of the inner shell electrons increases as we go from hydrogen to lithium to beryllium, because of the increase in nuclear charge. The lower energy electrons correspond to the $n = 1$ energy level of hydrogen and the higher energy electrons correspond to the $n = 2$ energy level.

Element	**Ionization Energy (MJ/mol)**					
H	1.31					
He	2.37					
Li	6.26	0.52				
Be	11.5	0.90				
B	19.3	1.36	0.80			
C	28.6	1.72	1.09			

continued on next page

N	39.6	2.45	1.40			
O	52.6	3.12	1.31			
F	67.2	3.88	1.68			
Ne	84.0	4.68	2.08			
Na	104	6.84	3.67	0.50		
Mg	126	9.07	5.31	0.74		
Al	151	12.1	7.79	1.09	0.58	
Si	178	15.1	10.3	1.46	0.79	
P	208	18.7	13.5	1.95	1.01	
S	239	22.7	16.5	2.05	1.00	
Cl	273	26.8	20.2	2.44	1.25	
Ar	309	31.5	24.1	2.82	1.52	
K	347	37.1	29.1	3.93	2.38	0.42
Ca	390	42.7	34.0	4.65	2.9	0.59

Table 5.1

Surprisingly, though, boron has three ionization energies, which does not seem consistent with the shell model. From the hydrogen atom energy levels, we would have expected that all $n = 2$ electrons would have the same energy. We can note that the two smaller ionization energies in boron are comparable in magnitude and smaller by more than a factor of ten than the ionization energy of the electrons in the inner shell. Thus, the electrons in the outer $n = 2$ shell apparently have comparable energies, but they are not identical. The separation of the second shell into two groups of electrons with two comparable but different energies is apparent for elements boron to neon.

As such, we conclude from the experimental data that the second shell of electrons should be described as two **subshells** with slightly different energies. For historical reasons, these subshells are referred to as the as the "2s" and "2p" subshells, with 2s electrons slightly lower in energy than 2p electrons. The energies of the 2s and 2p electrons decrease from boron to neon, consistent with the increase in the nuclear charge.

Beginning with sodium, we observe four distinct ionization energies, and beginning with aluminum there are five. Note for these elements that the fourth and fifth ionization energies are again roughly a factor of ten smaller than the second and third ionization energies, which are in turn at least a factor of ten less than the first ionization energy. Thus, it appears that there are three shells of electrons for these atoms, consistent with our previous shell model. As with $n = 2$, the $n = 3$ shell is again divided into two subshells, now called the 3s and 3p subshells.

These data also reveal how many electrons can reside in each subshell. In each n level, there are two elements which have only the ionization energy for the s subshell. Hence, s subshells can hold two electrons. By contrast, there are 6 elements which have both the s and p subshell ionization energies, so the p subshell can hold 6 electrons.

The shell and subshell organization of electron energies can also be observed by measuring the "electron affinity" of the atoms. Electron affinity is the energy released when an electron is added to an atom:

$$A\,(g) + e^{-}\,(g) \rightarrow A^{-}\,(g) \tag{5.7}$$

If there is a strong attraction between the atom A and the added electron, then a large amount of energy is released during this reaction, and the electron affinity is a large positive number. (As a note, this convention is the opposite of the one usually applied for energy changes in reactions: exothermic reactions, which give off energy, conventionally have negative energy changes.)

The electron affinities of the halogens are large positive values: the electron affinities of F, Cl, and Br are 328.0 kJ/mol, 348.8 kJ/mol, and 324.6 kJ/mol. Thus, the attached electrons are strongly attracted to the nucleus in each of these atoms. This is because there is room in the current subshell to add an additional electron, since each atom has 5 p electrons, and the core charge felt by the electron in that subshell is large.

By contrast, the electron affinities of the inert gases are **negative**: the addition of an electron to an inert gas atom actually requires the **input** of energy, in effect, to force the electron into place. This is because the added electron cannot fit in the current subshell and must be added to a new shell, farther from the nucleus. As such, the core charge felt by the added electron is very close to zero.

Similarly, the electron affinities of the elements Be, Mg, and Ca are all negative. This is again because the s subshell in these atoms already has two electrons, so the added electron must go into a higher energy subshell with a much smaller core charge.

5.7 Electron Waves, the Uncertainty Principle, and Electron Energies

We now have a fairly detailed description of the energies of the electrons in atoms. What we do not have is a model which tells us what factors determine the energy of an electron in a shell or subshell. Nor do we have a model to explain why these energies are similar but different for electrons in different subshells.

A complete answer to these questions requires a development of the quantum theory of electron motion in atoms. Because the postulates of this quantum theory cannot be readily developed from experimental observations, we will concern ourselves with a few important conclusions only.

The first important conclusion is that the motion of an electron in an atom is described by a wave function. Interpretation of the wave motion of electrons is a very complicated proposition, and we will only deal at present with a single important consequence, namely the **uncertainty principle**. A characteristic of wave motion is that, unlike a particle, the wave does not have a definite position at a single point in space. By contrast, the location of a particle is precise. Therefore, since an electron travels as a wave, we must conclude that we cannot determine the precise location of the electron in an atom. This is, for our purposes, the uncertainty principle of quantum mechanics. We **can** make measurements of the location of the electron, but we find that each measurement results in a different value. We are then forced to accept that we cannot determine the precise location. We are allowed, however, to determine a **probability distribution** for where the electron is observed.

This probability distribution is determined by quantum mechanics. The motion of the electron in a hydrogen atom is described by a function, often called the **wave function** or the **electron orbital** and typically designated by the symbol Ψ. Ψ is a function of the position of the electron r, and quantum mechanics tells us that $(|\Psi|)^2$ is the **probability** of observing the electron at the location r.

Each electron orbital has an associated constant value of the electronic energy, E_n, in agreement with our earlier conclusions. In fact, quantum mechanics exactly predicts the energy shells and the hydrogen atom spectrum we observe. The energy of an electron in an orbital is determined primarily by two characteristics of the orbital. The first, rather intuitive, property determines the average potential energy of the electron: an orbital which has substantial probability in regions of low potential energy will have a low total energy. By Coulomb's law, the potential energy arising from nucleus-electron attraction is lower when the electron is nearer the nucleus. In atoms with more than one electron, electron-electron repulsion also contributes to the potential energy, as Coulomb's law predicts an increase in potential energy arising from the repulsion of like charges.

A second orbital characteristic determines the contribution of kinetic energy, via a more subtle effect arising out of quantum mechanics. As a consequence of the uncertainty principle, quantum mechanics predicts that, the more confined an electron is to a smaller region of space, the higher must be its average kinetic energy. Since we cannot measure the position of electron precisely, we define the uncertainty in the measurement as $\Delta(x)$. Quantum mechanics also tells us that we cannot measure the momentum of an electron precisely either, so there is an uncertainty $\Delta(p)$ in the momentum. In mathematical detail, the uncertainty principle states that these uncertainties are related by an inequality:

$$\Delta(x)\,\Delta(p) \geq \frac{h}{4\pi} \tag{5.8}$$

where h is Planck's constant, $6.62 \times 10^{-34}\,(Js)$ (previously seen in Einstein's equation (5.3) for the energy of a photon). This inequality reveals that, when an electron moves in a small area with a correspondingly small uncertainty $\Delta(x)$, the uncertainty in the momentum $\Delta(p)$ must be large. For $\Delta(p)$ to be large, the momentum must also be large, and so must be the kinetic energy.

Therefore, the more compact an orbital is, the higher will be the average kinetic energy of an electron in that orbital. This extra kinetic energy, which can be regarded as the **confinement energy**, is comparable in magnitude to the average potential energy of electron-nuclear attraction. Therefore, in general, an electron orbital provides a compromise, somewhat localizing the electron in regions of low potential energy but somewhat delocalizing it to lower its confinement energy.

5.8 Electron Orbitals and Subshell Energies

We need to account for the differences in energies of the electrons in different subshells, since we know that, in a Hydrogen atom, the orbital energy depends only on the n quantum number. We recall that, in the Hydrogen atom, there is a **single** electron. The energy of that electron is thus entirely due to its kinetic energy and its attraction to the nucleus. The situation is different in all atoms containing more than one electron, because the energy of the electrons is affected by their mutual repulsion. This repulsion is very difficult to quantify, but our model must take it into account.

A simple way to deal with the effect of electron-electron repulsion is to examine the shell structure of the atom. The two $n = 1$ electrons in beryllium are in a shell with a comparatively short average distance from the nucleus. Therefore, the two $n = 2$ electrons are in a shell which is, on average, "outside" of the $n = 1$ shell. The $n = 1$ electrons are thus the "core" and the $n = 2$ electrons are in the valence shell. This structure allows us to see in a simple way the effect of electron-electron repulsion on the energies of the $n = 2$ electrons. Each $n = 2$ electron is attracted by the $+4$ charge on the tiny beryllium nucleus, but is repelled by the two -1 charges from the inner shell formed by the two $n = 1$ electrons. Net, then, an $n = 2$ electron effectively "sees" roughly a $+2$ nuclear charge. We refer to this $+2$ as the "core charge" since it is the net charge on the core resulting from the balance of attraction to the nucleus and repulsion from the core electrons. The nucleus is partially "shielded" from the valence electrons by the core electrons.

This shielding effect does not seem to account for the difference in ionization energies between 2s and 2p or for the lower ionization energy of boron compared to beryllium, since, in each atom, the valence electrons are in the $n = 2$ shell. However, the shielding effect is not perfect. Recall that we only know the **probabilities** for observing the positions of the electrons. Therefore, we cannot definitely state that the $n = 2$ electrons are outside of the $n = 1$ core. In fact, there is some probability that an $n = 2$ electron might be found inside the $n = 1$ core, an effect called "core penetration." When an $n = 2$ electron does penetrate the core, it is no longer shielded from the nucleus. In this case, the $n = 2$ electron is very strongly attracted to the nucleus and its energy is thus lowered. What is the extent of this penetration? We must consult quantum theory. The answer is in Figure 5.3 (Probability for an Electron at a Distance r from a Hydrogen Nucleus), which shows the probability of finding an electron a distance r away from the nucleus for each of the 1s, 2s, and 2p orbitals. We can see that there is a greater probability (though small) for the 2s electron to penetrate the core than for the 2p electron to do so.

Probability for an Electron at a Distance r from a Hydrogen Nucleus

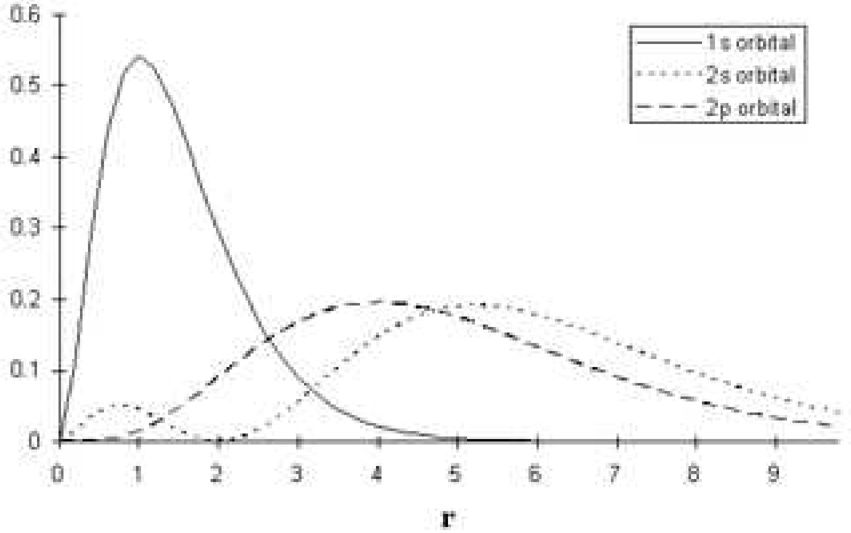


Figure 5.3

As a result of the core penetration, an electron in a 2s orbital feels a greater "effective nuclear charge" than just the core charge, which was approximated by assuming perfect shielding. Thus the effective nuclear charge for a 2s electron is greater than the effective nuclear charge for a 2p electron. Therefore, the energy of an electron in the 2s orbital in beryllium is lower than it would be in the 2p orbital.

A detailed analysis from quantum mechanics gives the following ordering of orbitals in order of increasing energy:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < ... \quad (5.9)$$

This ordering can be rationalized on the basis of effective nuclear charge, shielding, and core penetration.

5.9 Review and Discussion Questions

Exercise 5.1

The photoelectric effect demonstrates that radiation energy is quantized into "packets" or photons. Explain how and why this observation is of significance in understanding the structure of atoms.

Exercise 5.2

Explain how we can know that higher frequency light contains higher energy photons.

Exercise 5.3

Electron affinity is the energy released when an electron is attached to an atom. If an atom has a positive electron affinity, the added electron is attracted to the nucleus to form a stable negative ion. Why doesn't a Beryllium atom have a positive electron affinity? Explain how this demonstrates that the energy of a 2s orbital is less than the energy of a 2p orbital.

Exercise 5.4

Why does an inert gas atom have a high ionization energy but a low electron affinity? Why do these properties combine to make the atoms of inert gases unreactive?

Exercise 5.5

Consider electrons from two different subshells in the same atom. In photoelectron spectroscopy, the lower energy electron has a higher ionization energy but is observed to have lower kinetic energy after ionization. Reconcile the lower energy with the higher ionization energy with the lower kinetic energy.

Exercise 5.6

Chlorine atoms have 5 distinct ionization energies. Explain why. Predict the number of ionization energies for Bromine atoms, and explain your answer. (Hint: examine the structure of the periodic table.)

Exercise 5.7

Why does a Bromine atom have a much smaller radius than a Potassium atom, even though a Br atom has 16 more electrons than does a K atom?

Exercise 5.8

Explain why electrons confined to smaller orbitals are expected to have higher kinetic energies.

Exercise 5.9

Define "shielding" in the context of electron-electron repulsion. What is the significance of shielding in determining the energy of an electron? How is the affected by core penetration?

Chapter 6

Covalent Bonding and Electron Pair Sharing[1]

6.1 Foundation

We begin with our understanding of the relationship between chemical behavior and atomic structure. That is, we assume the Periodic Law that the chemical and physical properties of the elements are periodic functions of atomic number. We further assume the structure of the atom as a massive, positively charged nucleus, whose size is much smaller than that of the atom as a whole, surrounded by a vast open space in which move negatively charged electrons. These electrons can be effectively partitioned into a core and a valence shell, and it is only the electrons in the valence shell which are significant to the chemical properties of the atom. The number of valence electrons in each atom is equal to the group number of that element in the Periodic Table.

6.2 Goals

The atomic molecular theory is extremely useful in explaining what it means to form a compound its component elements. That is, a compound consists of identical molecules, each comprised of the atoms of the component elements in a simple whole number ratio. However, the atomic molecular theory also opens up a wide range of new questions. We would like to know what atomic properties determine the number of atoms of each type which combine to form stable compounds. Why are some combinations observed and other combinations not observed? Some elements with very dissimilar atomic masses (for example, iodine and chlorine) form very similar chemical compounds, but other elements with very similar atomic masses (for example, oxygen and nitrogen) form very dissimilar compounds. What factors are responsible for the bonding properties of the elements in a similar group? In general, we need to know what forces hold atoms together in forming a molecule.

We have developed a detail understanding of the structure of the atom. Our task now is to apply this understanding to develop a similar level of detail about how atoms bond together to form molecules.

6.3 Observation 1: Valence and the Periodic Table

To begin our analysis of chemical bonding, we define the **valence** of an atom by its tendencies to form molecules. The inert gases do not tend to combine with any other atoms. We thus assign their valence as 0, meaning that these atoms tend to form 0 bonds. Each halogen prefers to form molecules by combining with

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[1] This content is available online at <http://cnx.org/content/m12584/1.5/>.

a single hydrogen atom (*e.g.* HF, HCl). We thus assign their valence as 1, also taking hydrogen to also have a valence of 1. What we mean by a valence of 1 is that these atoms prefer to bind to only one other atom. The valence of oxygen, sulfur, etc. is assigned as 2, since two hydrogens are required to satisfy bonding needs of these atoms. Nitrogen, phosphorus, etc. have a valence of 3, and carbon and silicon have a valence of 4. This concept also applies to elements just following the inert gases. Lithium, sodium, potassium, and rubidium bind with a single halogen atom. Therefore, they also have a valence of 1. Correspondingly, it is not surprising to find that, for example, the combination of two potassium atoms with a single oxygen atom forms a stable molecule, since oxygen's valence of 2 is be satisfied by the two alkali atoms, each with valence 1. We can proceed in this manner to assign a valence to each element, by simply determining the number of atoms to which this element's atoms prefer to bind.

In doing so, we discover that the periodic table is a representation of the valences of the elements: elements in the same group all share a common valence. The inert gases with a valence of 0 sit to one side of the table. Each inert gas is immediately preceded in the table by one of the halogens: fluorine precedes neon, chlorine precedes argon, bromine precedes krypton, and iodine precedes xenon. And each halogen has a valence of one. This "one step away, valence of one" pattern can be extended. The elements just prior to the halogens (oxygen, sulfur, selenium, tellurium) are each two steps away from the inert gases in the table, and each of these elements has a valence of two (*e.g.* H_2O, H_2S). The elements just preceding these (nitrogen, phosphorus, antimony, arsenic) have valences of three (*e.g.* NH_3, PH_3), and the elements before that (carbon and silicon most notably) have valences of four (CH_4, SiH_4). The two groups of elements immediately after the inert gases, the alkali metals and the alkaline earths, have valences of one and two, respectively. Hence, for many elements in the periodic table, the valence of its atoms can be predicted from the number of steps the element is away from the nearest inert gas in the table. This systemization is quite remarkable and is very useful for remembering what molecules may be easily formed by a particular element.

Next we discover that there is a pattern to the valences: for elements in groups 4 through 8 (*e.g.* carbon through neon), the valence of each atom **plus** the number of electrons in the valence shell in that atom always equals **eight**. For examples, carbon has a valence of 4 and has 4 valence electrons, nitrogen has a valence of 3 and has 5 valence electrons, and oxygen has a valence of 2 and has 6 valence electrons. Hydrogen is an important special case with a single valence electron and a valence of 1. Interestingly, for each of these atoms, the number of bonds the atom forms is equal to the number of vacancies in its valence shell.

To account for this pattern, we develop a model assuming that each atom attempts to bond to other atoms so as to completely fill its valence shell with electrons. For elements in groups 4 through 8, this means that each atom attempts to complete an "octet" of valence shell electrons. (Why atoms should behave this way is a question unanswered by this model.) Consider, for example, the combination of hydrogen and chlorine to form hydrogen chloride, HCl. The chlorine atom has seven valence electrons and seeks to add a single electron to complete an octet. Hence, chlorine has a valence of 1. Either hydrogen or chlorine could satisfy its valence by "taking" an electron from the other atom, but this would leave the second atom now needing two electrons to complete its valence shell. The only way for both atoms to complete their valence shells simultaneously is to **share** two electrons. Each atom donates a single electron to the electron pair which is shared. It is this sharing of electrons that we refer to as a chemical bond, or more specifically, as a **covalent bond**, so named because the bond acts to satisfy the valence of both atoms. The two atoms are thus held together by the need to share the electron pair.

6.4 Observation 2: Compounds of Carbon and Hydrogen

Many of the most important chemical fuels are compounds composed entirely of carbon and hydrogen, *i.e.* hydrocarbons. The smallest of these is methane CH_4, a primary component of household natural gas. Other simple common fuels include ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, pentane C_5H_{12}, hexane C_6H_{14}, heptane C_7H_{16}, and octane C_8H_{18}. It is interesting to note that there is a consistency in these molecular formulae: in each case, the number of hydrogen atoms is two more than twice the number of carbon atoms, so that each compound has a molecular formula like C_nH_{2n+2}. This suggests that there are strong similarities in the valences of the atoms involved which should be understandable in terms of our valence shell electron pair sharing model. In each molecule, the carbon atoms must be directly bonded together, since they cannot be joined together with a hydrogen atom. In the easiest example of ethane, the two carbon atoms are bonded together, and each carbon atom is in turn bonded to three hydrogen atoms. Thus, in this case, it is relatively apparent that the valence of each carbon atom is 4, just as in methane, since each is bonded to four other atoms. Therefore, by sharing an electron pair with each of the four atoms to which it is bonded, each carbon atom has a valence shell of eight electrons.

In most other cases, it is not so trivial to determine which atoms are bonded to which, as there may be multiple possibilities which satisfy all atomic valences. Nor is it trivial, as the number of atoms and electrons increases, to determine whether each atom has an octet of electrons in its valence shell. We need a system of electron accounting which permits us to see these features more clearly. To this end, we adopt a standard notation for each atom which displays the number of valence electrons in the unbonded atom explicitly. In this notation, carbon and hydrogen look like Figure 6.1, representing the single valence electron in hydrogen and the four valence electrons in carbon.

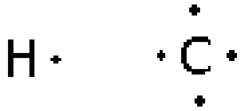

Figure 6.1

Using this notation, it is now relatively easy to represent the shared electron pairs and the carbon atom valence shell octets in methane and ethane. Linking bonded atoms together and pairing the valence shell electrons from each gives Figure 6.2.

Figure 6.2

Recall that each shared pair of electrons represents a chemical bond. These are examples of what are called **Lewis structures**, after G.N. Lewis who first invented this notation. These structures reveal, at a glance, which atoms are bonded to which, *i.e.* the structural formula of the molecule. We can also easily count the number of valence shell electrons around each atom in the bonded molecule. Consistent with our model of the octet rule, each carbon atom has eight valence electrons and each hydrogen has two in the molecule.

In a larger hydrocarbon, the structural formula of the molecule is generally not predictable from the number of carbon atoms and the number of hydrogen atoms, so the molecular structure must be given to deduce the Lewis structure and thus the arrangement of the electrons in the molecule. However, once given this information, it is straightforward to create a Lewis structure for molecules with the general molecular formula C_nH_{2n+2} such as propane, butane, etc. For example, the Lewis structure for "normal" butane (with all carbons linked one after another) is found here (Figure 6.3).

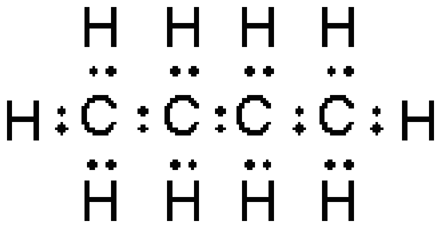

Figure 6.3

It is important to note that there exist no hydrocarbons where the number of hydrogens exceeds two more than twice the number of carbons. For example,

CH_5 does not exist, nor does C_2H_8. We correspondingly find that all attempts to draw Lewis structures which are consistent with the octet rule will fail for these molecules. Similarly, CH_3 and C_2H_5 are observed to be so extremely reactive that it is impossible to prepare stable quantities of either compound. Again we find that it is not possible to draw Lewis structures for these molecules which obey the octet rule.

We conclude from these examples that, when it is possible to draw a Lewis structure in which each carbon has a complete octet of electrons in its valence shell, the corresponding molecule will be stable and the hydrocarbon compound will exist under ordinary conditions. After working a few examples, it is apparent that this always holds for compounds with molecular formula C_nH_{2n+2}.

On the other hand, there are many stable hydrocarbon compounds with molecular formulae which do not fit the form C_nH_{2n+2}, particularly where the number of hydrogens is less than $2n+2$. In these compounds, the valences of the carbon atoms are not quite so obviously satisfied by electron pair sharing. For example, in ethene C_2H_4 and acetylene C_2H_2 there are not enough hydrogen atoms to permit each carbon atom to be bonded to four atoms each. In each molecule, the two carbon atoms must be bonded to one another. By simply arranging the electrons so that the carbon atoms share a single pair of electrons, we wind up with rather unsatisfying Lewis structures for ethene and acetylene, shown here (Figure 6.4).

Figure 6.4

Note that, in these structures, neither carbon atom has a complete octet of valence shell electrons. Moreover, these structures indicate that the carbon-carbon bonds in ethane, ethene, and acetylene should be very similar, since in each case a single pair of electrons is shared by the two carbons. However, these bonds are observed to be chemically and physically very different. First, we can compare the energy required to break each bond (the **bond energy** or **bond strength**). We find that the carbon-carbon bond energy is 347 kJ in C_2H_6, 589 kJ in C_2H_4, and 962 kJ in C_2H_2. Second, it is possible to observe the distance between the two carbon atoms, which is referred to as the **bond length**. It is found that carbon-carbon bond length is 154 pm in C_2H_6, 134 pm in C_2H_4, and 120 pm in C_2H_2. (1picometer = 1pm = $10^{-12}m$). These observations reveal clearly that the bonding between the carbon atoms in these three molecules must be very different.

Note that the bond in ethene is about one and a half times as strong as the bond in ethane; this suggests that the two unpaired and unshared electrons in the ethene structure above are also paired and shared as a second bond between the two carbon atoms. Similarly, since the bond in acetylene is about two and a half times stronger than the bond in ethane, we can imagine that this results from the sharing of three pairs of electrons between the two carbon atoms. These assumptions produce the Lewis structures here (Figure 6.5).

Figure 6.5

These structures appear sensible from two regards. First, the trend in carbon-carbon bond strengths can be understood as arising from the increasing number of shared pairs of electrons. Second, each carbon atom has a complete octet of electrons. We refer to the two pairs of shared electrons in ethene as a **double bond** and the three shared pairs in acetylene as a **triple bond**.

We thus extend our model of valence shell electron pair sharing to conclude that carbon atoms can bond by sharing one, two, or three pairs of electrons as needed to complete an octet of electrons, and that the strength of the bond is greater when more pairs of electrons are shared. Moreover, the data above tell us that the carbon-carbon bond in acetylene is shorter than that in ethene, which is shorter than that in ethane. We conclude that triple bonds are shorter than double bonds which are shorter than single bonds.

6.5 Observation 3: Compounds of Nitrogen, Oxygen, and the Halogens

Many compounds composed primarily of carbon and hydrogen also contain some oxygen or nitrogen, or one or more of the halogens. We thus seek to extend our understanding of bonding and stability by developing Lewis structures involving these atoms. Recall that a nitrogen atom has a valence of 3 and has five valence electrons. In our notation, we could draw a structure in which each of the five electrons appears separately in a ring, similar to what we drew for C. However, this would imply that a nitrogen atom would generally form five bonds to pair its five valence electrons. Since the valence is actually 3, our notation should reflect this. One possibility looks like this (Figure 6.6).

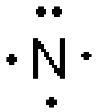

Figure 6.6

Note that this structure leaves three of the valence electrons "unpaired" and thus ready to join in a shared electron pair. The remaining two valence electrons are "paired," and this notation implies that they therefore are not generally available for sharing in a covalent bond. This notation is consistent with the available data, *i.e.* five valence electrons and a valence of 3. Pairing the two non-bonding electrons seems reasonable in analogy to the fact that electrons are paired in forming covalent bonds.

Analogous structures can be drawn for oxygen, as well as for fluorine and the other halogens, as shown here (Figure 6.7).

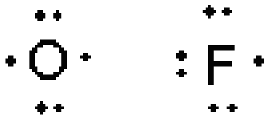

Figure 6.7

With this notation in hand, we can now analyze structures for molecules including nitrogen, oxygen, and the halogens. The hydrides are the easiest, shown here (Figure 6.8).

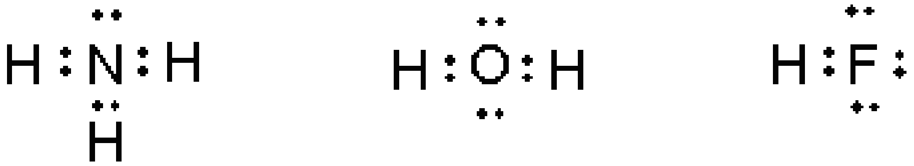

Figure 6.8

Note that the octet rule is clearly obeyed for oxygen, nitrogen, and the halogens.

At this point, it becomes very helpful to adopt one new convention: a pair of bonded electrons will now be more easily represented in our Lewis structures by a straight line, rather than two dots. Double bonds and triple bonds are represented by double and triple straight lines between atoms. We will continue to show non-bonded electron pairs explicitly.

As before, when analyzing Lewis structures for larger molecules, we must already know which atoms are bonded to which. For example, two very different compounds, ethanol and dimethyl ether, both have molecular formula C_2H_6O. In ethanol, the two carbon atoms are bonded together and the oxygen atom is attached to one of the two carbons; the hydrogens are arranged to complete the valences of the carbons and the oxygen shown here (Figure 6.9).

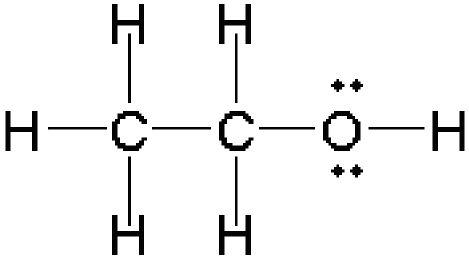

Figure 6.9

This Lewis structure reveals not only that each carbon and oxygen atom has a completed octet of valence shell electrons but also that, in the stable molecule, there are four non-bonded electrons on the oxygen atom. Ethanol is an example of an **alcohol**. Alcohols can be easily recognized in Lewis structures by the C-O-H group. The Lewis structures of all alcohols obey the octet rule.

In dimethyl ether, the two carbons are each bonded to the oxygen, in the middle, shown here (Figure 6.10).

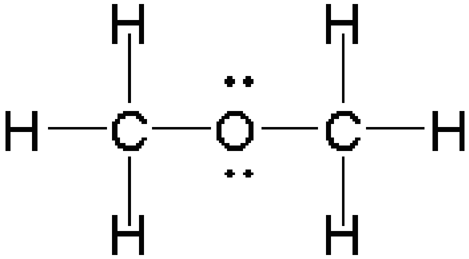

Figure 6.10

Ethers can be recognized in Lewis structures by the C-O-C arrangement. Note that, in both ethanol and dimethyl ether, the octet rule is obeyed for all carbon and oxygen atoms. Therefore, it is not usually possible to predict the structural formula of a molecule from Lewis structures. We must know the molecular structure prior to determining the Lewis structure.

Ethanol and dimethyl ether are examples of **isomers**, molecules with the same molecular formula but different structural formulae. In general, isomers have rather different chemical and physical properties arising from their differences in molecular structures.

A group of compounds called **amines** contain hydrogen, carbon, and nitrogen. The simplest amine is methyl amine, whose Lewis structure is here (Figure 6.11).

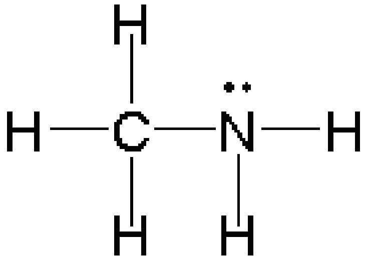

Figure 6.11

"Halogenated" hydrocarbons have been used extensively as refrigerants in air conditioning systems and refrigerators. These are the notorious "chlorofluorocarbons" or "CFCs" which have been implicated in the destruction of stratospheric ozone. Two of the more important CFCs include Freon 11, $CFCl_3$, and Freon 114, $C_2F_4Cl_2$, for which we can easily construct appropriate Lewis structures, shown here (Figure 6.12).

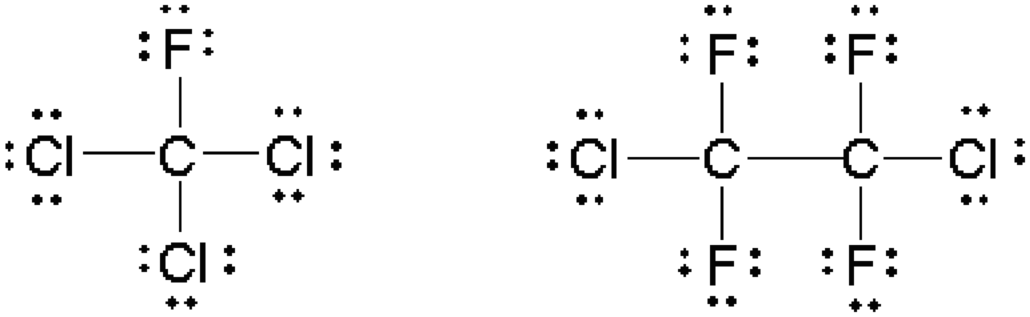

Figure 6.12

Finally, Lewis structures account for the stability of the diatomic form of the elemental halogens, F_2, Cl_2, Br_2, and I_2. The single example of F_2 is sufficient, shown here (Figure 6.13).

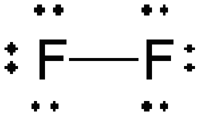

Figure 6.13

We can conclude from these examples that molecules containing oxygen, nitrogen, and the halogens are expected to be stable when these atoms all have octets of electrons in their valence shells. The Lewis structure of each molecule reveals this character explicitly.

On the other hand, there are many examples of common molecules with apparently unusual valences, including: carbon dioxide CO_2, in which the carbon is bonded to only two atoms and each oxygen is only bonded to one; formaldehyde H_2CO; and hydrogen cyanide HCN. Perhaps most conspicuously, we have yet to understand the bonding in two very important elemental diatomic molecules, O_2 and N_2, each of which has fewer atoms than the valence of either atom.

We first analyze CO_2, noting that the bond strength of one of the CO bonds in carbon dioxide is 532 kJ, which is significantly greater than the bond strength of the CO bond in ethanol, 358 kJ. By analogy to the comparison of bonds strengths in ethane to ethene, we can imagine that this difference in bond strengths results from double bonding in CO_2. Indeed, a Lewis structure of CO_2 in which only single electron pairs are shared (Figure 6.14) does not obey the octet rule, but one in which we pair and share the extra electrons reveals that double bonding permits the octet rule to be obeyed (Figure 6.15).

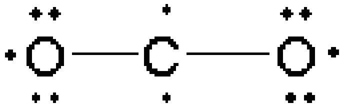

Figure 6.14

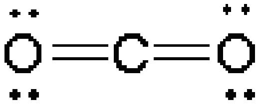

Figure 6.15

A comparison of bond lengths is consistent with our reasoning: the single CO bond in ethanol is 148 pm, whereas the double bond in CO_2 is 116.

Knowing that oxygen atoms can double-bond, we can easily account for the structure of formaldehyde. The strength of the CO bond in H_2CO is comparable to that in CO_2, consistent with the Lewis structure here (Figure 6.16).

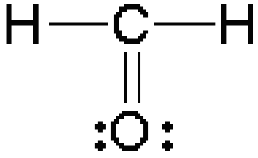

Figure 6.16

What about nitrogen atoms? We can compare the strength of the CN bond in HCN, 880 kJ, to that in methyl amine, 290 kJ. This dramatic disparity again suggests the possibility of multiple bonding, and an appropriate Lewis structure for HCN is shown here (Figure 6.17).

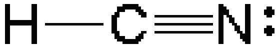

Figure 6.17

We can conclude that oxygen and nitrogen atoms, like carbon atoms, are capable of multiple bonding. Furthermore, our observations of oxygen and nitrogen reinforce our earlier deduction that multiple bonds are stronger than single bonds, and their bond lengths are shorter.

As our final examples in this section, we consider molecules in which oxygen atoms are bonded to oxygen atoms. Oxygen-oxygen bonds appear primarily in two types of molecules. The first is simply the oxygen diatomic molecule, O_2, and the second are the peroxides, typified by hydrogen peroxide, H_2O_2. In a comparison of bond energies, we find that the strength of the OO bond in O_2 is 499 kJ whereas the strength of the OO bond in H_2O_2 is 142 kJ. This is easily understood in a comparison of the Lewis structures of these molecules, showing that the peroxide bond is a single bond, whereas the O_2 bond is a double bond, shown here (Figure 6.18).

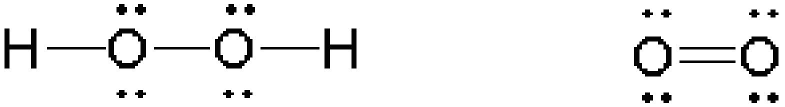

Figure 6.18

We conclude that an oxygen atom can satisfy its valence of 2 by forming two single bonds or by forming one double bond. In both cases, we can understand the stability of the resulting molecules by in terms of an octet of valence electrons.

6.6 Interpretation of Lewis Structures

Before further developing our model of chemical bonding based on Lewis structures, we pause to consider the interpretation and importance of these structures. It is worth recalling that we have developed our model based on observations of the numbers of bonds formed by individual atoms and the number of valence electrons in each atom. In general, these structures are useful for predicting whether a molecule is expected to be stable under normal conditions. If we cannot draw a Lewis structure in which each carbon, oxygen, nitrogen, or halogen has an octet of valence electrons, then the corresponding molecule probably is not stable. Consideration of bond strengths and bond lengths enhances the model by revealing the presence of double and triple bonds in the Lewis structures of some molecules.

At this point, however, we have observed no information regarding the geometries of molecules. For example, we have not considered the angles measured between bonds in molecules. Consequently, the Lewis structure model of chemical bonding does not at this level predict or interpret these bond angles. (This will be considered here (Chapter 7).) Therefore, although the Lewis structure of methane is drawn as shown here (Figure 6.19).

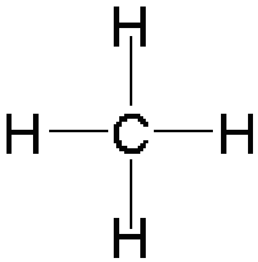

Figure 6.19

This does **not** imply that methane is a flat molecule, or that the angles between CH bonds in methane is $90\,^{\circ}$. Rather, the structure simply reveals that the carbon atom has a complete octet of valence electrons in a methane molecule, that all bonds are single bonds, and that there are no non-bonding electrons. Similarly, one can write the Lewis structure for a water molecule in two apparently different ways, shown here (Figure 6.20).

Figure 6.20

However, it is very important to realize that these two structures are **identical** in the Lewis model, because both show that the oxygen atom has a complete octet of valence electrons, forms two single bonds with hydrogen atoms, and has two pairs of unshared electrons in its valence shell. In the same way, the two structures for Freon 114 shown here (Figure 6.21) are also **identical**.

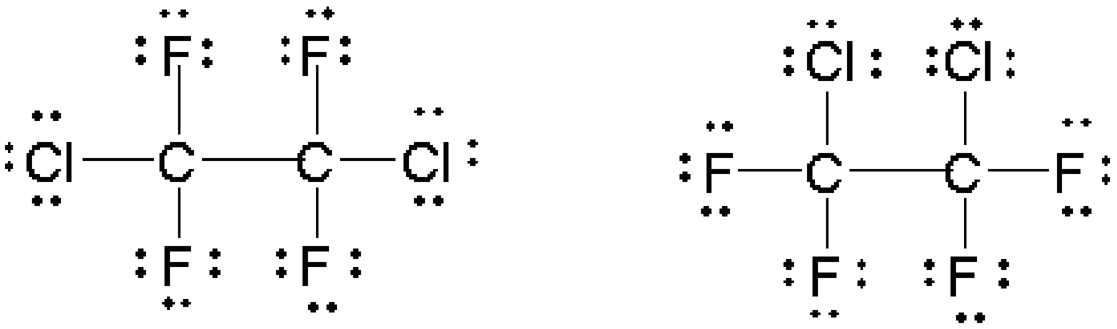

Figure 6.21

These two drawings do not represent different structures or arrangements of the atoms in the bonds.

Finally, we must keep in mind that we have drawn Lewis structures strictly as a convenient tool for our understanding of chemical bonding and molecular stability. It is based on commonly observed trends in valence, bonding, and bond strengths. These structures must not be mistaken as observations themselves, however. As we encounter additional experimental observations, we must be prepared to adapt our Lewis structure model to fit these observations, but we must never adapt our observations to fit the Lewis model.

6.7 Extensions of the Lewis Structure Model

With these thoughts in mind, we turn to a set of molecules which challenge the limits of the Lewis model in describing molecular structures. First, we note that there are a variety of molecules for which atoms clearly must bond in such a way as to have more than eight valence electrons. A conspicuous example is SF_6, where the sulfur atom is bonded to six F atoms. As such, the S atom must have 12 valence shell electrons to form 6 covalent bonds. Similarly, the phosphorous atom in PCl_5 has 10 valence electrons in 5 covalent bonds, the Cl atom in ClF_3 has 10 valence electrons in 3 covalent bonds and two lone pairs. We also observe the interesting compounds of the noble gas atoms, *e.g.* XeO_3, where noble gas atom begins with eight valence electrons even before forming any bonds. In each of these cases, we note that the valence of the atoms S, P, Cl, and Xe are normally 2, 3, 1, and 0, yet more bonds than this are formed. In such cases, it is not possible to draw Lewis structures in which S, P, Cl, and Xe obey the octet rule. We refer to these molecules as "expanded valence" molecules, meaning that the valence of the central atom has expanded beyond the expected octet.

There are also a variety of molecules for which there are too few electrons to provide an octet for every atom. Most notably, Boron and Aluminum, from Group III, display bonding behavior somewhat different than we have seen and thus less predictable from the model we have developed so far. These atoms have three valence shell electrons, so we might predict a valence of 5 on the basis of the octet rule. However, compounds in which boron or aluminum atoms form five bonds are never observed, so we must conclude that simple predictions based on the octet rule are not reliable for Group III.

Consider first boron trifluoride, BF_3. The bonding here (Figure 6.22) is relatively simple to model with a Lewis structure if we allow each valence shell electron in the boron atom to be shared in a covalent bond with each fluorine atom.

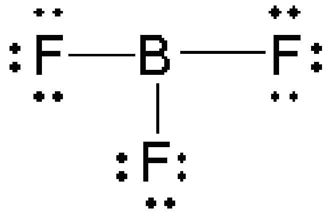

Figure 6.22

Note that, in this structure, the boron atom has only six valence shell electrons, but the octet rule is obeyed by the fluorine atoms.

We might conclude from this one example that boron atoms obey a sextet rule. However, boron will form a stable ion with hydrogen, BH_4^-, in which the boron atom does have a complete octet. In addition, BF_3 will react with ammonia NH_3 for form a stable compound, NH_3BF_3, for which a Lewis structure can be drawn in which boron has a complete octet, shown here (Figure 6.23).

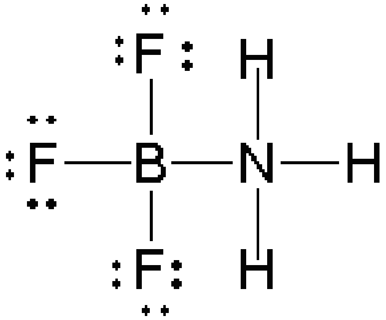

Figure 6.23

Compounds of aluminum follow similar trends. Aluminum trichloride, $AlCl_3$, aluminum hydride, AlH_3, and aluminum hydroxide, $Al(OH)_3$, all indicate a valence of 3 for aluminum, with six valence electrons in the bonded molecule. However, the stability of aluminum hydride ions, AlH_4^-, indicates that Al can also support an octet of valence shell electrons as well.

We conclude that, although the octet rule can still be of some utility in understanding the chemistry of Boron and Aluminum, the compounds of these elements are less predictable from the octet rule. This should not be disconcerting, however. The octet rule was developed in Section 6.3 (Observation 1: Valence and the Periodic Table) on the basis of the observation that, for elements in Groups IV through VIII, the number of valence electrons plus the most common valence is equal to eight. Elements in Groups I, II, and III do not follow this observation most commonly.

6.8 Resonance Structures

Another interesting challenge for the Lewis model we have developed is the set of molecules for which it is possible to draw more than one structure in agreement with the octet rule. A notable example is the nitric acid molecule, HNO_3, where all three oxygens are bonded to the nitrogen. Two structures can be drawn for nitric acid with nitrogen and all three oxygens obeying the octet rule.

In each structure, of the oxygens not bonded to hydrogen, one shares a single bond with nitrogen while the other shares a double bond with nitrogen. These two structures are not identical, unlike the two freon structures in Figure 6.12, because the atoms are bonded differently in the two structures.

6.9 Review and Discussion Questions

Exercise 6.1
Compounds with formulae of the form C_nH_{2n+2} are often referred to as "saturated" hydrocarbons. Using Lewis structures, explain how and in what sense these molecules are "saturated."

Exercise 6.2
Molecules with formulae of the form C_nH_{2n+1} (*e.g.* CH_3, C_2H_5) are called "radicals" and are extremely reactive. Using Lewis structures, explain the reactivity of these molecules.

Exercise 6.3
State and explain the experimental evidence and reasoning which shows that multiple bonds are stronger and shorter than single bonds.

Exercise 6.4
Compare N_2 to H_4N_2. Predict which bond is stronger and explain why.

Exercise 6.5
Explain why the two Lewis structures for Freon 114, shown in Figure 21Figure 6.21, are identical. Draw a Lewis structures for an isomer of Freon 114, that is, another molecule with the same molecular formula as Freon 114 but a different structural formula.

Chapter 7

Molecular Geometry and Electron Domain Theory[1]

7.1 Foundation

We begin by assuming a **Lewis structure model** for chemical bonding based on valence shell electron pair sharing and the octet rule. We thus assume the nuclear structure of the atom, and we further assume the existence of a valence shell of electrons in each atom which dominates the chemical behavior of that atom. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. A number of atoms, including C, N, O, P, and S, can form double or triple bonds as needed to complete an octet. We know that double bonds are generally stronger and have shorter lengths than single bonds, and triple bonds are stronger and shorter than double bonds.

7.2 Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. The relationship between bonding, structure, and properties is comparatively simple in **diatomic** molecules, which contain two atoms only, *e.g.* HCl or O_2. A **polyatomic** molecule contains more than two atoms. An example of the complexities which arise with polyatomic molecules is molecular geometry: how are the atoms in the molecule arranged with respect to one another? In a diatomic molecule, only a single molecular geometry is possible since the two atoms must lie on a line. However, with a triatomic molecule (three atoms), there are two possible geometries: the atoms may lie on a line, producing a linear molecule, or not, producing a bent molecule. In molecules with more than three atoms, there are many more possible geometries. What geometries are actually observed? What determines which geometry will be observed in a particular molecule? We seek a model which allows us to understand the observed geometries of molecules and thus to predict these geometries.

Once we have developed an understanding of the relationship between molecular structure and chemical bonding, we can attempt an understanding of the relationship of he structure and bonding in a polyatomic molecule to the physical and chemical properties we observe for those molecules.

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[1] This content is available online at <http://cnx.org/content/m12594/1.1/>.

7.3 Observation 1: Geometries of molecules

The geometry of a molecule includes a description of the arrangements of the atoms in the molecule. At a simple level, the molecular structure tells us which atoms are bonded to which. At a more detailed level, the geometry includes the lengths of all of these bonds, that is, the distances between the atoms which are bonded together, and the angles between pairs of bonds. For example, we find that in water, H_2O, the two hydrogens are bonded to the oxygen and each O-H bond length is 95.72pm (where 1pm = $10^{-12}m$). Furthermore, H_2O is a bent molecule, with the H-O-H angle equal to 104.5 °. (The measurement of these geometric properties is difficult, involving the measurement of the frequencies at which the molecule rotates in the gas phase. In molecules in crystalline form, the geometry of the molecule is revealed by irradiating the crystal with x-rays and analyzing the patterns formed as the x-rays diffract off of the crystal.)

Not all triatomic molecules are bent, however. As a common example, CO_2 is a linear molecule. Larger polyatomics can have a variety of shapes, as illustrated in Figure 7.1 (Molecular Structures). Ammonia, NH_3, is a pyramid-shaped molecule, with the hydrogens in an equilateral triangle, the nitrogen above the plane of this triangle, and a H-N-H angle equal to 107 °. The geometry of CH_4 is that of a tetrahedron, with all H-C-H angles equal to 109.5 °. (See also Figure 7.2(a).) Ethane, C_2H_6, has a geometry related to that of methane. The two carbons are bonded together, and each is bonded to three hydrogens. Each H-C-H angle is 109.5 ° and each H-C-C angle is 109.5 °. By contrast, in ethene, C_2H_4, each H-C-H bond angle is 116.6 ° and each H-C-C bond angle is 121.7 °. All six atoms of ethene lie in the same plane. Thus, ethene and ethane have very different geometries, despite the similarities in their molecular formulae.

Molecular Structures

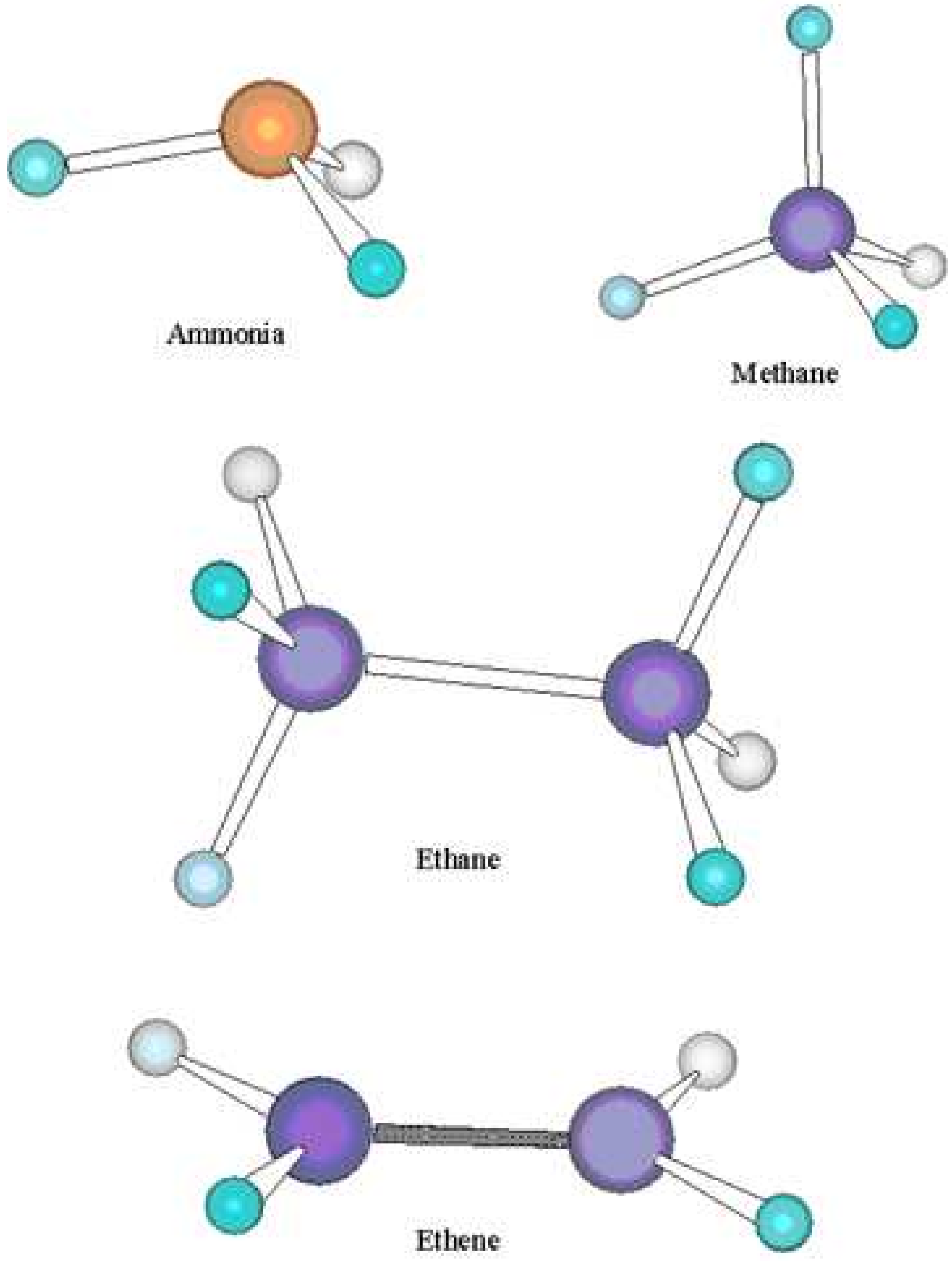


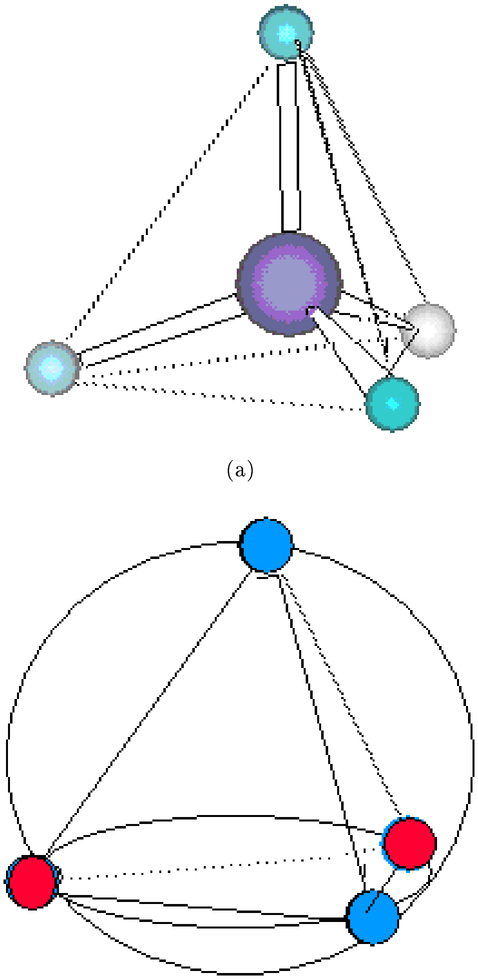
Figure 7.1

We begin our analysis of these geometries by noting that, in the molecules listed above which do **not** contain double or triple bonds (H_2O, NH_3, $CH_4$and C_2H_6), the bond angles are very similar, each equal to or very close to the tetrahedral angle 109.5 °. To account for the observed angle, we begin with our valence shell electron pair sharing model, and we note that, in the Lewis structures of these molecules, the central atom in each bond angle of these molecules contains four pairs of valence shell electrons. For methane and ethane, these four electron pairs are all shared with adjacent bonded atoms, whereas in

ammonia or water, one or two (respectively) of the electron pairs are not shared with any other atom. These unshared electron pairs are called **lone pairs** . Notice that, in the two molecules with no lone pairs, all bond angles are **exactly** equal to the tetrahedral angle, whereas the bond angles are only close in the molecules with lone pairs

One way to understand this result is based on the mutual repulsion of the negative charges on the valence shell electrons. Although the two electrons in each bonding pair must remain relatively close together in order to form the bond, different pairs of electrons should arrange themselves in such a way that the distances between the pairs are as large as possible. Focusing for the moment on methane, the four pairs of electrons must be equivalent to one another, since the four C-H bonds are equivalent, so we can assume that the electron pairs are all the same distance from the central carbon atom. How can we position four electron pairs at a fixed distance from the central atom but as far apart from one another as possible? A little reflection reveals that this question is equivalent to asking how to place four points on the surface of a sphere spread out from each other as far apart as possible. A bit of experimentation reveals that these four points must sit at the corners of a tetrahedron, an equilateral triangular pyramid, as may be seen in Figure 7.2(b). If the carbon atom is at the center of this tetrahedron and the four electron pairs at placed at the corners, then the hydrogen atoms also form a tetrahedron about the carbon. This is, as illustrated in Figure 7.2(a), the correct geometry of a methane molecule. The angle formed by any two corners of a tetrahedron and the central atom is 109.5 °, exactly in agreement with the observed angle in methane. This model also works well in predicting the bond angles in ethane.

Tetrahedral Structure of Methane



(a)

(b)

Figure 7.2: (a) The dotted lines illustrate that the hydrogens form a tetrahedron about the carbon atom. (b) The same tetrahedron is formed by placing four points on a sphere as far apart from one another as possible.

We conclude that molecular geometry is determined by minimizing the mutual repulsion of the valence shell electron pairs. As such, this model of molecular geometry is often referred to as the **valence shell electron pair repulsion (VSEPR) theory** . For reasons that will become clear, extension of this model implies that a better name is the **Electron Domain (ED) Theory** .

This model also accounts, at least approximately, for the bond angles of H_2O and NH_3. These molecules are clearly not tetrahedral, like CH_4, since neither contains the requisite five atoms to form the tetrahedron. However, each molecule does contain a central atom surrounded by four pairs of valence shell electrons. We expect from our Electron Domain model that those four pairs should be arrayed in a tetrahedron, without regard to whether they are bonding or lone-pair electrons. Then attaching the hydrogens (two for oxygen, three for nitrogen) produces a prediction of bond angles of 109.5 °, very close indeed to the observed angles of 104.5 ° in H_2O and 107 ° in NH_3.

Note, however, that we do not describe the geometries of H_2O and NH_3 as "tetrahedral," since the **atoms** of the molecules do not form tetrahedrons, even if the valence shell electron pairs do. (It is worth noting that these angles are not exactly equal to 109.5 °, as in methane. These deviations will be discussed later (Section 7.5: Observation 3: Distortions from Expected Geometries).)

We have developed the Electron Domain model to this point only for geometries of molecules with four pairs of valence shell electrons. However, there are a great variety of molecules in which atoms from Period 3 and beyond can have more than an octet of valence electrons. We consider two such molecules illustrated in Figure 7.3 (More Molecular Structures).

More Molecular Structures

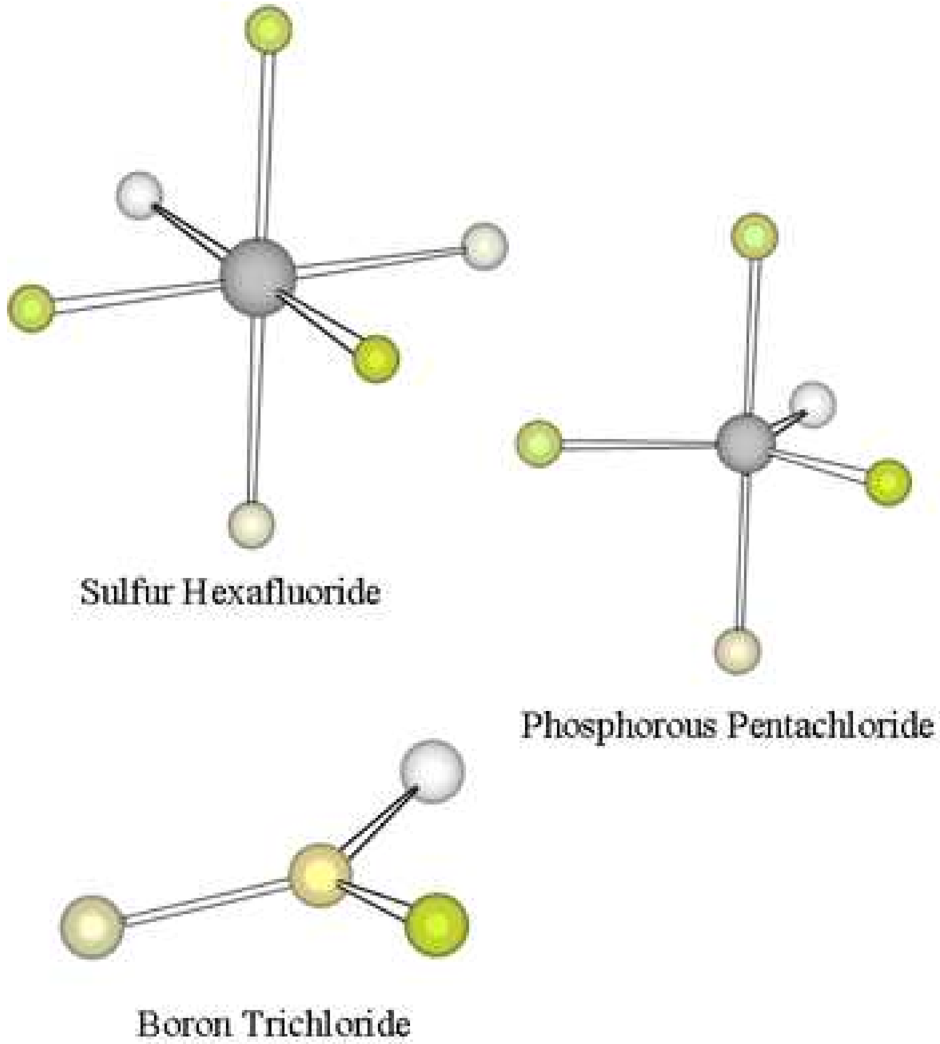


Figure 7.3

First, PCl_5 is a stable gaseous compound in which the five chlorine atoms are each bonded to the phosphorous atom. Experiments reveal that the geometry of PCl_5 is that of a **trigonal bipyramid** : three of the chlorine atoms form an equilateral triangle with the P atom in the center, and the other two chlorine atoms are on top of and below the P atom. Thus there must be 10 valence shell electrons around the phosphorous atom. Hence, phosphorous exhibits what is called an **expanded valence** in PCl_5. Applying our Electron Domain model, we expect the five valence shell electron pairs to spread out optimally to minimize their repulsions. The required geometry can again be found by trying to place five points on the surface of a sphere with maximum distances amongst these points. A little experimentation reveals that this can be achieved by placing the five points to form a trigonal bipyramid. Hence, Electron Domain theory accounts for the geometry of PCl_5.

Second, SF_6 is a fairly unreactive gaseous compound in which all six fluorine atoms are bonded to the central sulfur atom. Again, it is clear that the octet rule is violated by the sulfur atom, which must therefore have an expanded valence. The observed geometry of SF_6, as shown in Figure 7.3 (More Molecular Structures), is highly symmetric: all bond lengths are identical and all bond angles are 90 °. The F atoms form an **octahedron** about the central S atom: four of the F atoms form a square with the S atom at the center, and the other two F atoms are above and below the S atom. To apply our Electron Domain model to understand this geometry, we must place six points, representing the six electron pairs about the central S atom, on the surface of a sphere with maximum distances between the points. The requisite geometry is found, in fact, to be that of an octahedron, in agreement with the observed geometry.

As an example of a molecule with an atom with less than an octet of valence shell electrons, we consider boron trichloride, BCl_3. The geometry of BCl_3 is also given in Figure 7.3 (More Molecular Structures): it is **trigonal planar** , with all four atoms lying in the same plane, and all Cl-B-Cl bond angles equal to 120 °. The three Cl atoms form an equilateral triangle. The Boron atom has only three pairs of valence shell electrons in BCl_3. In applying Electron Domain theory to understand this geometry, we must place three points on the surface of a sphere with maximum distance between points. We find that the three points form an equilateral triangle in a plane with the center of the sphere, so Electron Domain is again in accord with the observed geometry.

We conclude from these predictions and observations that the Electron Domain model is a reasonably accurate way to understand molecular geometries, even in molecules which violate the octet rule.

7.4 Observation 2: Molecules with Double or Triple Bonds

In each of the molecules considered up to this point, the electron pairs are either in single bonds or in lone pairs. In current form, the Electron Domain model does **not** account for the observed geometry of C_2H_4, in which each H-C-H bond angle is 116.6 ° and each H-C-C bond angle is 121.7 ° and all six atoms lie in the same plane. Each carbon atom in this molecule is surrounded by four pairs of electrons, all of which are involved in bonding, *i.e.* there are no lone pairs. However, the arrangement of these electron pairs, and thus the bonded atoms, about each carbon is not even approximately tetrahedral. Rather, the H-C-H and H-C-C bond angles are much closer to 120 °, the angle which would be expected if **three** electron pairs were separated in the optimal arrangement, as just discussed for BCl_3.

This observed geometry can be understood by re-examining the Lewis structure. Recall that, although there are four electron pairs about each carbon atom, two of these pairs form a double bond between the carbon atoms. It is tempting to assume that these four electron pairs are forced apart to form a tetrahedron as in previous molecules. However, if this were this case, the two pairs involved in the double bond would be separated by an angle of 109.5 ° which would make it impossible for both pairs to be localized between the carbon atoms. To preserve the double bond, we must assume that the two electron pairs in the double bond remain in the same vicinity. Given this assumption, separating the three **independent** groups of electron pairs about a carbon atom produces an expectation that all three pairs should lie in the same plane as the carbon atom, separated by 120 ° angles. This agrees very closely with the observed bond angles. We conclude that the our model can be extended to understanding the geometries of molecules with double (or triple) bonds by treating the multiple bond as two electron pairs confined to a single **domain**. It is for this reason that we refer to the model as Electron Domain theory.

Applied in this form, Electron Domain theory can help us understand the linear geometry of CO_2. Again, there are four electron pairs in the valence shell of the carbon atom, but these are grouped into only two domains of two electron pairs each, corresponding to the two C=O double bonds. Minimizing the repulsion between these two domains forces the oxygen atoms to directly opposite sides of the carbon, producing a linear molecule. Similar reasoning using Electron Domain theory as applied to triple bonds correctly predicts that acetylene, $HCCH$, is a linear molecule. If the electron pairs in the triple bond are treated as a single domain, then each carbon atom has only two domains each. Forcing these domains to opposite sides from one another accurately predicts 180 ° H-C-C bond angles.

7.5 Observation 3: Distortions from Expected Geometries

It is interesting to note that some molecular geometries (CH_4, CO_2, $HCCH$) are exactly predicted by the Electron Domain model, whereas in other molecules, the model predictions are only approximately correct. For examples, the observed angles in ammonia and water each differ slightly from the tetrahedral angle. Here again, there are four pairs of valence shell electrons about the central atoms. As such, it is reasonable to conclude that the bond angles are determined by the mutual repulsion of these electron pairs, and are thus expected to be 109.5 °, which is close but not exact.

One clue as to a possible reason for the discrepancy is that the bond angles in ammonia and water are both **less** than 109.5 °. Another is that both ammonia and water molecules have lone pair electrons, whereas there are no lone pairs in a methane molecule, for which the Electron Domain prediction is exact. Moreover, the bond angle in water, with two lone pairs, is less than the bond angles in ammonia, with a single lone pair. We can straightforwardly conclude from these observations that the lone pairs of electrons must produce a greater repulsive effect than do the bonded pairs. Thus, in ammonia, the three bonded pairs of electrons are forced together slightly compared to those in methane, due to the greater repulsive effect of the lone pair. Likewise, in water, the two bonded pairs of electrons are even further forced together by the two lone pairs of electrons.

This model accounts for the comparative bond angles observed experimentally in these molecules. The valence shell electron pairs repel one another, establishing the geometry in which the energy of their interaction is minimized. Lone pair electrons apparently generate a greater repulsion, thus slightly reducing the angles between the bonded pairs of electrons. Although this model accounts for the observed geometries, why should lone pair electrons generate a greater repulsive effect? We must guess at a qualitative answer to this question, since we have no description at this point for where the valence shell electron pairs actually are or what it means to share an electron pair. We can assume, however, that a pair of electrons shared by two atoms must be located somewhere between the two nuclei, otherwise our concept of "sharing" is quite meaningless. Therefore, the powerful tendency of the two electrons in the pair to repel one another must be significantly offset by the localization of these electrons between the two nuclei which share them. By contrast, a lone pair of electrons need not be so localized, since there is no second nucleus to draw them into the same vicinity. Thus more free to move about the central atom, these lone pair electrons must have a more significant repulsive effect on the other pairs of electrons.

These ideas can be extended by more closely examining the geometry of ethene, C_2H_4 . Recall that each H-C-H bond angle is 116.6 ° and each H-C-C bond angle is 121.7 °, whereas the Electron Domain theory prediction is for bond angles exactly equal to 120 °. We can understand why the H-C-H bond angle is slightly less than 120 ° by assuming that the two pairs of electrons in the C=C double bond produce a greater repulsive effect than do either of the single pairs of electrons in the C-H single bonds. The result of this greater repulsion is a slight "pinching" of the H-C-H bond angle to less than 120 °.

The concept that lone pair electrons produce a greater repulsive effect than do bonded pairs can be used to understand other interesting molecular geometries. Sulfur tetrafluoride, SF_4, is a particularly interesting example, shown in Figure 7.4 (Molecular Structure of SF4).

Molecular Structure of SF4

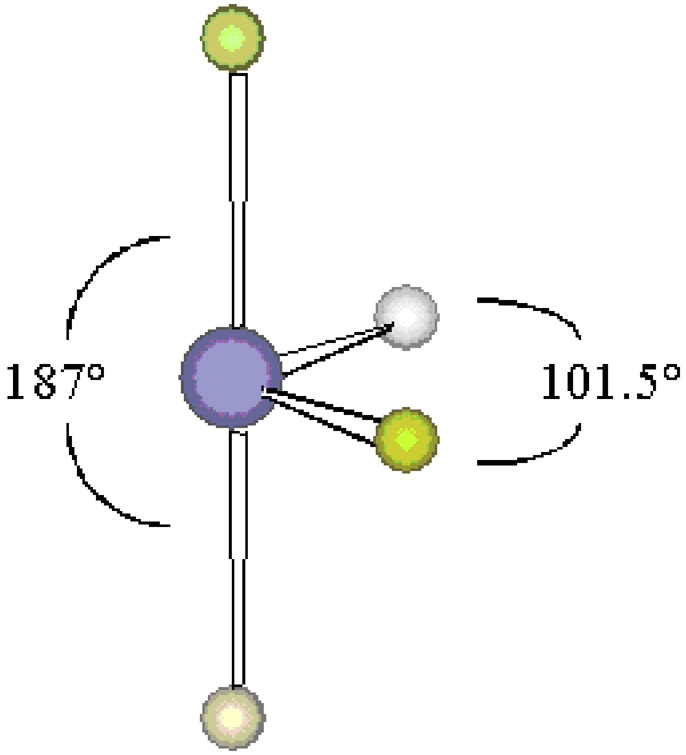


Figure 7.4

Note that two of the fluorines form close to a straight line with the central sulfur atom, but the other two are approximately perpendicular to the first two and at an angle of 101.5 ° to each other. Viewed sideways, this structure looks something like a seesaw.

To account for this structure, we first prepare a Lewis structure. We find that each fluorine atom is singly bonded to the sulfur atom, and that there is a lone pair of electrons on the sulfur. Thus, with five electron pairs around the central atom, we expect the electrons to arrange themselves in a trigonal bipyramid, similar to the arrangement in PCl_5 in Figure 7.3 (More Molecular Structures). In this case, however, the fluorine atoms and the lone pair could be arranged in two different ways with two different resultant molecular structures. The lone pair can either go on the axis of the trigonal bipyramid (*i.e.* "above" the sulfur) or on the equator of the bipyramid (*i.e.* "beside" the sulfur).

The actual molecular structure in Figure 7.4 (Molecular Structure of SF4) shows clearly that the lone pair goes on the equatorial position. This can be understood if we assume that the lone pair produces a greater repulsive effect than do the bonded pairs. With this assumption, we can deduce that the lone pair should be placed in the trigonal bipyramidal arrangement as far as possible from the bonded pairs. The equatorial position does a better job of this, since only two bonding pairs of electrons are at approximately 90 ° angles from the lone pair in this position. By contrast, a lone pair in the axial position is approximately 90 ° away from three bonding pairs. Therefore, our Electron Domain model assumptions are consistent with the observed geometry of SF_4. Note that these assumptions also correctly predict the observed distortions away from the 180 ° and 120 ° angles which would be predicted by a trigonal bipyramidal arrangement of the five electron pairs.

7.6 Review and Discussion Questions

Exercise 7.1
Using a styrofoam or rubber ball, prove to yourself that a tetrahedral arrangement provides the maximum separation of four points on the surface of the ball. Repeat this argument to find the expected arrangements for two, three, five, and six points on the surface of the ball.

Exercise 7.2
Explain why arranging points on the surface of a sphere can be considered equivalent to arranging electron pairs about a central atom.

Exercise 7.3
The valence shell electron pairs about the central atom in each of the molecules H_2O, NH_3, and CH_4 are arranged approximately in a tetrahedron. However, only CH_4 is considered a tetrahedral molecule. Explain why these statements are not inconsistent.

Exercise 7.4
Explain how a comparison of the geometries of H_2O and CH_4 leads to a conclusion that lone pair electrons produce a greater repulsive effect than do bonded pairs of electrons. Give a physical reason why this might be expected.

Exercise 7.5
Explain why the octet of electrons about each carbon atom in ethene, C_2H_4, are not arranged even approximately in a tetrahedron.

Exercise 7.6
Assess the accuracy of the following reasoning and conclusions:

A trigonal bipyramid forms when there are five electron domains. If one ED is a lone pair, then the lone pair takes an equatorial position and the molecule has a seesaw geometry. If two EDs are lone pairs, we have to decide among the following options: both axial, both equatorial, or one axial and one equatorial. By placing both lone pairs in the axial positions, the lone pairs are as far apart as possible, so the trigonal planar structure is favored.

Exercise 7.7
Assess the accuracy of the following reasoning and conclusions:

The Cl-X-Cl bond angles in the two molecules (Figure 7.5) are identical, because the bond angle is determined by the repulsion of the two Cl atoms, which is identical in the two molecules.

Figure 7.5

Chapter 8

Molecular Structure and Physical Properties[1]

8.1 Foundation

We begin with our knowledge of the structure and properties of atoms. We know that atoms have a nuclear structure, meaning that all of the positive charge and virtually all of the mass of the atom are concentrated in a nucleus which is a very small fraction of the volume of the atom. In addition, we know that many of the properties of atoms can be understood by a model in which the electrons in the atom are arranged in "shells" about the nucleus, with each shell farther from the nucleus that the previous. The electrons in outer shells are more weakly attached to the atom than the electrons in the inner shells, and only a limited number of electrons can fit in each shell. Within each shell are subshells, each of which can also hold a limited number of electrons. The electrons in different subshells have different energies and different locations for motion about the nucleus. We also assume a knowledge of the a **Lewis structure** model for chemical bonding based on valence shell electron pair sharing and the octet rule. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. We finally assume the **Electron Domain Model** for understanding and predicting molecular geometries. The pairs of valence shell electrons are arranged in bonding and non-bonding domains, and these domains are separated in space to minimize electron-electron repulsions. This electron domain arrangement determines the molecular geometry.

8.2 Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. Now that we have developed an understanding of the relationship between molecular structure and chemical bonding, we analyze physical properties of the molecules and compounds of these molecules to relate to this bonding and structure. Simple examples of physical properties which can be related to molecular properties are the melting and boiling temperatures. These vary dramatically from substance to substance, even for substances which appear similar in molecular formulae, with some melting temperatures in the hundreds or thousands of degrees Celsius and others well below 0 °C. We seek to understand these variations by analyzing molecular structures.

To develop this understanding, we will have to apply more details of our understanding of atomic structure and electronic configurations. In our covalent bonding model, we have assumed that atoms "share" electrons to form a bond. However, our knowledge of the properties of atoms reveals that different atoms attract

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[1] This content is available online at <http://cnx.org/content/m12595/1.1/>.

electrons with different strengths, resulting in very strong variations in ionization energies, atomic radii, and electron affinities. We seek to incorporate this information into our understanding of chemical bonding

8.3 Observation 1: Compounds of Groups I and II

We begin by analyzing compounds formed from elements from Groups I and II (*e.g.* sodium and magnesium). These compounds are not currently part of our Lewis structure model. For example, Sodium, with a single valence electron, is unlikely to gain seven additional electrons to complete an octet. Indeed, the common valence of the alkali metals in Group I is 1, not 7, and the common valence of the alkaline earth metals is 2, not 6. Thus, our current model of bonding does not apply to elements in these groups.

To develop an understanding of bonding in these compounds, we focus on the halides of these elements. In Table 8.1: Melting Points and Boiling Points of Chloride Compounds, we compare physical properties of the chlorides of elements in Groups I and II to the chlorides of the elements of Groups IV, V, and VI, and we see enormous differences. All of the alkali halides and alkaline earth halides are solids at room temperature and have melting points in the hundreds of degrees centigrade. The melting point of $NaCl$ is 808 °C, for example. By contrast, the melting points of the non-metal halides from Periods 2 and 3, such as CCl_4, PCl_3, and SCl_2, are below 0 °C, so that these materials are liquids at room temperature. Furthermore, all of these compounds have low boiling points, typically in the range of 50 °C to 80 °C.

Melting Points and Boiling Points of Chloride Compounds

	Melting Point (°C)	**Boiling Point (°C)**
$LiCl$	610	1382
$BeCl_2$	405	488
CCl_4	-23	77
NCl_3	-40	71
OCl_2	-20	4
FCl	-154	-101
$NaCl$	808	1465
$MgCl_2$	714	1418
$SiCl_4$	-68	57
PCl_3	-91	74
SCl_2	-122	59
Cl_2	-102	-35
KCl	772	1407
$CaCl_2$	772	>1600

Table 8.1

Second, the non-metal halide liquids are electrical insulators, that is, they do not conduct an electrical current. By contrast, when we melt an alkali halide or alkaline earth halide, the resulting liquid is an excellent electrical conductor. This indicates that these molten compounds consist of ions, whereas the non-metal halides do not.

We must conclude that the bonding of atoms in alkali halides and alkaline earth halides differs significantly from bonding in non-metal halides. We need to extend our valence shell electron model to account for this bonding, and in particular, we must account for the presence of ions in the molten metal halides. Consider the prototypical example of $NaCl$. We have already deduced that Cl atoms react so as to form a complete octet of valence shell electrons. Such an octet could be achieved by covalently sharing the single valence shell electron from a sodium atom. However, such a covalent sharing is clearly inconsistent with the presence of ions in molten sodium chloride. Furthermore, this type of bond would predict that $NaCl$ should have similar properties to other covalent chloride compounds, most of which are liquids at room temperature. By contrast, we might imagine that the chlorine atom completes its octet by taking the valence shell electron from a sodium atom, without covalent sharing. This would account for the presence of Na^+ and Cl^- ions in molten sodium chloride.

In the absence of a covalent sharing of an electron pair, though, what accounts for the stability of sodium chloride as a compound? It is relatively obvious that a negatively charged chloride ion will be attracted electrostatically to a positively charged sodium ion. We must also add to this model, however, the fact that individual molecules of $NaCl$ are not generally observed at temperatures less than 1465 °C, the boiling point of sodium chloride. Note that, if solid sodium chloride consists of individual sodium ions in proximity to individual chloride ions, then each positive ion is not simply attracted to a single specific negative ion but rather to all of the negative ions in its near vicinity. Hence, solid sodium chloride cannot be viewed as individual $NaCl$ molecules, but must be viewed rather as a lattice of positive sodium ions interacting with negative chloride ions. This type of "ionic" bonding, which derives from the electrostatic attraction of interlocking lattices of positive and negative ions, accounts for the very high melting and boiling points of the alkali halides.

We can now draw modified Lewis structures to account for ionic bonding, but these are very different from our previous drawings. Sodium chloride can be represented as shown in Figure 8.1.

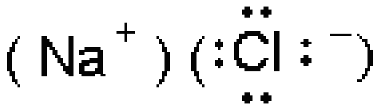

Figure 8.1

This indicates explicitly that the bonding is due to positive-negative ion attraction, and not due to sharing of an electron pair. The only sense in which the Na^+ ion has obeyed an octet rule is perhaps that, in having emptied its valence shell of electrons, the remaining outer shell of electrons in the ion has the same octet as does a neon atom. We must keep in mind, however, that the positive sodium ion is attracted to many negative chloride ions, and not just the single chloride ion depicted in the Lewis structure.

8.4 Observation 2: Molecular Dipole Moments

Our Lewis model of bonding, as currently developed, incorporates two extreme views of the distribution of electrons in a bond. In a covalent bond, we have assumed up to this point that the electron pair is shared perfectly. In complete contrast, in ionic bonding we have assumed that the electrons are not shared at all. Rather, one of the atoms is assumed to entirely extract one or more electrons from the other. We might expect that a more accurate description of the reality of chemical bonds falls in general somewhere between these two extremes. To observe this intermediate behavior, we can examine molecular dipole moments.

An electric dipole is a spatial separation of positive and negative charges. In the simplest case, a positive charge Q and a negative charge $-Q$ separated by a distance R produce a measurable **dipole moment**, μ equal to $Q \times R$. An electric field can interact with an electric dipole and can even orient the dipole in the direction of the field.

We might initially expect that molecules do not in general have dipole moments. Each atom entering into a chemical bond is electrically neutral, with equal numbers of positive and negative charges. Consequently, a molecule formed from neutral atoms must also be electrically neutral. Although electron pairs are shared between bonded nuclei, this does not affect the total number of negative charges. We might from these simple statements that molecules would be unaffected by electric or magnetic fields, each molecule behaving as a single uncharged particle.

This prediction is incorrect, however. To illustrate, a stream of water can be deflected by an electrically charged object near the stream, indicating that individual water molecules exhibit a dipole moment. A water molecule is rather more complicated than a simple separation of a positive and negative charges, however. Recall though that a water molecule has equal total numbers of positive and negative charges, consisting of three positively charged nuclei surrounded by ten electrons. Nevertheless, measurements reveal that water has a dipole moment of $6.17 \times 10^{-30} \, (Cm) = 1.85$debye. (The debye is a unit used to measure dipole moments: 1debye $= 3.33 \times 10^{-30} \, (Cm)$.) Water is not unique: the molecules of most substances have dipole moments. A sampling of molecules and their dipole moments is given in Table 8.2: Dipole Moments of Specific Molecules.

Dipole Moments of Specific Molecules

	μ **(debye)**
H_2O	1.85
HF	1.91
HCl	1.08
HBr	0.80
HI	0.42
CO	0.12
CO_2	0
NH_3	1.47
PH_3	0.58
AsH_3	0.20
CH_4	0
$NaCl$	9.00

Table 8.2

Focusing again on the water molecule, how can we account for the existence of a dipole moment in a neutral molecule? The existence of the dipole moment reveals that a water molecule must have an internal separation of positive partial charge δ and negative partial charge $-\delta$. Thus, it must be true that the electrons in the covalent bond between hydrogen and oxygen are not **equally** shared. Rather, the shared electrons must spend more time in the vicinity of one nucleus than the other. The molecule thus has one region where, on average, there is a net surplus of negative charge and one region where, on average, there is a compensating surplus of positive charge, thus producing a molecular dipole. Additional observations reveal that the oxygen "end" of the molecule holds the partial negative charge. Hence, the covalently shared electrons spend more time near the oxygen atom than near the hydrogen atoms. We conclude that oxygen atoms have a greater ability to attract the shared electrons in the bond than do hydrogen atoms.

We should not be surprised by the fact that individual atoms of different elements have differing abilities to attract electrons to themselves. We have previously seen that different atoms have greatly varying ionization energies, representing great variation in the extent to which atoms cling to their electrons. We have also seen great variation in the electron affinities of atoms, representing variation in the extent to which atoms attract an added electron. We now define the **electronegativity** of an atom as the ability of the atom to attract electrons in a chemical bond. This is different than either ionization energy or electron affinity, because electronegativity is the attraction of electrons **in a chemical bond**, whereas ionization energy and electron affinity refer to removal and attachment of electrons in free atoms. However, we can expect electronegativity to be correlated with electron affinity and ionization energy. In particular, the electronegativity of an atom arises from a combination of properties of the atom, including the size of the atom, the charge on the nucleus, the number of electrons about the nuclei, and the number of electrons in the valence shell.

Because electronegativity is an abstractly defined property, it cannot be directly measured. In fact, there are many definitions of electronegativity, resulting in many different scales of electronegativities. However, relative electronegativities can be observed indirectly by measuring molecular dipole moments: in general, the greater the dipole moment, the greater the separation of charges must be, and therefore, the less equal the sharing of the bonding electrons must be.

With this in mind, we refer back to the dipoles given in Table 8.2: Dipole Moments of Specific Molecules. There are several important trends in these data. Note that each hydrogen halide (HF, HCl, HBr, and HI) has a significant dipole moment. Moreover, the dipole moments increase as we move **up** the periodic table in the halogen group. We can conclude that fluorine atoms have a greater electronegativity than do chlorine atoms, *etc.* Note also that HF has a greater dipole moment than H_2O, which is in turn greater than that of NH_3. We can conclude that electronegativity increases as we move **across** the periodic table from left to right in a single period. These trends hold generally in comparisons of the electronegativities of the individual elements. One set of relative electronegativities of atoms in the first three rows of the periodic table is given in Table 8.3: Electronegativities of Selected Atoms.

Electronegativities of Selected Atoms

	χ
H	2.1
He	-
Li	1.0
Be	1.5
B	2.0
C	2.5
N	3.0
O	3.5
F	4.0
Ne	-
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0
Ar	-
K	0.8
Ca	1.0

Table 8.3

8.5 Observation 3: Dipole Moments in Polyatomic Molecules

We might reasonably expect from our analysis to observe a dipole moment in any molecule formed from atoms with different electronegativities. Although this must be the case for a diatomic molecule, this is not necessarily true for a polyatomic molecule, *i.e.* one with more than two atoms. For example, carbon is more electronegative than hydrogen. However, the simplest molecule formed from carbon and hydrogen (*e.g.* CH_4) does **not** possess a dipole moment, as we see in Table 8.2: Dipole Moments of Specific Molecules. Similarly, oxygen is significantly more electronegative than carbon, yet CO_2 is a non-polar molecule. An analysis of molecular dipole moments in polyatomic molecules requires us to apply our understanding of molecular geometry.

Note that each CO bond is expected to be polar, due to the unequal sharing of the electron pairs between the carbon and the oxygen. Thus, the carbon atom should have a slight positive charge and the oxygen atom a slight negative charge in each CO bond. However, since each oxygen atom should have the same net negative charge, neither end of the molecule would display a greater affinity for an electric field. Moreover, because CO_2 is linear, the dipole in one CO bond is exactly offset by the dipole in the opposite direction due to the other CO bond. As measured by an electric field from a distance, the CO_2 molecule does not appear to have separated positive and negative charges and therefore does not display polarity. Thus, in predicting molecular dipoles we must take into account both differences in electronegativity, which affect bond polarity, and overall molecular geometry, which can produce cancellation of bond polarities.

Using this same argument, we can rationalize the zero molecular dipole moments observed for other molecules, such as methane, ethene and acetylene. In each of these molecules, the individual CH bonds are polar. However, the symmetry of the molecule produces a cancellation of these bond dipoles overall, and none of these molecules have a molecular dipole moment.

As an example of how a molecular property like the dipole moment can affect the macroscopic property of a substance, we can examine the boiling points of various compounds. The boiling point of a compound is determined by the strength of the forces between molecules of the compound: the stronger the force, the more energy is required to separate the molecules, the higher the temperature required to provide this energy. Therefore, molecules with strong intermolecular forces have high boiling points.

We begin by comparing molecules which are similar in size, such as the hydrides SiH_4, PH_3, and SH_2 from the third period. The boiling points at standard pressure for these molecules are, respectively, -111.8 °C, -87.7 °C, and -60.7 °C. All three compounds are thus gases at room temperature and well below. These molecules have very similar masses and have exactly the same number of electrons. However, the dipole moments of these molecules are very different. The dipole moment of SiH_4, is 0.0D, the dipole moment of PH_3 is 0.58D, and the dipole moment of SH_2 is 0.97D. Note that, for these similar molecules, the higher the dipole moment, the higher the boiling point. Thus, molecules with larger dipole moments generally have stronger intermolecular forces than similar molecules with smaller dipole moments. This is because the positive end of the dipole in one molecule can interact electrostatically with the negative end of the dipole in another molecules, and vice versa.

We note, however, that one cannot generally predict from dipole moment information only the relative boiling points of compounds of very dissimilar molecules

8.6 Review and Discussion Questions

Exercise 8.1
Compare and contrast the chemical and physical properties of KCl and CCl_4, and compare and contrast how the chemical bonding model can be used to account for these properties.

Exercise 8.2
Why is the dipole moment of $NaCl$ extremely large?

Exercise 8.3
Explain why CO has a dipole moment but CO_2 does not.

Exercise 8.4
Explain why an atom with a high ionization energy is expected to have a high electronegativity. Explain why an atom with a high electron affinity is expected to have a high electronegativity.

Exercise 8.5
Would you predict that a Kr atom has high electronegativity or low electronegativity? Predict the relative electronegativity of Kr and F.

Exercise 8.6
Explain why S has a greater electronegativity than P but a smaller electronegativity than O.

Exercise 8.7
N atoms have a high electronegativity. However, N atoms have no electron affinity, meaning that N atoms do not attract electrons. Explain how and why these facts are not inconsistent.

Exercise 8.8
Explain why compounds formed from elements with large differences in electronegativities are ionic.

Exercise 8.9
Explain why ionic compounds have much higher melting points than covalent compounds.

Chapter 9

Chemical Bonding and Molecular Energy Levels[1]

9.1 Foundation

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

9.2 Goals

Our model of valence describes a chemical bond as resulting from the sharing of a pair of electrons in the valence shell of the bonded atoms. This sharing allows each atom to complete an octet of electrons in its valence shell, at least in the sense that we count the shared electrons as belonging to both atoms. However, it is not clear that this electron counting picture has any basis in physical reality. What is meant, more precisely, by the sharing of the electron pair in a bond, and why does this result in the bonding of two atoms together? Indeed, what does it mean to say that two atoms are bound together? Furthermore, what is the significance of sharing a pair of electrons? Why aren't chemical bonds formed by sharing one or three electrons, for example?

We seek to understand how the details of chemical bonding are related to the properties of the molecules formed, particularly in terms of the strengths of the bonds formed.

9.3 Observation 1: Bonding with a Single Electron

We began our analysis of the energies and motions of the electrons in atoms by observing the properties of the simplest atom, hydrogen, with a single electron. Similarly, to understand the energies and motions of electrons which lead to chemical bonding, we begin our observations with the simplest particle with a chemical bond, which is the H_2^+ molecular ion. Each hydrogen nucleus has a charge of $+1$. An H_2^+ molecular ion therefore has a single electron. It seems inconsistent with our notions of valence that a single electron, rather than an electron pair, can generate a chemical bond. However, these concepts have been based on observations on molecules, not molecular ions like H_2^+. And it is indeed found that H_2^+ is a stable bound molecular ion.

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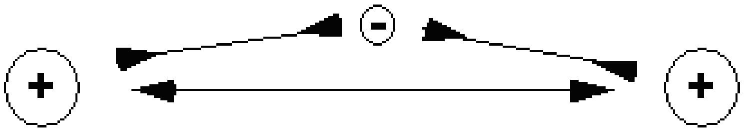
[1] This content is available online at <http://cnx.org/content/m14777/1.3/>.

What forces and motions hold the two hydrogen nuclei close together in the H_2^+ ion? It is worth keeping in mind that the two nuclei must repel one another, since they are both positively charged. In the absence of the electron, the two nuclei would accelerate away from one another, rather than remaining in close proximity. What is the role of the electron? Clearly, the electron is attracted to both nuclei at the same time, and, in turn, each nucleus is attracted to the electron. The effect of this is illustrated in Fig. 1. In Fig. 1a, the electron is "outside" of the two nuclei. In this position, the electron is primarily attracted to the nucleus on the left, to which it is closer. More importantly, the nucleus on the right feels a greater repulsion from the other nucleus than attraction to the electron, which is farther away. As a result, the nucleus on the right experiences a strong force driving it away from the hydrogen atom on the left. This arrangement does not generate chemical bonding, therefore. By contrast, in Fig. 1b, the electron is between the two nuclei. In this position, the electron is roughly equally attracted to the two nuclei, and very importantly, each nucleus feels an attractive force to the electron which is greater than the repulsive force generated by the other nucleus. Focusing on the electron's energy, the proximity of the two nuclei provides it a doubly attractive environment with a very low potential energy. If we tried to pull one of the nuclei away, this would raise the potential energy of the electron, since it would lose attraction to that nucleus. Hence, to pull one nucleus away requires us to add energy to the molecular ion. This is what is meant by a chemical bond: the energy of the electrons is lower when the atoms are in close proximity than when the atoms are far part. This "holds" the nuclei close together, since we must do work (add energy) to take the nuclei apart.

Figure 1

Electrostatic Interactions in H_2^+

(a) When the electron is outside of the region between the two nuclei, the repulsion of the nuclei exceeds the attraction of the electron to the nuclei, and no bonding force is expected.



(b) When the electron is in the region between the two nuclei, the attraction of the electron to the two nuclei exceeds the repulsion of the nuclei, lowering the total energy of the molecule and producing bonding.

Figure 9.1

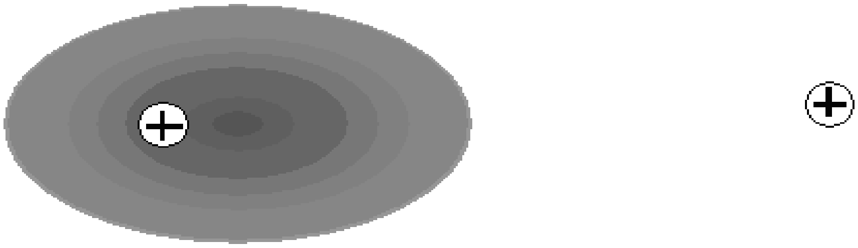
Note that the chemical bond in Fig. 1b results from the electron's position between the nuclei. On first thought, this appears to answer our question of what we mean by "sharing an electron pair" to form a chemical bond. An electron positioned between two nuclei is "shared" to the extent that its potential energy is lowered due to attraction to both nuclei simultaneously.

On second thought, though, this description must be inaccurate. We have learned our study of Energy Levels in Atoms that an electron must obey the uncertainty principle and that, as a consequence, the electron does not have a definite position, between the nuclei or otherwise. We can only hope to specify a probability for observing an electron in a particular location. This probability is, from quantum mechanics, provided by the wave function. What does this probability distribution look like for the H_2^+ molecular ion?

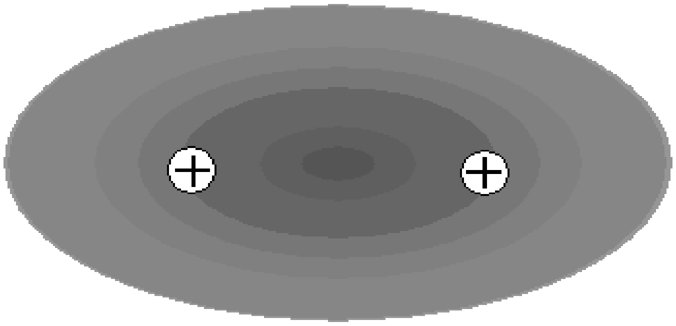
To answer this question, we begin by experimenting with a distribution that we know: the 1s electron orbital in a hydrogen atom. This we recall has the symmetry of a sphere, with equal probability in all directions away from the nucleus. To create an H_2^+ molecular ion from a hydrogen atom, we must add a bare second hydrogen nucleus (an H^+ion). Imagine bringing this nucleus closer to the hydrogen atom from a very great distance (see Fig. 2a). As the H^+ion approaches the neutral atom, both the hydrogen atom's nucleus and electron respond to the electric potential generated by the positive charge. The electron is attracted and the hydrogen atom nucleus is repelled. As a result, the distribution of probability for the electron about the nucleus must become distorted, so that the electron has a greater probability of being near the H^+ ion and the nucleus has a greater probability of being farther from the ion. This distortion, illustrated in Fig. 2b, is called "polarization": the hydrogen atom has become like a "dipole", with greater negative charge to one side and greater positive charge to the other.

Figure 2
Polarization and Bonding in H_2^+

(a) When the nuclei are separated to a great distance, the electron probability is described by a hydrogenic 1s orbital, which is spherical.



(b) As the bare nucleus approaches the hydrogen atom, the electron probability becomes "polarized" in the direction of the positive charge.



(c) When the nuclei are close enough together, the electron probability is distributed equally over both nuclei, resulting in a "molecular orbital."

Figure 9.2

This polarization must increase as the H^+ ion approaches the hydrogen atom until, eventually, the electron orbital must be sufficiently distorted that there is equal probability for observing the electron in proximity to either hydrogen nucleus (see Fig. 2c). The electron probability distribution in Fig. 2c now describes the motion of the electron, not in a hydrogen atom, but in an H_2^+ molecular ion. As such, we refer to this distribution as a "molecular orbital."

We note that the molecular orbital in Fig. 2c is more delocalized than the atomic orbital in Fig. 2a, and this is also important in producing the chemical bond. We recall from the discussion of Atomic Energy Levels that the energy of an electron in an orbital is determined, in part, by the compactness of the orbital. The more the orbital confines the motion of the electron, the higher is the kinetic energy of the electron, an effect we referred to as the "confinement energy." Applying this concept to the orbitals in Fig. 2, we can conclude that the confinement energy is lowered when the electron is delocalized over two nuclei in a molecular orbital. This effect contributes significantly to the lowering of the energy of an electron resulting from sharing by two nuclei.

Recall that the electron orbitals in the hydrogen atom are described by a set of quantum numbers. One of these quantum numbers is related to the symmetry or shape of the atomic orbital and is generally depicted by a letter. Recall that an "s" orbital is spherical in shape, and a "p" orbital has two lobes aligned along one axis. Similarly, the molecular orbitals for the H_2^+ molecular ion are described by a set of numbers which give the symmetry (or shape) of the orbital. For our purposes, we need only one of these descriptors, based on the symmetry of the orbital along the bond: if the molecular orbital has the symmetry of a cylinder, we refer to it as a " σ orbital." The orbital in Fig. 2c satisfies this condition.

We conclude that chemical bonding results from an electron in a molecular orbital which has substantial probability for the electron to be between two nuclei. However, this example illustrates chemical bonding with a single electron. Our rules of valence indicate that bonding typically occurs with a pair of electrons, rather than a single electron. Furthermore, this model of bonding does not tell us how to handle molecules with many electrons (say, F_2) where most of the electrons do not participate in the bonding at all.

9.4 Observation 2: Bonding and Non-Bonding in Diatomic Molecules

We now consider molecules with more than one electron. These are illustrated most easily by diatomic molecules (molecules with only two atoms) formed by like atoms, beginning with the hydrogen molecule, H_2. The most direct experimental observation of a chemical bond is the amount of energy required to break it. This is called the bond energy, or somewhat less precisely, the bond strength. Experimentally, it is observed that the bond energy of the hydrogen molecule H_2 is 458 kJ/mol. By contrast, the bond energy of the H_2^+ molecular ion is 269 kJ/mol. Therefore, the bond in H_2 is stronger than the bond in H_2^+. Thus, the pair of shared electrons in H_2 generates a stronger attractive force than does the single electron in H_2^+.

Before deducing an explanation of this in terms of electron orbitals, we first recall the valence shell electron pair description of the bonding in H_2. Each hydrogen atom has a single electron. By sharing these two electrons, each hydrogen atom can fill its valence shell, attaining the electron configuration of helium.

How does this translate into the electron orbital picture of electron sharing that we have just described for the H_2^+ molecular ion? There are two ways to deduce the answer to this question, and, since they are both useful, we will work through them both. The first way is to imagine that we form an H_2 molecule by starting with an H_2^+ molecular ion and adding an electron to it. As a simple approximation, we might imagine that the first electron's probability distribution (its orbital) is not affected by the addition of the second electron. The second electron must have a probability distribution describing its location in the molecule as well. We recall that, in atoms, it is possible to put two electrons into a single electron orbital, provided that the two electrons have opposite values of the spin quantum number, ms. Therefore, we expect this to be true for molecules as well, and we place the added second electron in H_2 into the same σ orbital as the first. This results in two electrons in the region between the two nuclei, thus adding to the force of attraction of the two nuclei into the bond. This explains our observation that the bond energy of H_2 is almost (although not quite) twice the bond energy of H_2^+.

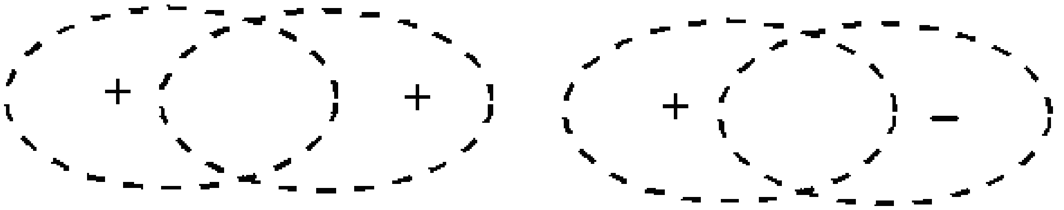
The second way to understand the electron orbital picture of H_2 is to imagine that we form the molecule by starting with two separated hydrogen atoms. Each of these atoms has a single electron in a 1s orbital. As the two atoms approach one another, each electron orbital is polarized in the direction of the other atom. Once the atoms are close enough together, these two orbitals become superimposed. Now we must recall that these orbitals describe the wave-like motion of the electron, so that, when these two wave functions overlap, they must interfere, either constructively or destructively. In Fig. 3, we see the consequences of constructive and destructive interference. We can deduce that, in H_2 the electron orbitals from the atoms must constructively interfere, because that would increase the electron probability in the region between the nuclei, resulting in bonding as before. Therefore, the σ molecular orbital describing the two electrons in H_2 can be understood as resulting from the constructive overlap of two atomic 1s electron orbitals.

We now add to our observations of diatomic molecules by noting that, of the diatomic molecules formed from like atoms of the first ten elements, H_2, Li_2, B_2, C_2, N_2, O_2, and F_2 are stable molecules with chemical bonds, whereas He_2, Be_2, and Ne_2 are not bound. In examining the electron configurations of the atoms of these elements, we discover a correspondence with which diatomic molecules are bound and which ones are not. $H, Li, B, N, \text{and} F$ all have odd numbers of electrons, so that at least one electron in each atom is unpaired. By contrast, He, Be, and Ne all have even numbers of electrons, none of which are unpaired. The other atoms, C and O both have an even number of electrons. However, as deduced in our understanding of the electron configurations in atoms, electrons will, when possible, distribute themselves into different orbitals of the same energy so as to reduce the effect of their mutual repulsion. Thus, in C and O, there are three 2p orbitals into which 2 and 4 electrons are placed, respectively. Therefore, in both atoms, there are two unpaired electrons. We conclude that bonds will form between atoms if and only if there are unpaired electrons in these atoms.

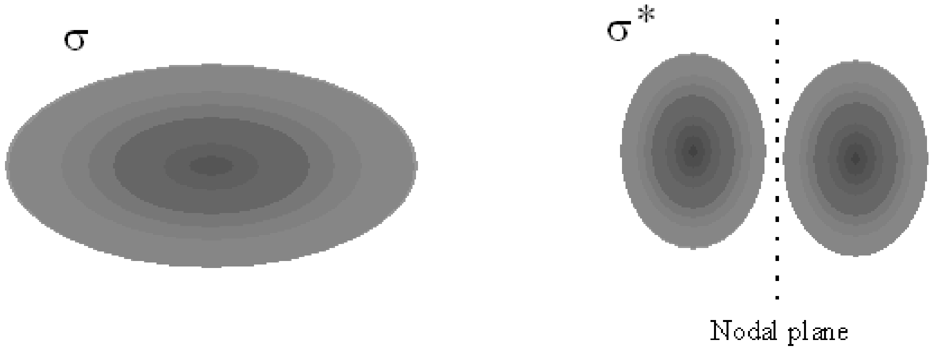
In H_2, the unpaired electrons from the separated atoms become paired in a molecular orbital formed from the overlap of the 1s atomic electron orbitals. In the case of a hydrogen atom, then, there are of course no paired electrons in the atom to worry about. In all other atoms, there certainly are paired electrons, regardless of whether there are or are not unpaired electrons. For example, in a lithium atom, there are two paired electrons in a 1s orbital and an unpaired electron in the 2s orbital. To form Li_2, the unpaired electron from each atom can be placed into a molecular orbital formed from the overlap of the 2s atomic electron orbitals. However, what becomes of the two electrons paired in the 1s orbital in a Li atom during the bonding of Li_2?

To answer this question, we examine He_2, in which each atom begins with only the two 1s electrons. As we bring the two He atoms together from a large distance, these 1s orbitals should become polarized, as in the hydrogen atom. When the polarized 1s orbitals overlap, constructive interference will again result in a σ molecular orbital, just as in H_2. Yet, we observe that He_2 is not a stable bound molecule. The problem which prevents bonding for He_2 arises from the Pauli Exclusion Principle: only two of the four electrons in He_2 can be placed into this σ bonding molecular orbital. The other two must go into a different orbital with a different probability distribution. To deduce the form of this new orbital, we recall that the bonding orbital discussed so far arises from the constructive interference of the atomic orbitals, as shown in Fig. 3. We could, instead, have assumed destructive interference of these orbitals. Destructive interference of two waves eliminates amplitude in the region of overlap of the waves, also shown in Fig. 3. In the case of the atomic orbitals, this means that the molecular orbital formed from destructive interference decreases probability for the electron to be between in the nuclei. Therefore, it increases probability for the electron to be outside the nuclei, as in Fig. 1a. As discussed there, this arrangement for the electron does not result in bonding; instead, the nuclei repel each other and the atoms are forced apart. This orbital is thus called an anti-bonding orbital. This orbital also has the symmetry of a cylinder along the bond axis, so it is also a σorbital; to indicate that it is an anti-bonding orbital, we designate it with an asterisk, σ^*

Figure 3
Formation of Bonding and Anti-bonding Orbitals



(a) When two s orbitals overlap, they can interfere constructively (same signs) or destructively (different signs).



(b) Constructive interference produces a bonding σ molecular orbital; destructive intereference produces an antibonding σ^* molecular orbital, with a nodal plane between the nuclei.

Figure 9.3

In He_2, both the bonding and the anti-bonding orbitals must be used in order to accommodate four electrons. The two electrons in the bonding orbital lower the energy of the molecule, but the two electrons in the anti-bonding orbital raise it. Since two He atoms will not bind together, then the net effect must be that the anti-bonding orbital more than offsets the bonding orbital.

We have now deduced an explanation for why the paired electrons in an atom do not contribute to bonding. Both bonding and anti-bonding orbitals are always formed when two atomic orbitals overlap.

When the electrons are already paired in the atomic orbitals, then there are too many electrons for the bonding molecular orbital. The extra electrons must go into the anti-bonding orbital, which raises the energy of the molecule, preventing the bond from forming.

Returning to the Li_2 example discussed above, we can develop a simple picture of the bonding. The two 1s electrons from each atom do not participate in the bonding, since the anti-bonding more than offsets the bonding. Thus, the paired "core" electrons remain in their atomic orbitals, unshared, and we can ignore them in describing the bond. The bond is formed due to overlap of the 2s orbitals and sharing of these electrons only. This is also consistent with our earlier view that the core electrons are closer to the nucleus, and thus unlikely to be shared by two atoms.

The model we have constructed seems to describe fairly well the bonding in the bound diatomic molecules listed above. For example, in a fluorine atom, the only unpaired electron is in a 2p orbital. Recall that a 2p orbital has two lobes, directed along one axis. If these lobes are assumed to lie along the axis between the two nuclei in F_2, then we can overlap them to form a bonding orbital. Placing the two unpaired electrons into this orbital then results in a single shared pair of electrons and a stable molecular bond.

9.5 Observation 3: Ionization energies of diatomic molecule

The energies of electrons in molecular orbitals can be observed directly by measuring the ionization energy. This is the energy required to remove an electron, in this case, from a molecule:

$H_2\,(g) \rightarrow H_2^+\,(g) + e^-\,(g)$

The measured ionization energy of H_2 is 1488 kJ/mol. This number is primarily important in comparison to the ionization energy of a hydrogen atom, which is 1312 kJ/mol. Therefore, it requires more energy to remove an electron from the hydrogen molecule than from the hydrogen atom, so we can conclude that the electron has a lower energy in the molecule. If we attempt to pull the atoms apart, we must raise the energy of the electron. Hence, energy is required to break the bond, so the molecule is bound.

We conclude that a bond is formed when the energy of the electrons in the molecule is lower than the energy of the electrons in the separated atoms. This conclusion seems consistent with our previous view of shared electrons in bonding molecular orbitals.

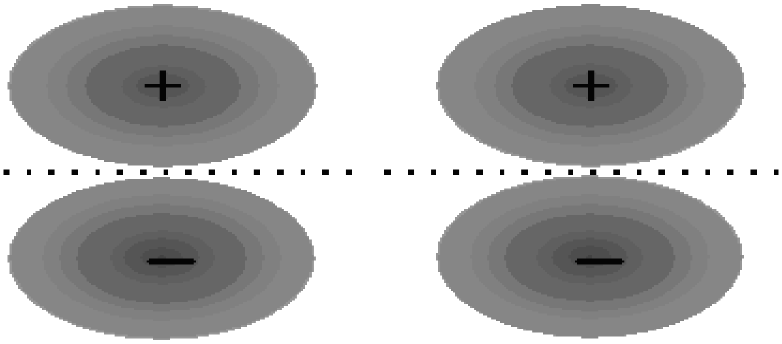
As a second example, we consider the nitrogen molecule, N_2. We find that the ionization energy of molecular nitrogen is 1503 kJ/mol, and that of atomic nitrogen is 1402 kJ/mol. Once again, we conclude that the energy of the electrons in molecular nitrogen is lower than that of the electrons in the separated atoms, so the molecule is bound.

As a third example, we consider fluorine, F_2. In this case, we find that the ionization energy of molecular fluorine is 1515 kJ/mol, which is smaller than the ionization energy of a fluorine atom, 1681 kJ/mol. This seems inconsistent with the bonding orbital concept we have developed above, which states that the electrons in the bond have a lower energy than in the separated atoms. If the electron being ionized has a higher energy in F_2 than in F, why is F_2 a stable molecule? Apparently, we need a more complete description of the molecular orbital concept of chemical bonding.

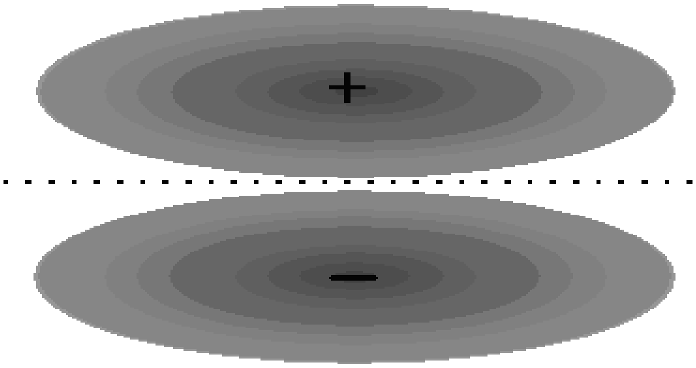
To proceed further, we compare bond energies in several molecules. Recall that the bond energy (or bond strength) is the energy required to separate the bonded atoms. We observe that the bond energy of N_2 is 956 kJ/mol. This is very much larger than the bond energy of H_2, 458 kJ/mol, and of F_2, which is 160 kJ/mol. We can account for the unusually strong bond in nitrogen using both our valence shell electron pair sharing model and our electron orbital descriptions. A nitrogen atom has three unpaired electrons in its valence shell, because the three 2p electrons distribute themselves over the three 2p orbitals, each oriented along a different axis. Each of these unpaired electrons is available for sharing with a second nitrogen atom. The result, from valence shell electron pair sharing concepts, is that three pairs of electrons are shared between two nitrogen atoms, and we call the bond in N_2 a "triple bond." It is somewhat intuitive that the triple bond in N_2 should be much stronger than the single bond in H_2 or in F_2.

Now consider the molecular orbital description of bonding in N_2. Each of the three 2p atomic orbitals in each nitrogen atom must overlap to form a bonding molecular orbital, if we are to accommodate three electron pairs. Each 2p orbital is oriented along a single axis. One 2p orbital from each atom is oriented in the direction of the other atom, that is, along the bond axis. When these two atomic orbitals overlap, they form a molecular orbital which has the symmetry of a cylinder and which is therefore a σ orbital. Of course, they also form a σ^*orbital. The two electrons are then paired in the bonding orbital.

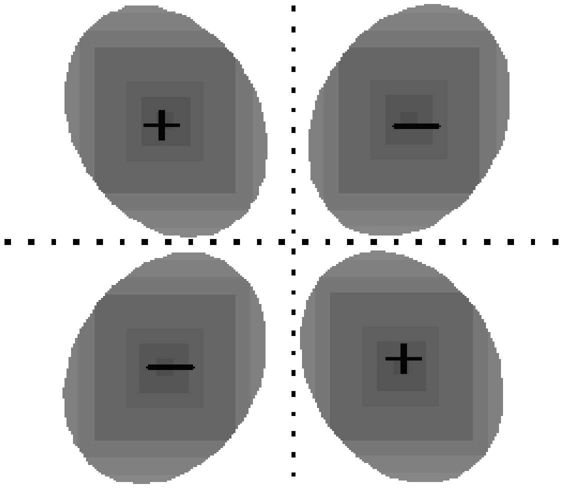
Figure 4
π and π^* orbitals



(a) Two p orbitals perpendicular to the bond axis will overlap and interfere to produce π and π^* molecular orbitals.



(b) Constructive interference results in formation of a bonding π molecular orbital.



(c) Destructive interference results in formation of an anti-bonding π^* molecular orbital.

Figure 9.4

The other two 2p orbitals on each nitrogen atom are perpendicular to the bond axis. The constructive overlap between these orbitals from different atoms must therefore result in a molecular orbital somewhat different that what we have discussed before. As shown in Fig. 4, the molecular orbital which results now does not have the symmetry of a cylinder, and in fact, looks something more like a cylinder cut into two pieces. This we call a π orbital. There are two such π orbitals since there are two sets of p orbitals perpendicular to the bond axis. Figure 4 also shows that an anti-bonding orbital is formed from the destructive overlap of 2p orbitals, and this is called a π^* orbital. There are also two π^* orbitals formed from destructive overlap of 2p orbitals. In N_2, the three shared electron pairs are thus in a single σ orbital and in two π orbitals. Each of these orbitals is a bonding orbital, therefore all six electrons have their energy lowered in comparison to the separated atoms.

This is depicted in Fig. 5 in what is called a "molecular orbital energy diagram." Each pair of atomic orbitals, one from each atom, is overlapped to form a bonding and an anti-bonding orbital. The three 2p orbitals from each atom form one σ and σ^* pair and two π and π^* pairs. The lowering of the energies of the electrons in the $\sigma$and π orbitals is apparent. The ten n=2 electrons from the nitrogen atoms are then placed pairwise, in order of increasing energy, into these molecular orbitals. Note that, in agreement with the Pauli Exclusion Principle, each pair in a single orbital consists of one spin up and one spin down electron.

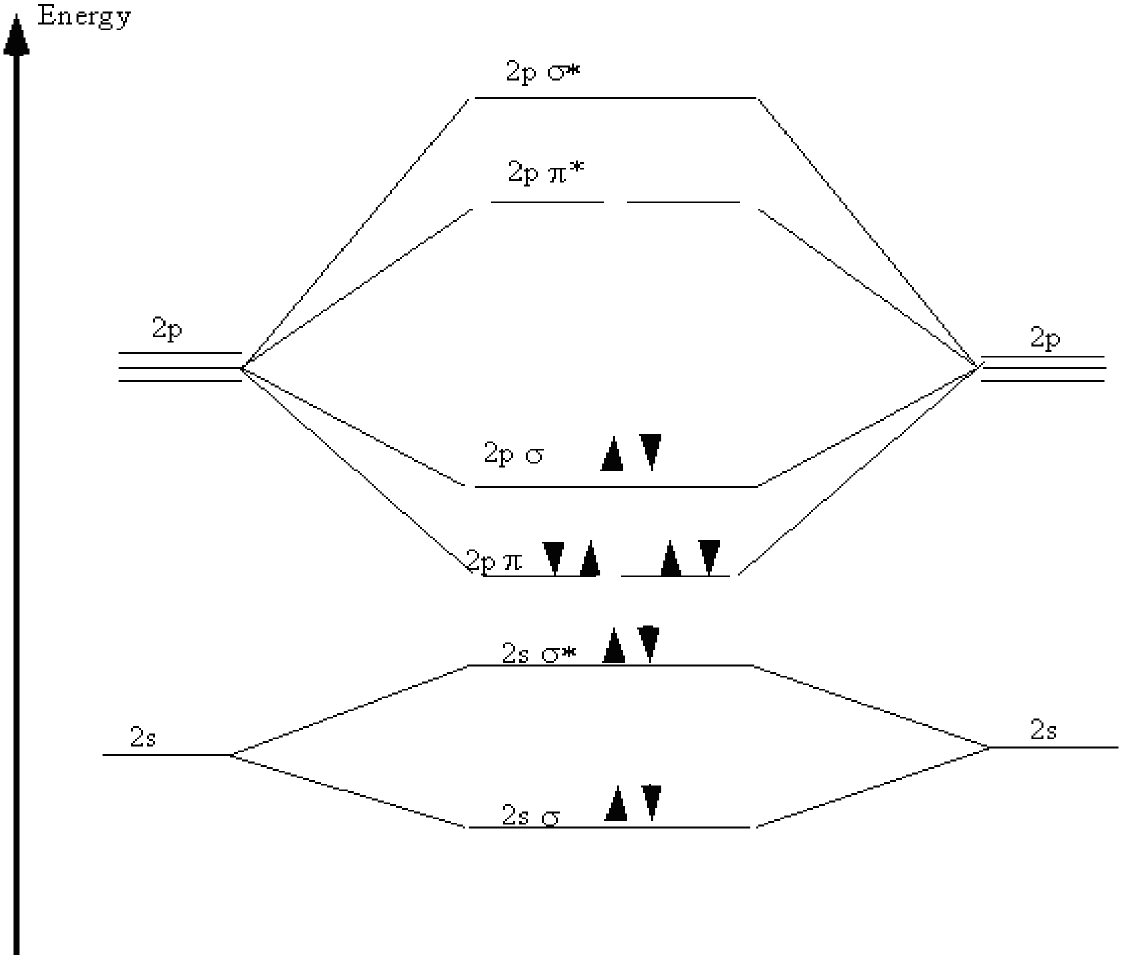


Figure 5
Molecular Orbital Energy Diagram
for Nitrogen

Figure 9.5

Recall now that we began the discussion of bonding in N_2 because of the curious result that the ionization energy of an electron in F_2 is less than that of an electron in an F atom. By comparing the molecular orbital energy level diagrams for N_2 and F_2 we are now prepared to answer this puzzle. There are five p electrons in each fluorine atom. These ten electrons must be distributed over the molecular orbitals whose energies are shown in Fig. 6. (Note that the ordering of the bonding 2p orbitals differ between N_2 and F_2.) We place two electrons in the σ orbital, four more in the two π orbitals, and four more in the two π^* orbitals. Overall, there are six electrons in bonding orbitals and four in anti-bonding orbitals. Since F_2 is a stable molecule, we must conclude that the lowering of energy for the electrons in the bonding orbitals is greater than the raising of energy for the electrons in the antibonding orbitals. Overall, this distribution of electrons is, net, equivalent to having two electrons paired in a single bonding orbital.

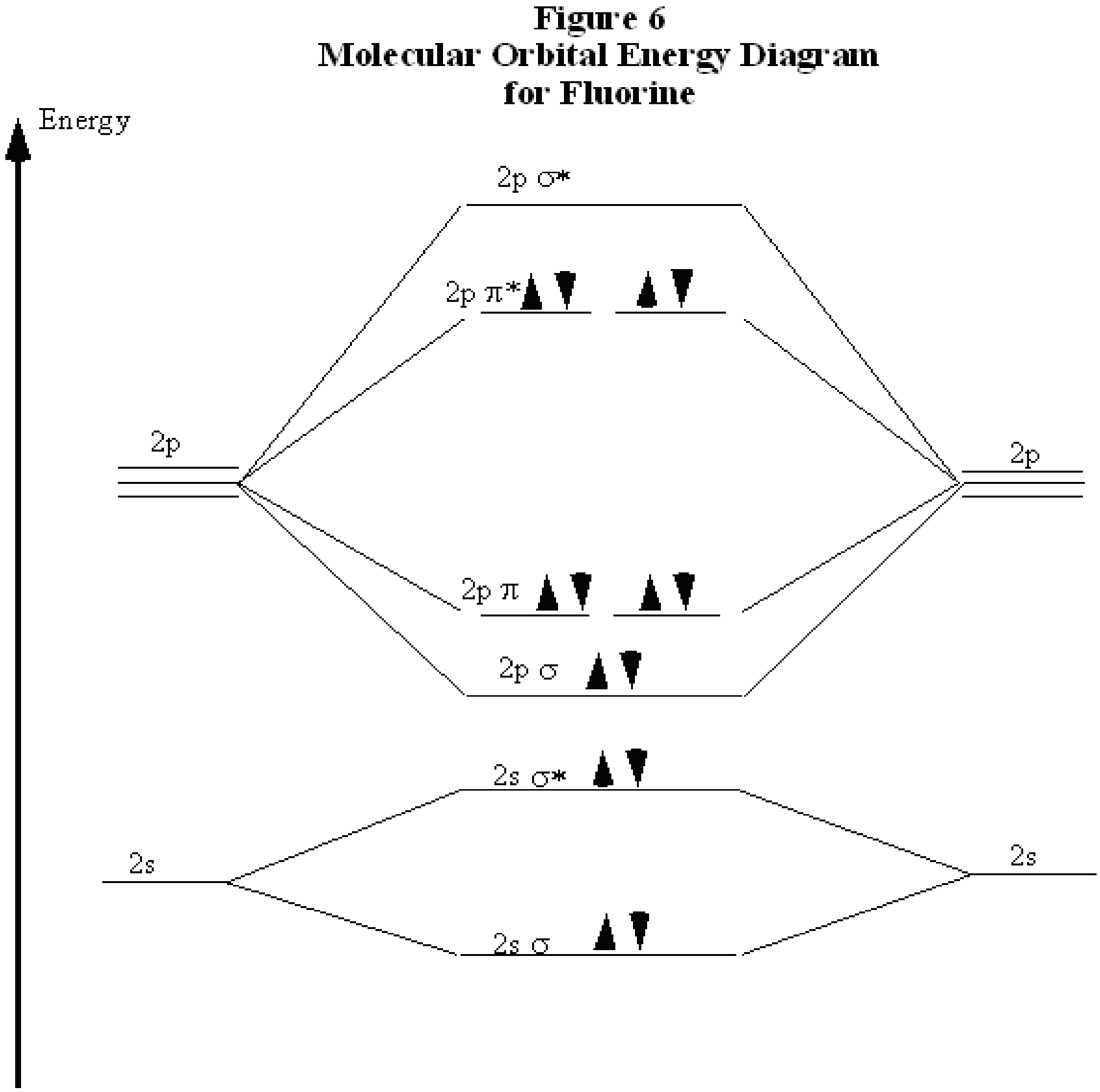


Figure 9.6

This also explains why the ionization energy of F_2 is less than that of an F atom. The electron with the highest energy requires the least energy to remove from the molecule or atom. The molecular orbital energy diagram in Fig. 6 clearly shows that the highest energy electrons in F_2 are in anti-bonding orbitals. Therefore, one of these electrons is easier to remove than an electron in an atomic 2p orbital, because the energy of an anti-bonding orbital is higher than that of the atomic orbitals. (Recall that this is why an anti-bonding orbital is, indeed, anti-bonding.) Therefore, the ionization energy of molecular fluorine is less than that of atomic fluorine. This clearly demonstrates the physical reality and importance of the anti-bonding orbitals.

A particularly interesting case is the oxygen molecule, O_2. In completing the molecular orbital energy level diagram for oxygen, we discover that we must decide whether to pair the last two electrons in the same $2p\pi^*$ orbital, or whether they should be separated into different $2p\pi^*$ orbitals. To determine which, we note that oxygen molecules are paramagnetic, meaning that they are strongly attracted to a magnetic field. To account for this paramagnetism, we recall that electron spin is a magnetic property. In most molecules, all electrons are paired, so for each "spin up" electron there is a "spin down" electron and their magnetic fields cancel out. When all electrons are paired, the molecule is diamagnetic meaning that it responds only weakly to a magnetic field.

If the electrons are not paired, they can adopt the same spin in the presence of a magnetic field. This accounts for the attraction of the paramagnetic molecule to the magnetic field. Therefore, for a molecule to be paramagnetic, it must have unpaired electrons. The correct molecular orbital energy level diagram for an O_2 molecule is shown in Fig. 7.

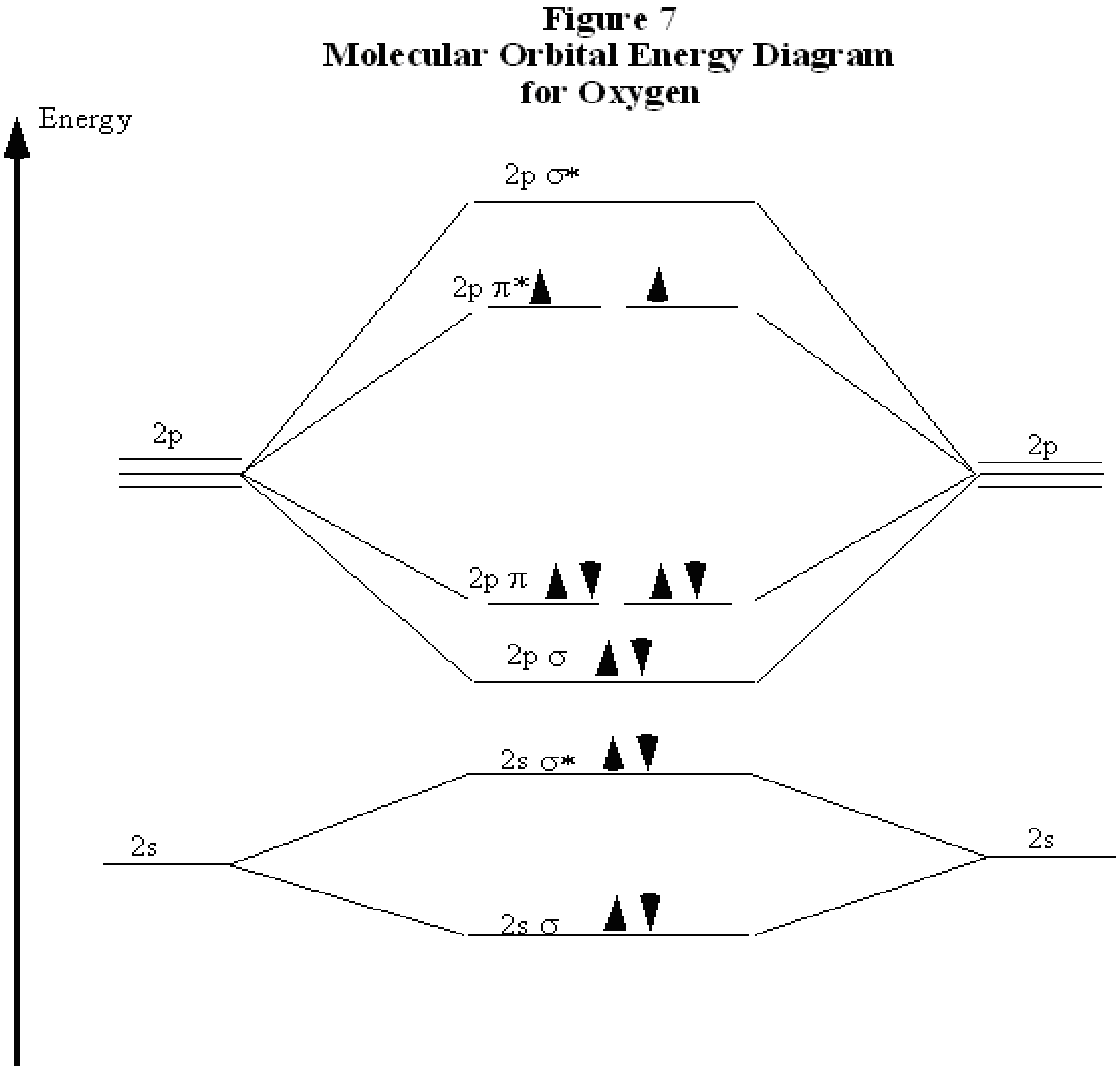


Figure 9.7

In comparing these three diatomic molecules, we recall that N_2 has the strongest bond, followed by O_2 and F_2. We have previously accounted for this comparison with Lewis structures, showing that N_2 is a triple bond, O_2 is a double bond, and F_2 is a single bond. The molecular orbital energy level diagrams in Figs. 5 to 7 cast a new light on this analysis. Note that, in each case, the number of bonding electrons in these molecules is eight. The difference in bonding is entirely due to the number of antibonding electrons: 2 for N_2 , 4 for O_2 , and six for F_2. Thus, the strength of a bond must be related to the relative numbers of bonding and antibonding electrons in the molecule. Therefore, we now define the bond order as

BondOrder $= \frac{1}{2}$ (# bonding electrons − # antibonding electrons)

Note that, defined this way, the bond order for N_2 is 3, for O_2 is 2, and for F_2 is 1, which agrees with our conclusions from Lewis structures. We conclude that we can predict the relative strengths of bonds by comparing bond orders.

9.6 Review and Discussion Questions

1. Why does an electron shared by two nuclei have a lower potential energy than an electron on a single atom? Why does an electron shared by two nuclei have a lower kinetic energy than an electron on a single atom? How does this sharing result in a stable molecule? How can this affect be measured experimentally?
2. Explain why the bond in an H_2 molecule is almost twice as strong as the bond in the H_2^+ ion. Explain why the H_2 bond is less than twice as strong as the H_2^+ bond.
3. Be_2 is not a stable molecule. What information can we determine from this observation about the energies of molecular orbitals?
4. Less energy is required to remove an electron from an F_2 molecule than to remove an electron from an F atom. Therefore, the energy of that electron is higher in the molecule than in the atom. Explain why, nevertheless, F_2 is a stable molecule, i.e., the energy of an F_2 molecule is less than the energy of two F atoms.
5. Why do the orbitals of an atom "hybridize" when forming a bond?
6. Calculate the bond orders of the following molecules and predict which molecule in each pair has the stronger bond:
    a. C_2 or C_2^+
    b. B_2 or B_2^+
    c. F_2 or F_2^-
    d. O_2 or O_2^+
7. Which of the following diatomic molecules are paramagnetic: CO, Cl_2, NO, N_2 ?
8. B_2 is observed to be paramagnetic. Using this information, draw an appropriate molecular orbital energy level diagram for B_2.

Chapter 10

Energetics of Chemical Reactions[1]

10.1 The Foundation

We begin our study of the energetics of chemical reactions with our understanding of mass relationships, determined by the stoichiometry of balanced reactions and the relative atomic masses of the elements. We will assume a conceptual understanding of energy based on the physics of mechanics, and in particular, we will assume the law of conservation of energy. In developing a molecular understanding of the reaction energetics, we will further assume our understanding of chemical bonding via valence shell electron pair sharing and molecular orbital theory.

10.2 Goals

The heat released or consumed in a chemical reaction is typically amongst the most easily observed and most readily appreciated consequences of the reaction. Many chemical reactions are performed routinely specifically for the purpose of utilizing the heat released by the reaction.

We are interested here in an understanding of the energetics of chemical reactions. Specifically, we wish to know what factors determine whether heat is absorbed or released during a chemical reaction. With that knowledge, we seek to quantify and predict the amount of heat anticipated in a chemical reaction. We expect to find that the quantity of heat absorbed or released during a reaction is related to the bonding of the molecules involved in the reaction.

Prior to answering these questions, we must first answer a few questions regarding the nature of heat. Despite our common familiarity with heat (particularly in Houston), the concept of heat is somewhat elusive to define. We recognize heat as "whatever it is that makes things hot," but this definition is too imprecise to permit measurement or any other conceptual progress. Exactly how do we define and measure heat?

10.3 Observation 1: Measurement of Heat by Temperature

We can define in a variety of ways a temperature scale which permits quantitative measurement of "how hot" an object is. Such scales are typically based on the expansion and contraction of materials, particularly of liquid mercury, or on variation of resistance in wires or thermocouples. Using such scales, we can easily show that heating an object causes its temperature to rise.

It is important, however, to distinguish between heat and temperature. These two concepts are not one and the same. To illustrate the difference, we begin by measuring the temperature rise produced by a given amount of heat, focusing on the temperature rise in 1000g of water produced by burning 1.0g of methane gas. We discover by performing this experiment repeatedly that the temperature of this quantity of water

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[1] This content is available online at <http://cnx.org/content/m12592/1.1/>.

always rises by exactly 13.3 °C. Therefore, the same quantity of heat must always be produced by reaction of this quantity of methane.

If we burn 1.0g of methane to heat 500g of water instead, we observe a temperature rise of 26.6 °C. If we burn 1.0g of methane to heat 1000g of iron, we observe a temperature rise of 123 °C. Therefore, the temperature rise observed is a function of the quantity of material heated as well as the nature of the material heated. Consequently, 13.3 °C is not an appropriate measure of this quantity of heat, since we cannot say that the burning of 1.0g of methane "produces 13.3 °C of heat." Such a statement is clearly revealed to be nonsense, so the concepts of temperature and heat must be kept distinct.

Our observations do reveal that we can relate the temperature rise produced in a substance to a fixed quantity of heat, provided that we specify the type and amount of the substance. Therefore, we define a property for each substance, called the **heat capacity**, which relates the temperature rise to the quantity of heat absorbed. We define q to be the quantity of heat, and $\Delta(T)$ to be the temperature rise produced by this heat. The heat capacity C is defined by

$$q = C\Delta(T) \tag{10.1}$$

This equation, however, is only a definition and does not help us calculate either q or C, since we know neither one.

Next, however, we observe that we can also elevate the temperature of a substance **mechanically**, that is, by doing work on it. As simple examples, we can warm water by stirring it, or warm metal by rubbing or scraping it. (As an historical note, these observations were crucial in establishing that heat is equivalent to work in its effect on matter, demonstrating that heat is therefore a form of energy.) Although it is difficult to do, we can measure the amount of work required to elevate the temperature of 1g of water by 1 °C. We find that the amount of work required is invariably equal to 4.184J. Consequently, adding 4.184J of energy to 1g of water must elevate the energy of the water molecules by an amount measured by 1 °C. By conservation of energy, the energy of the water molecules does not depend on how that energy was acquired. Therefore, the increase in energy measured by a 1 °C temperature increase is the same regardless of whether the water was heated or stirred. As such, 4.184J must also be the amount of energy added to the water molecules when they are **heated** by 1 °C rather than stirred. We have therefore effectively measured the heat q required to elevate the temperature of 1g of water by 1 °C. Referring back to (10.1), we now can calculate that the heat capacity of 1g of water must be $4.184\frac{J}{^{\circ}C}$. The heat capacity **per gram** of a substance is referred to as the **specific heat** of the substance, usually indicated by the symbol c_s. The specific heat of water is $4.184\frac{J}{^{\circ}C}$.

Determining the heat capacity (or specific heat) of water is an extremely important measurement for two reasons. First, from the heat capacity of water we can determine the heat capacity of any other substance very simply. Imagine taking a hot 5.0g iron weight at 100 °C and placing it in 10.0g of water at 25 °C. We know from experience that the iron bar will be cooled and the water will be heated until both have achieved the same temperature. This is an easy experiment to perform, and we find that the final temperature of the iron and water is 28.8 °C. Clearly, the temperature of the water has been raised by 3.8 °C. From (10.1) and the specific heat of water, we can calculate that the water must have absorbed an amount of heat $q = (10.0g)\left(\left(4.184\frac{J}{g\,^{\circ}C}\right)\right)(3.8\,^{\circ}C) = 159J$. By conservation of energy, this must be the amount of heat **lost** by the 1g iron weight, whose temperature was lowered by 71.2 °C. Again referring to (10.1), we can calculate the specific heat of the iron bar to be $c_s = \frac{-159J}{(-71.2\,^{\circ}C)(5.0g)} = 0.45\frac{J}{g\,^{\circ}C}$. Following this procedure, we can easily produce extensive tables of heat capacities for many substances.

Second, and perhaps more importantly for our purposes, we can use the known specific heat of water to measure the heat released in any chemical reaction. To analyze a previous example, we observed that the combustion of 1.0g of methane gas released sufficient heat to increase the temperature of 1000g of water by 13.3 °C. The heat capacity of 1000g of water must be $(1000g)\left(4.184\frac{J}{g\,^{\circ}C}\right) = 4184\frac{J}{^{\circ}C}$. Therefore, by (10.1), elevating the temperature of 1000g of water by 13.3 °C must require $55,650J =$ 55.65kJ of heat. Therefore, burning 1.0g of methane gas produces exactly 55.65kJ of heat.

The method of measuring reaction energies by capturing the heat evolved in a water bath and measuring the temperature rise produced in that water bath is called **calorimetry**. This method is dependent on the equivalence of heat and work as transfers of energy, and on the law of conservation of energy. Following this procedure, we can straightforwardly measure the heat released or absorbed in any easily performed chemical reaction. For reactions which are difficult to initiate or which occur only under restricted conditions or which are exceedingly slow, we will require alternative methods.

10.4 Observation 2: Hess' Law of Reaction Energies

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

$$C\,(s) + 2H_2O\,(g) \rightarrow CO_2\,(g) + 2H_2\,(g) \tag{10.2}$$

Calorimetry reveals that this reaction requires the **input** of 90.1kJ of heat for every mole of $C\,(s)$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an **endothermic** reaction. When heat is evolved, the reaction is **exothermic** and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction (10.2) converts one fuel, $C\,(s)$, into another, $H_2\,(g)$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \tag{10.3}$$

produces 393.5kJ for one mole of carbon burned; hence $q = -393.5\text{kJ}$. The reaction

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g) \tag{10.4}$$

produces 483.6kJ for two moles of hydrogen gas burned, so $q = -483.6\text{kJ}$. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy.

Of considerable importance is the observation that the heat input in (10.2), 90.1kJ, is exactly equal to the **difference** between the heat evolved, -393.5kJ, in the combustion of carbon (10.3) and the heat evolved, -483.6kJ, in the combustion of hydrogen (10.4). This is not a coincidence: if we take the combustion of carbon (10.3) and add to it the **reverse** of the combustion of hydrogen (10.4), we get

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$$

$$2H_2O\,(g) \rightarrow 2H_2\,(g) + O_2\,(g)$$

$$C\,(s) + O_2\,(g) + 2H_2O\,(g) \rightarrow CO_2\,(g) + 2H_2\,(g) + O_2\,(g) \tag{10.5}$$

Canceling the $O_2\,(g)$ from both sides, since it is net neither a reactant nor product, (10.5) is equivalent to (10.2). Thus, taking the combustion of carbon (10.3) and "subtracting" the combustion of hydrogen (10.4) (or more accurately, adding the reverse of the combustion of hydrogen (10.4)) yields (10.2). And, the heat of the combustion of carbon (10.3) **minus** the heat of the combustion of hydrogen (10.4) equals the heat of (10.2).

By studying many chemical reactions in this way, we discover that this result, known as **Hess' Law**, is general.

Law 10.1: Hess' Law
The heat of any reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction.

(Although we have not considered the restriction, applicability of this law requires that all reactions considered proceed under similar conditions: we will consider all reactions to occur at constant pressure.)

A pictorial view of Hess' Law as applied to the heat of (10.2) is illustrative. In Figure 10.1 (A Pictorial View of Hess' Law), the reactants $C(s) + 2H_2O(g)$ are placed together in a box, representing the **state** of the materials involved in the reaction prior to the reaction. The products $CO_2(g) + 2H_2(g)$ are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing $C(s)$, $O_2(g)$, and $2H_2(g)$. This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in (10.3) and (10.4).

A Pictorial View of Hess' Law

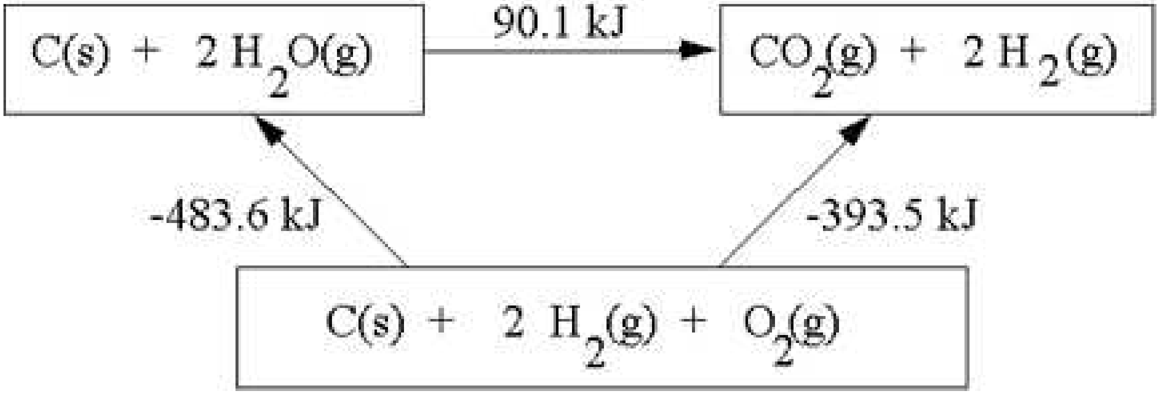


Figure 10.1

This picture of Hess' Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $C(s)$, $O_2(g)$, and $2H_2(g)$. A consequence of our observation of Hess' Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product. (This statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions.)

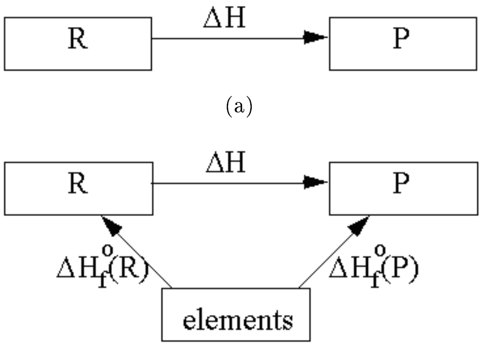
A slightly different view of Figure 10.1 (A Pictorial View of Hess' Law) results from beginning at the reactant box and following a complete circuit through the other boxes leading back to the reactant box, summing the net heats of reaction as we go. We discover that the net heat transferred (again provided that all reactions occur under constant pressure) is exactly zero. This is a statement of the conservation of energy: the energy in the reactant state does not depend upon the processes which produced that state. Therefore, we cannot extract any energy from the reactants by a process which simply recreates the reactants. Were this not the case, we could endlessly produce unlimited quantities of energy by following the circuitous path which continually reproduces the initial reactants.

By this reasoning, we can define an energy function whose value for the reactants is independent of how the reactant state was prepared. Likewise, the value of this energy function in the product state is independent of how the products are prepared. We choose this function, H, so that the change in the function, $\Delta(H) = H_{\text{products}} - H_{\text{reactants}}$, is equal to the heat of reaction q under constant pressure conditions. H, which we call the **enthalpy**, is a **state function**, since its value depends only on the state of the materials under consideration, that is, the temperature, pressure and composition of these materials.

The concept of a state function is somewhat analogous to the idea of elevation. Consider the difference in elevation between the first floor and the third floor of a building. This difference is independent of the path we choose to get from the first floor to the third floor. We can simply climb up two flights of stairs, or we can climb one flight of stairs, walk the length of the building, then walk a second flight of stairs. Or we can ride the elevator. We could even walk outside and have a crane lift us to the roof of the building, from which we climb down to the third floor. Each path produces exactly the same elevation gain, even though the distance traveled is significantly different from one path to the next. This is simply because the elevation is a "state function." Our elevation, standing on the third floor, is independent of how we got to the third floor, and the same is true of the first floor. Since the elevation thus a state function, the elevation gain is independent of the path.

Now, the existence of an energy state function H is of considerable importance in calculating heats of reaction. Consider the prototypical reaction in Figure 10.2(a), with reactants R being converted to products P. We wish to calculate the heat absorbed or released in this reaction, which is $\Delta (H)$. Since H is a state function, we can follow any path from R to P and calculate $\Delta (H)$ along that path. In Figure 10.2(b), we consider one such possible path, consisting of two reactions passing through an intermediate state containing all the atoms involved in the reaction, each in elemental form. This is a useful intermediate state since it can be used for any possible chemical reaction. For example, in Figure 10.1 (A Pictorial View of Hess' Law), the atoms involved in the reaction are C, H, and O, each of which are represented in the intermediate state in elemental form. We can see in Figure 10.2(b) that the $\Delta (H)$ for the overall reaction is now the difference between the $\Delta (H)$ in the formation of the products P from the elements and the $\Delta (H)$ in the formation of the reactants R from the elements.

Calculation of ΔH



(a)

(b)

Figure 10.2

The $\Delta (H)$ values for formation of each material from the elements are thus of general utility in calculating $\Delta (H)$ for any reaction of interest. We therefore define the **standard formation reaction** for reactant R, as

$$\text{elements in standard state} \rightarrow R$$

and the heat involved in this reaction is the **standard enthalpy of formation**, designated by $\Delta \left(H_f^\circ\right)$. The subscript f, standing for "formation," indicates that the $\Delta (H)$ is for the reaction creating the material from the elements in standard state. The superscript ° indicates that the reactions occur under constant standard pressure conditions of 1 atm. From Figure 10.2(b), we see that the heat of any reaction can be calculated from

$$\Delta\left(H_f^\circ\right) = \Delta\left(H_{f\,\text{products}}^\circ\right) - \Delta\left(H_{f\,\text{reactants}}^\circ\right) \tag{10.6}$$

Extensive tables of $\Delta\left(H_f^\circ\right)$ have been compiled and published. This allows us to calculate with complete confidence the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react.

10.5 Observation 3: Bond Energies in Polyatomic Molecules

The **bond energy** for a molecule is the energy required to separate the two bonded atoms to great distance. We recall that the total energy of the bonding electrons is lower when the two atoms are separated by the bond distance than when they are separated by a great distance. As such, the energy input required to separate the atoms elevates the energy of the electrons when the bond is broken.

We can use diatomic bond energies to calculate the heat of reaction $\Delta(H)$ for any reaction involving only diatomic molecules. We consider two simple examples. First, the reaction

$$H_2(g) + Br(g) \rightarrow H(g) + HBr(g) \tag{10.7}$$

is observed to be endothermic with heat of reaction $70\frac{\text{kJ}}{\text{mol}}$. Note that this reaction can be viewed as consisting entirely of the breaking of the H_2 bond followed by the formation of the HBr bond. Consequently, we must input energy equal to the bond energy of H_2 ($436\frac{\text{kJ}}{\text{mol}}$), but in forming the HBr bond we recover output energy equal to the bond energy of HBr ($366\frac{\text{kJ}}{\text{mol}}$). Therefore the heat of (10.7) at constant pressure must be equal to difference in these bond energies, $70\frac{\text{kJ}}{\text{mol}}$.

Now we can answer the question, at least for this reaction, of where the energy "goes" during the reaction. The reason this reaction absorbs energy is that the bond which must be broken, H_2, is stronger than the bond which is formed, HBr. Note that energy is released when the HBr bond is formed, but the amount of energy released is less than the amount of energy required to break the H_2 bond in the first place.

The second example is similar:

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \tag{10.8}$$

This reaction is exothermic with $\Delta\left(H^\circ\right) = -103\frac{\text{kJ}}{\text{mol}}$. In this case, we must break an H_2 bond, with energy $436\frac{\text{kJ}}{\text{mol}}$, and a Br_2 bond, with energy $193\frac{\text{kJ}}{\text{mol}}$. Since two HBr molecules are formed, we must form two HBr bonds, each with bond energy $366\frac{\text{kJ}}{\text{mol}}$. In total, then, breaking the bonds in the reactants requires $629\frac{\text{kJ}}{\text{mol}}$, and forming the new bonds releases $732\frac{\text{kJ}}{\text{mol}}$, for a net release of $103\frac{\text{kJ}}{\text{mol}}$. This calculation reveals that the reaction is exothermic because, although we must break one very strong bond and one weaker bond, we form two strong bonds.

There are two items worth reflection in these examples. First, energy is released in a chemical reaction due to the **formation** of strong bonds. Breaking a bond, on the other hand, always requires the **input** of energy. Second, (10.8) does not actually proceed by the two-step process of breaking both reactant bonds, thus forming four free atoms, followed by making two new bonds. The actual process of the reaction is significantly more complicated. The details of this process are irrelevant to the energetics of the reaction, however, since, as we have shown, the heat of reaction $\Delta(H)$ does not depend on the path of the reaction. This is another example of the utility of Hess' law.

We now proceed to apply this bond energy analysis to the energetics of reactions involving polyatomic molecules. A simple example is the combustion of hydrogen gas discussed previously here (10.4). This is an explosive reaction, producing 483.6kJ per mole of oxygen. Calculating the heat of reaction from bond energies requires us to know the bond energies in H_2O. In this case, we must break not one but two bonds:

$$H_2O(g) \rightarrow 2H(g) + O(g) \tag{10.9}$$

The energy required to perform this reaction is measured to be $926.9 \frac{\text{kJ}}{\text{mol}}$. (10.4) can proceed by a path in which we first break two H_2 bonds and one O_2 bond, then we follow the reverse of (10.9) twice:

$$2H_2\left(g\right) + O_2\left(g\right) \rightarrow 4H\left(g\right) + 2O\left(g\right) \tag{10.10}$$

$$4H\left(g\right) + 2O\left(g\right) \rightarrow 2H_2O\left(g\right)$$

$$2H_2\left(g\right) + O_2\left(g\right) \rightarrow 2H_2O\left(g\right)$$

Therefore, the energy of (10.4) must be the energy required to break two H_2 bonds and one O_2 bond minus twice the energy of (10.9). We calculate that $\Delta\left(H^{\circ}\right) = 2 \times \left(436 \frac{\text{kJ}}{\text{mol}}\right) + 498.3 \frac{\text{kJ}}{\text{mol}} - 2 \times \left(926.9 \frac{\text{kJ}}{\text{mol}}\right) = -483.5 \frac{\text{kJ}}{\text{mol}}$. It is clear from this calculation that (10.4) is strongly exothermic because of the very large amount of energy released when two hydrogen atoms and one oxygen atom form a water molecule.

It is tempting to use the heat of (10.9) to calculate the energy of an O-H bond. Since breaking the two O-H bonds in water requires $926.9 \frac{\text{kJ}}{\text{mol}}$, then we might infer that breaking a single O-H bond requires $\frac{926.9 \frac{\text{kJ}}{\text{mol}}}{2} = 463.5 \frac{\text{kJ}}{\text{mol}}$. However, the reaction

$$H_2O\left(g\right) \rightarrow OH\left(g\right) + H\left(g\right) \tag{10.11}$$

has $\Delta\left(H^{\circ}\right) = 492 \frac{\text{kJ}}{\text{mol}}$. Therefore, the energy required to break an O-H bond in H_2O is not the same as the energy required to break the O-H bond in the OH diatomic molecule. Stated differently, it requires more energy to break the first O-H bond in water than is required to break the second O-H bond.

In general, we find that the energy required to break a bond between any two particular atoms depends upon the molecule those two atoms are in. Considering yet again oxygen and hydrogen, we find that the energy required to break the O-H bond in methanol (CH_3OH) is $437 \frac{\text{kJ}}{\text{mol}}$, which differs substantially from the energy of (10.11). Similarly, the energy required to break a single C-H bond in methane (CH_4) is $435 \frac{\text{kJ}}{\text{mol}}$, but the energy required to break all four C-H bonds in methane is $1663 \frac{\text{kJ}}{\text{mol}}$, which is not equal to four times the energy of one bond. As another such comparison, the energy required to break a C-H bond is $400 \frac{\text{kJ}}{\text{mol}}$ in trichloromethane ($HCCl_3$), $414 \frac{\text{kJ}}{\text{mol}}$ in dichloromethane (H_2CCl_2), and $422 \frac{\text{kJ}}{\text{mol}}$ in chloromethane (H_3CCl).

These observations are somewhat discouraging, since they reveal that, to use bond energies to calculate the heat of a reaction, we must first measure the bond energies for all bonds for all molecules involved in that reaction. This is almost certainly more difficult than it is desirable. On the other hand, we can note that the bond energies for similar bonds in similar molecules are close to one another. The C-H bond energies in the three chloromethanes above illustrate this quite well. We can estimate the C-H bond energy in any one of these chloromethanes by the average C-H bond energy in the three chloromethanes molecule, which is $412 \frac{\text{kJ}}{\text{mol}}$. Likewise, the average of the C-H bond energies in methane is $\frac{1663 \frac{\text{kJ}}{\text{mol}}}{4} = 416 \frac{\text{kJ}}{\text{mol}}$ and is thus a reasonable approximation to the energy required to break a single C-H bond in methane.

By analyzing many bond energies in many molecules, we find that, in general, we can approximate the bond energy in any particular molecule by the average of the energies of similar bonds. These average bond energies can then be used to estimate the heat of a reaction without measuring all of the required bond energies.

Consider for example the combustion of methane to form water and carbon dioxide:

$$CH_4\left(g\right) + 2O_2\left(g\right) \rightarrow CO_2\left(g\right) + 2H_2O\left(g\right) \tag{10.12}$$

We can estimate the heat of this reaction by using average bond energies. We must break four C-H bonds at an energy cost of approximately $4 \times 412 \frac{\text{kJ}}{\text{mol}}$ and two O_2 bonds at an energy cost of approximately $2 \times 496 \frac{\text{kJ}}{\text{mol}}$. Forming the bonds in the products releases approximately $2 \times 743 \frac{\text{kJ}}{\text{mol}}$ for the two C=O double bonds and $4 \times 463 \frac{\text{kJ}}{\text{mol}}$ for the O-H bonds. Net, the heat of reaction is thus approximately $\Delta\left(H^{\circ}\right) = 1648 + 992 - 1486 - 1852 = -698 \frac{\text{kJ}}{\text{mol}}$. This is a rather rough approximation to the actual heat of combustion of methane, $-890 \frac{\text{kJ}}{\text{mol}}$. Therefore, we cannot use average bond energies to predict accurately the heat of a reaction. We can get an estimate, which may be sufficiently useful. Moreover, we can use these calculations to gain insight into the energetics of the reaction. For example, (10.12) is strongly exothermic, which is why methane gas (the primary component in natural gas) is an excellent fuel. From our calculation, we can see that the reaction involved breaking six bonds and forming six new bonds. The bonds formed are substantially stronger than those broken, thus accounting for the net release of energy during the reaction.

10.6 Review and Discussion Questions

Exercise 10.1
Assume you have two samples of two different metals, X and Z. The samples are exactly the same mass.

10.6.1

Both samples are heated to the same temperature. Then each sample is placed into separate glasses containing identical quantities of cold water, initially at identical temperatures below that of the metals. The final temperature of the water containing metal X is greater than the final temperature of the water containing metal Z. Which of the two metals has the larger heat capacity? Explain your conclusion.

10.6.2

If each sample, initially at the same temperature, is heated with exactly 100J of energy, which sample has the higher final temperature?

Exercise 10.2
Explain how Hess' Law is a consequence of conservation of energy.

Exercise 10.3
Consider the reaction

$$N_2O_4\left(g\right) \rightarrow 2NO_2\left(g\right)$$

Draw Lewis structures for each of $N_2O_4$and NO_2. On the basis of these structures, predict whether the reaction is endothermic or exothermic, and explain your reasoning.

Exercise 10.4
Why is the bond energy of H_2 not equal to $\Delta\left(H_f^{\circ}\right)$ of H_2? For what species is the enthalpy of formation related to the bond energy of H_2?

Exercise 10.5
Suggest a reason why $\Delta\left(H^{\circ}\right)$ for the reaction

$$CO_2\left(g\right) \rightarrow CO\left(g\right) + O\left(g\right)$$

is not equal to $\Delta\left(H^{\circ}\right)$ for the reaction

$$CO\left(g\right) \rightarrow C\left(g\right) + O\left(g\right)$$

Exercise 10.6
Determine whether the reaction is exothermic or endothermic for each of the following circumstances:

10.6.1

The heat of combustion of the products is greater than the heat of combustion of the reactants.

10.6.2

The enthalpy of formation of the products is greater than the enthalpy of formation of the reactants.

10.6.3

The total of the bond energies of the products is greater than the total of the bond energies for the reactants.

Chapter 11

The Ideal Gas Law[1]

11.1 Foundation

We assume as our starting point the atomic molecular theory. That is, we assume that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound.

11.2 Goals

The individual molecules of different compounds have characteristic properties, such as mass, structure, geometry, bond lengths, bond angles, polarity, diamagnetism or paramagnetism. We have not yet considered the properties of mass quantities of matter, such as density, phase (solid, liquid or gas) at room temperature, boiling and melting points, reactivity, and so forth. These are properties which are not exhibited by individual molecules. It makes no sense to ask what the boiling point of one molecule is, nor does an individual molecule exist as a gas, solid, or liquid. However, we do expect that these material or bulk properties are related to the properties of the individual molecules. Our ultimate goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise.

Achieving this goal will require considerable analysis. In this Concept Development Study, we begin at a somewhat more fundamental level, with our goal to know more about the nature of gases, liquids and solids. We need to study the relationships between the physical properties of materials, such as density and temperature. We begin our study by examining these properties in gases.

11.3 Observation 1: Pressure-Volume Measurements on Gases

It is an elementary observation that air has a "spring" to it: if you squeeze a balloon, the balloon rebounds to its original shape. As you pump air into a bicycle tire, the air pushes back against the piston of the pump. Furthermore, this resistance of the air against the piston clearly increases as the piston is pushed farther in. The "spring" of the air is measured as a pressure, where the pressure P is defined

$$P = \frac{F}{A} \tag{11.1}$$

F is the force exerted by the air on the surface of the piston head and A is the surface area of the piston head.

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[1] This content is available online at <http://cnx.org/content/m12598/1.2/>.

For our purposes, a simple pressure gauge is sufficient. We trap a small quantity of air in a syringe (a piston inside a cylinder) connected to the pressure gauge, and measure both the volume of air trapped inside the syringe and the pressure reading on the gauge. In one such sample measurement, we might find that, at atmospheric pressure (760 torr), the volume of gas trapped inside the syringe is 29.0 ml. We then compress the syringe slightly, so that the volume is now 23.0 ml. We feel the increased spring of the air, and this is registered on the gauge as an increase in pressure to 960 torr. It is simple to make many measurements in this manner. A sample set of data appears in Table 11.1: Sample Data from Pressure-Volume Measurement. We note that, in agreement with our experience with gases, the pressure increases as the volume decreases. These data are plotted here (Figure 11.1: Measurements on Spring of the Air).

Sample Data from Pressure-Volume Measurement

Pressure (torr)	Volume (ml)
760	29.0
960	23.0
1160	19.0
1360	16.2
1500	14.7
1650	13.3

Table 11.1

Measurements on Spring of the Air

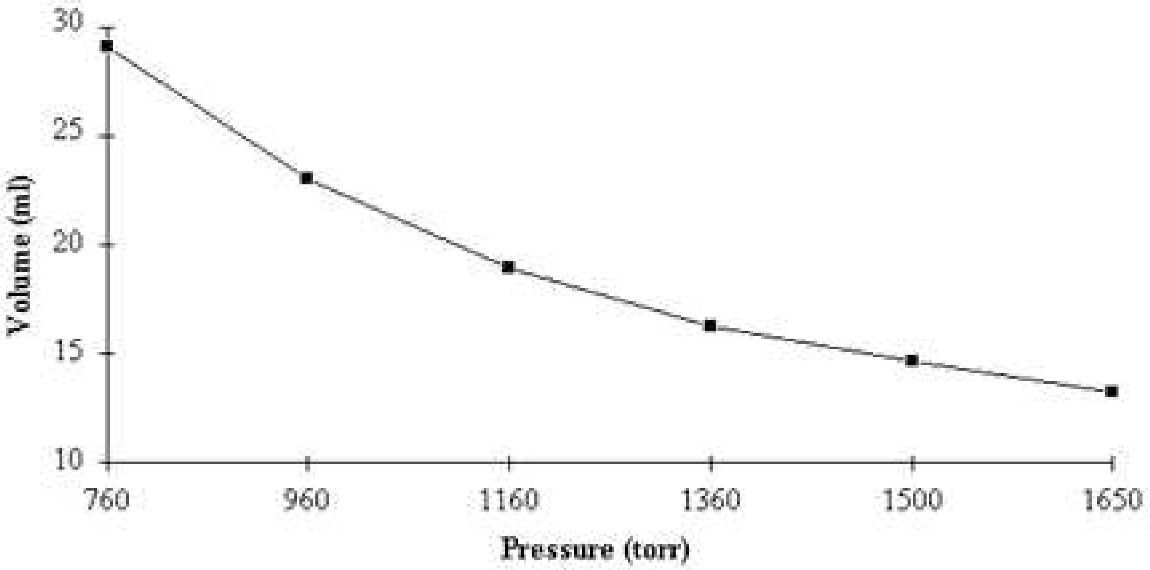

Figure 11.1

An initial question is whether there is a quantitative relationship between the pressure measurements and the volume measurements. To explore this possibility, we try to plot the data in such a way that both quantities increase together. This can be accomplished by plotting the pressure versus the inverse of the volume, rather than versus the volume. The data are given in Table 11.2: Analysis of Sample Data and plotted here (Figure 11.2: Analysis of Measurements on Spring of the Air).

Analysis of Sample Data

Pressure (torr)	**Volume (ml)**	**1/Volume (1/ml)**	**Pressure × Volume**
760	29.0	0.0345	22040
960	23.0	0.0435	22080
1160	19.0	0.0526	22040
1360	16.2	0.0617	22032
1500	14.7	0.0680	22050
1650	13.3	0.0752	21945

Table 11.2

Analysis of Measurements on Spring of the Air

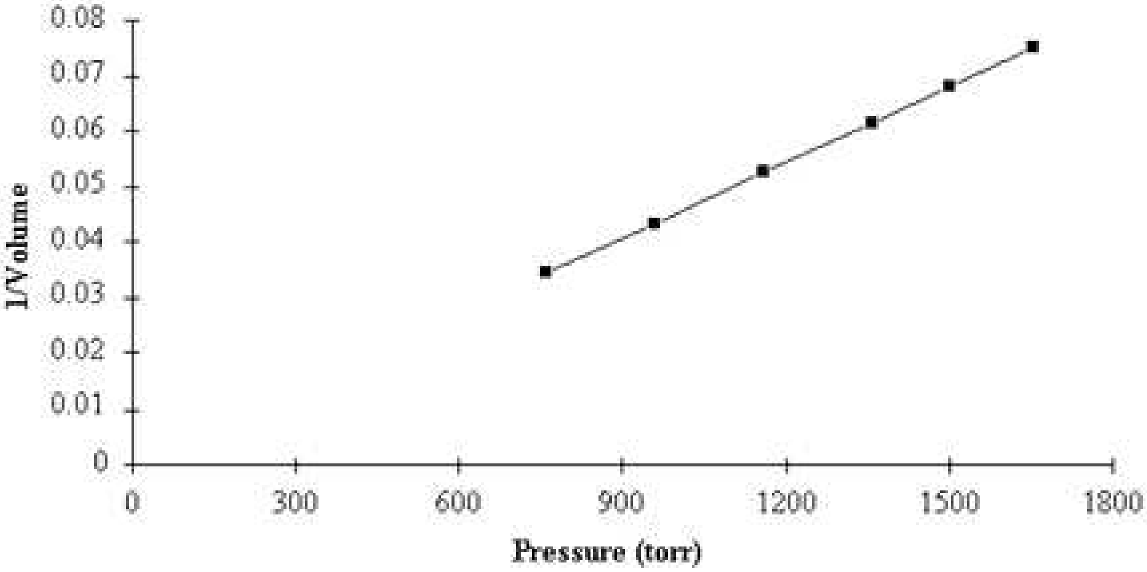

Figure 11.2

Notice also that, with elegant simplicity, the data points form a straight line. Furthermore, the straight line seems to connect to the origin $\{0, 0\}$. This means that the pressure must simply be a constant multiplied by $\frac{1}{V}$:

$$P = k \times \frac{1}{V} \tag{11.2}$$

If we multiply both sides of this equation by V, then we notice that

$$PV = k \tag{11.3}$$

In other words, if we go back and multiply the pressure and the volume together for each experiment, we should get the same number each time. These results are shown in the last column of Table 11.2: Analysis of Sample Data, and we see that, within the error of our data, all of the data points give the same value of the product of pressure and volume. (The volume measurements are given to three decimal places and hence are accurate to a little better than 1%. The values of Pressure × Volume are all within 1% of each other, so the fluctuations are not meaningful.)

We should wonder what significance, if any, can be assigned to the number 22040 (torrml) we have observed. It is easy to demonstrate that this "constant" is not so constant. We can easily trap any amount of air in the syringe at atmospheric pressure. This will give us any volume of air we wish at 760 torr pressure. Hence, the value 22040 (torrml) is only observed for the particular amount of air we happened to choose in our sample measurement. Furthermore, if we heat the syringe with a fixed amount of air, we observe that the volume increases, thus changing the value of the 22040 (torrml). Thus, we should be careful to note that the **product of pressure and volume is a constant for a given amount of air at a fixed temperature**. This observation is referred to as **Boyle's Law**, dating to 1662.

The data given in Table 11.1: Sample Data from Pressure-Volume Measurement assumed that we used air for the gas sample. (That, of course, was the only gas with which Boyle was familiar.) We now experiment with varying the composition of the gas sample. For example, we can put oxygen, hydrogen, nitrogen, helium, argon, carbon dioxide, water vapor, nitrogen dioxide, or methane into the cylinder. In each case we start with 29.0 ml of gas at 760 torr and 25 °C. We then vary the volumes as in Table 11.1: Sample Data from Pressure-Volume Measurement and measure the pressures. Remarkably, we find that the pressure of each gas is exactly the same as every other gas at each volume given. For example, if we press the syringe to a volume of 16.2 ml, we observe a pressure of 1360 torr, no matter which gas is in the cylinder. This result also applies equally well to mixtures of different gases, the most familiar example being air, of course.

We conclude that the pressure of a gas sample depends on the volume of the gas and the temperature, but not on the composition of the gas sample. We now add to this result a conclusion from a previous study (Chapter 3). Specifically, we recall the Law of Combining Volumes (Law 3.1, Law of Combining Volumes, p. 10), which states that, when gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios. We further recall that this result can be explained in the context of the atomic molecular theory by hypothesizing that equal volumes of gas contain equal numbers of gas particles, independent of the type of gas, a conclusion we call **Avogadro's Hypothesis**. Combining this result with Boyle's law reveals that the **pressure** of a gas depends on the **number** of gas particles, the **volume** in which they are contained, and the **temperature** of the sample. The pressure does **not** depend on the type of gas particles in the sample or whether they are even all the same.

We can express this result in terms of Boyle's law by noting that, in the equation $PV = k$, the "constant" k is actually a function which varies with both number of gas particles in the sample and the temperature of the sample. Thus, we can more accurately write

$$PV = k\,(N, t) \tag{11.4}$$

explicitly showing that the product of pressure and volume depends on N, the number of particles in the gas sample, and t,the temperature.

It is interesting to note that, in 1738, Bernoulli showed that the inverse relationship between pressure and volume could be proven by assuming that a gas consists of individual particles colliding with the walls of the container. However, this early evidence for the existence of atoms was ignored for roughly 120 years, and the atomic molecular theory was not to be developed for another 70 years, based on mass measurements rather than pressure measurements.

11.4 Observation 2: Volume-Temperature Measurements on Gases

We have already noted the dependence of Boyle's Law on temperature. To observe a constant product of pressure and volume, the temperature must be held fixed. We next analyze what happens to the gas when the temperature is allowed to vary. An interesting first problem that might not have been expected is the question of how to measure temperature. In fact, for most purposes, we think of temperature only in the rather non-quantitative manner of "how hot or cold" something is, but then we measure temperature by examining the length of mercury in a tube, or by the electrical potential across a thermocouple in an electronic thermometer. We then briefly consider the complicated question of just what we are measuring when we measure the temperature.

Imagine that you are given a cup of water and asked to describe it as "hot" or "cold." Even without a calibrated thermometer, the experiment is simple: you put your finger in it. Only a qualitative question was asked, so there is no need for a quantitative measurement of "how hot" or "how cold." The experiment is only slightly more involved if you are given two cups of water and asked which one is hotter or colder. A simple solution is to put one finger in each cup and to directly compare the sensation. You still don't need a calibrated thermometer or even a temperature scale at all.

Finally, imagine that you are given a cup of water each day for a week at the same time and are asked to determine which day's cup contained the hottest or coldest water. Since you can no longer trust your sensory memory from day to day, you have no choice but to define a temperature scale. To do this, we make a physical measurement on the water by bringing it into contact with something else whose properties depend on the "hotness" of the water in some unspecified way. (For example, the volume of mercury in a glass tube expands when placed in hot water; certain strips of metal expand or contract when heated; some liquid crystals change color when heated; *etc.*) We assume that this property will have the same value when it is placed in contact with two objects which have the same "hotness" or temperature. Somewhat obliquely, this defines the temperature measurement.

For simplicity, we illustrate with a mercury-filled glass tube thermometer. We observe quite easily that when the tube is inserted in water we consider "hot," the volume of mercury is larger than when we insert the tube in water that we consider "cold." Therefore, the volume of mercury is a measure of how hot something is. Furthermore, we observe that, when two very different objects appear to have the same "hotness," they also give the same volume of mercury in the glass tube. This allows us to make quantitative comparisons of "hotness" or temperature based on the volume of mercury in a tube.

All that remains is to make up some numbers that define the scale for the temperature, and we can literally do this in any way that we please. This arbitrariness is what allows us to have two different, but perfectly acceptable, temperature scales, such as Fahrenheit and Centigrade. The latter scale simply assigns zero to be the temperature at which water freezes at atmospheric pressure. We then insert our mercury thermometer into freezing water, and mark the level of the mercury as "0". Another point on our scale assigns 100 to be the boiling point of water at atmospheric pressure. We insert our mercury thermometer into boiling water and mark the level of mercury as "100." Finally, we just mark off in increments of $\frac{1}{100}$ of the distance between the "0" and the "100" marks, and we have a working thermometer. Given the arbitrariness of this way of measuring temperature, it would be remarkable to find a quantitative relationship between temperature and any other physical property.

Yet that is what we now observe. We take the same syringe used in the previous section and trap in it a small sample of air at room temperature and atmospheric pressure. (From our observations above, it should be clear that the type of gas we use is irrelevant.) The experiment consists of measuring the volume of the gas sample in the syringe as we vary the temperature of the gas sample. In each measurement, the pressure of the gas is held fixed by allowing the piston in the syringe to move freely against atmospheric pressure. A sample set of data is shown in Table 11.3: Sample Data from Volume-Temperature Measurement and plotted here (Figure 11.3: Volume vs. Temperature of a Gas).

Sample Data from Volume-Temperature Measurement

Temperature (°C)	Volume (ml)
11	95.3
25	100.0
47	107.4
73	116.1
159	145.0
233	169.8
258	178.1

Table 11.3

Volume vs. Temperature of a Gas

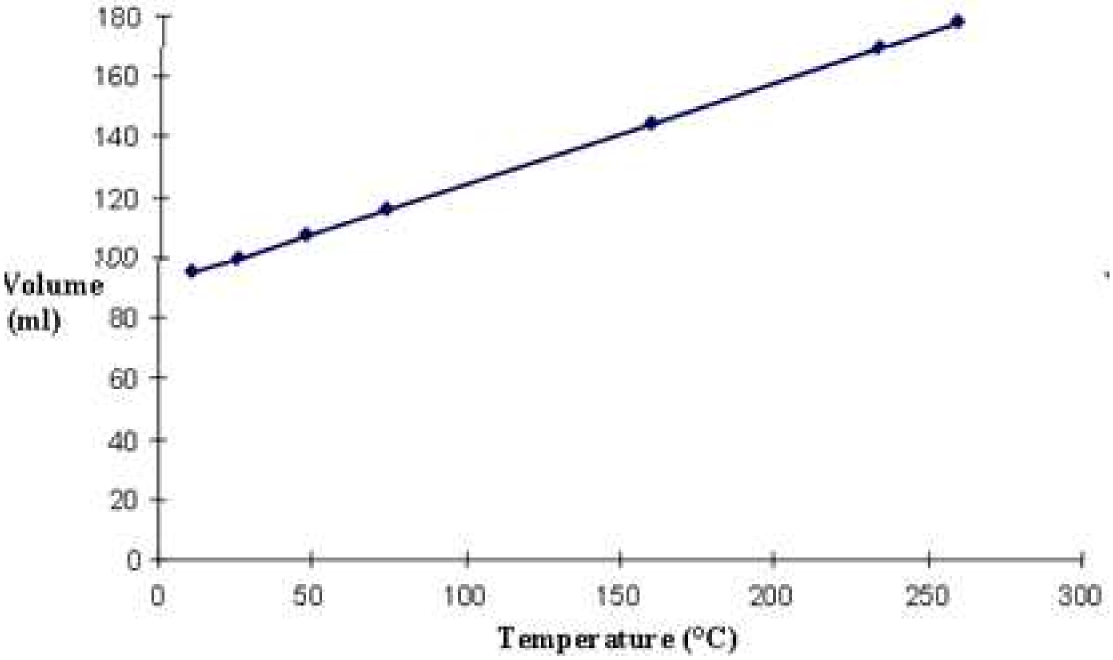

Figure 11.3

We find that there is a simple linear (straight line) relationship between the volume of a gas and its temperature as measured by a mercury thermometer. We can express this in the form of an equation for a line:

$$V = \alpha t + \beta \tag{11.5}$$

where V is the volume and t is the temperature in °C. α and β are the slope and intercept of the line, and in this case, $\alpha = 0.335$ and, $\beta = 91.7$. We can rewrite this equation in a slightly different form:

$$V = \alpha \left(t + \frac{\beta}{\alpha} \right) \tag{11.6}$$

This is the same equation, except that it reveals that the quantity $\frac{\beta}{\alpha}$ must be a temperature, since we can add it to a temperature. This is a particularly important quantity: if we were to set the temperature of the gas equal to $-\frac{\beta}{\alpha} = -273\,°\mathrm{C}$, we would find that the volume of the gas would be exactly 0! (This assumes that this equation can be extrapolated to that temperature. This is quite an optimistic extrapolation, since we haven't made any measurements near to $-273\,°\mathrm{C}$. In fact, our gas sample would condense to a liquid or solid before we ever reached that low temperature.)

Since the volume depends on the pressure and the amount of gas (Boyle's Law), then the values of α and β also depend on the pressure and amount of gas and carry no particular significance. However, when we repeat our observations for many values of the amount of gas and the fixed pressure, we find that the **ratio** $-\frac{\beta}{\alpha} = -273\,°\mathrm{C}$ does not vary from one sample to the next. Although we do not know the physical significance of this temperature at this point, we can assert that it is a true constant, independent of any choice of the conditions of the experiment. We refer to this temperature as **absolute zero**, since a temperature below this value would be predicted to produce a negative gas volume. Evidently, then, we cannot expect to lower the temperature of any gas below this temperature.

This provides us an "absolute temperature scale" with a zero which is not arbitrarily defined. This we define by adding 273 (the value of $\frac{\beta}{\alpha}$) to temperatures measured in °C, and we define this scale to be in units of degrees Kelvin (K). The data in Table 11.3: Sample Data from Volume-Temperature Measurement are now recalibrated to the absolute temperature scale in Table 11.4: Analysis of Volume-Temperature Data and plotted here (Figure 11.4: Volume vs. Absolute Temperature of a Gas).

Analysis of Volume-Temperature Data

Temperature (°C)	**Temperature (K)**	**Volume (ml)**
11	284	95.3
25	298	100.0
47	320	107.4
73	350	116.1
159	432	145.0
233	506	169.8
258	531	178.1

Table 11.4

Volume vs. Absolute Temperature of a Gas

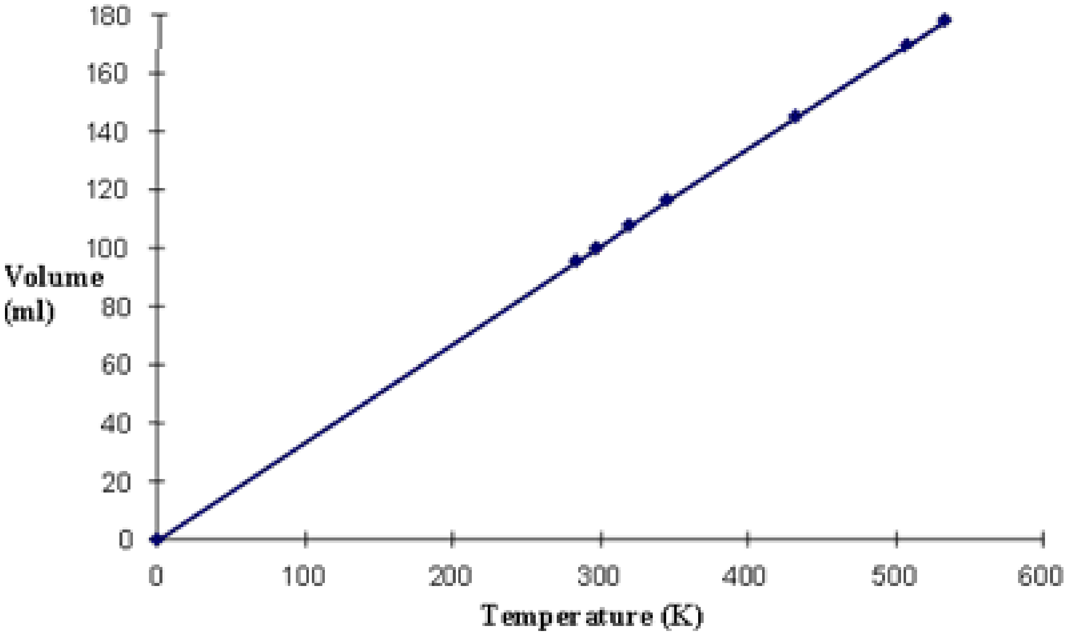

Figure 11.4

Note that **the volume is proportional to the absolute temperature** in degrees Kelvin,

$$V = kT \tag{11.7}$$

provided that the pressure and amount of gas are held constant. This result is known as **Charles' Law**, dating to 1787.

As with Boyle's Law, we must now note that the "constant" k is not really constant, since the volume also depends on the pressure and quantity of gas. Also as with Boyle's Law, we note that Charles' Law does not depend on the **type** of gas on which we make the measurements, but rather depends only the number of particles of gas. Therefore, we slightly rewrite Charles' Law to explicit indicate the dependence of k on the pressure and number of particles of gas

$$V = k(N, P)T \tag{11.8}$$

11.5 The Ideal Gas Law

We have been measuring four properties of gases: pressure, volume, temperature, and "amount", which we have assumed above to be the number of particles. The results of three observations relate these four properties pairwise. Boyle's Law relates the pressure and volume at constant temperature and amount of gas:

$$P \times V = k_1(N, T) \tag{11.9}$$

Charles' Law relates the volume and temperature at constant pressure and amount of gas:

$$V = k_2\left(N, P\right) T \tag{11.10}$$

The Law of Combining Volumes leads to Avogadro's Hypothesis that the volume of a gas is proportional to the number of particles (N) provided that the temperature and pressure are held constant. We can express this as

$$V = k_3\left(P, T\right) N \tag{11.11}$$

We will demonstrate below that these three relationships can be combined into a single equation relating P, V, T, and N. Jumping to the conclusion, however, we can more easily show that these three relationships can be considered as special cases of the more general equation known as the **Ideal Gas Law**:

$$PV = nRT \tag{11.12}$$

where R is a constant, n is the number of moles of gas, related to the number of particles N by Avogadro's number, N_A

$$n = \frac{N}{N_A} \tag{11.13}$$

In Boyle's Law, we examine the relationship of P and V when n (or N) and T are fixed. In the Ideal Gas Law, when n and T are constant, nRT is constant, so the product PV is also constant. Therefore, Boyle's Law is a special case of the Ideal Gas Law. If n and P are fixed in the Ideal Gas Law, then $V = \frac{nR}{P}T$ and $\frac{nR}{P}$ is a constant. Therefore, Charles' Law is also a special case of the Ideal Gas Law. Finally, if P and T are constant, then in the Ideal Gas Law, $V = \frac{RT}{P}n$ and the volume is proportional the number of moles or particles. Hence, Avogadro's hypothesis is a special case of the Ideal Gas Law.

We have now shown that the each of our experimental observations is consistent with the Ideal Gas Law. We might ask, though, how did we get the Ideal Gas Law? We would like to derive the Ideal Gas Law from the three experiemental observations. To do so, we need to learn about the functions $k_1\left(N, T\right)$, $k_2\left(N, P\right)$, $k_3\left(P, T\right)$.

We begin by examining Boyle's Law in more detail: if we hold N and P fixed in Boyle's Law and allow T to vary, the volume must increase with the temperature in agreement with Charles' Law. In other words, with N and P fixed, the volume must be proportional to T. Therefore, k_1 in Boyle's Law must be proportional to T:

$$k_1\left(N, T\right) = k_4\left(N\right) \times T \tag{11.14}$$

where k_4 is a new function which depends only on N. (11.9) then becomes

$$P \times V = k_4\left(N\right) T \tag{11.15}$$

Avogadro's Hypothesis tells us that, at constant pressure and temperature, the volume is proportional to the number of particles. Therefore k_4 must also increase proportionally with the number of particles:

$$k_4\left(N\right) = k \times N \tag{11.16}$$

where k is yet another new constant. In this case, however, there are no variables left, and k is truly a constant. Combining (11.15) and (11.16) gives

$$P \times V = k \times N \times T \tag{11.17}$$

This is very close to the Ideal Gas Law, except that we have the number of particles, N, instead of the number of the number of moles, n. We put this result in the more familiar form by expressing the number of particles in terms of the number of moles, n, by dividing the number of particles by Avogadro's number, N_A, from (11.13). Then, from (11.17),

$$P \times V = k \times N_A \times n \times T \tag{11.18}$$

The two constants, k and N_A, can be combined into a single constant, which is commonly called R, the gas constant. This produces the familiar conclusion of (11.12).

11.6 Observation 3: Partial Pressures

We referred briefly above to the pressure of mixtures of gases, noting in our measurements leading to Boyle's Law that the total pressure of the mixture depends only on the number of moles of gas, regardless of the types and amounts of gases in the mixture. The Ideal Gas Law reveals that the pressure exerted by a mole of molecules does not depend on what those molecules are, and our earlier observation about gas mixtures is consistent with that conclusion.

We now examine the actual process of mixing two gases together and measuring the total pressure. Consider a container of fixed volume 25.0L. We inject into that container 0.78 moles of N_2 gas at 298K. From the Ideal Gas Law, we can easily calculate the measured pressure of the nitrogen gas to be 0.763 atm. We now take an identical container of fixed volume 25.0L, and we inject into that container 0.22 moles of O_2 gas at 298K. The measured pressure of the oxygen gas is 0.215 atm. As a third measurement, we inject 0.22 moles of O_2 gas at 298K into the **first** container which already has 0.78 moles of N_2. (Note that the mixture of gases we have prepared is very similar to that of air.) The measured pressure in this container is now found to be 0.975 atm.

We note now that the **total** pressure of the mixture of N_2 and O_2 in the container is equal to the sum of the pressures of the N_2 and O_2 samples taken separately. We now define the **partial pressure** of each gas in the mixture to be the pressure of each gas as if it were the only gas present. Our measurements tell us that the partial pressure of N_2, P_{N_2}, is 0.763 atm, and the partial pressure of O_2, P_{O_2}, is 0.215 atm.

With this definition, we can now summarize our observation by saying that the total pressure of the mixture of oxygen and nitrogen is equal to the sum of the partial pressures of the two gases. This is a general result: **Dalton's Law of Partial Pressures**.

Law 11.1: Dalton's Law of Partial Pressures
The total pressure of a mixture of gases is the sum of the partial pressures of the component gases in the mixture

11.7 Review and Discussion Questions

Exercise 11.1
Sketch a graph with two curves showing Pressure vs. Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise 11.2
Sketch a graph with two curves showing Pressure vs. 1/Volume for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same temperature. Explain the comparison of the two curves.

Exercise 11.3
Sketch a graph with two curves showing Volume vs. Temperature for two different values of the number of moles of gas, with $n_2 > n_1$, both at the same pressure. Explain the comparison of the two curves.

Exercise 11.4
Sketch a graph with two curves showing Volume vs Temperature for two different values of the pressure of the gas, with $P_2 > P_1$, both for the same number of moles. Explain the comparison of the two curves.

Exercise 11.5
Explain the significance of the fact that, in the volume-temperature experiments, $\frac{\beta}{\alpha}$ is observed to have the same value, independent of the quantity of gas studied and the type of gas studied. What is the significance of the quantity $\frac{\beta}{\alpha}$? Why is it more significant than either β or α?

Exercise 11.6
Amonton's Law says that the pressure of a gas is proportional to the absolute temperature for a fixed quantity of gas in a fixed volume. Thus, $P = k\left(N, V\right)T$. Demonstrate that Amonton's Law can be derived by combining Boyle's Law and Charles' Law.

Exercise 11.7
Using Boyle's Law in your reasoning, demonstrate that the "constant" in Charles' Law, *i.e.* $k_2\left(N, P\right)$, is inversely proportional to P.

Exercise 11.8
Explain how Boyle's Law and Charles' Law may be combined to the general result that, for constant quantity of gas, $P \times V = kT$.

Exercise 11.9
Using Dalton's Law and the Ideal Gas Law, show that the partial pressure of a component of a gas mixture can be calculated from

$$P_i = PX_i \tag{11.19}$$

Where P is the total pressure of the gas mixture and X_i is the **mole fraction** of component i, defined by

$$X_i = \frac{n_i}{n_{\text{total}}} \tag{11.20}$$

Exercise 11.10
Dry air is 78.084% nitrogen, 20.946% oxygen, 0.934% argon, and 0.033% carbon dioxide. Determine the mole fractions and partial pressures of the components of dry air at standard pressure.

Exercise 11.11
Assess the accuracy of the following statement:

Boyle's Law states that $PV = k_1$, where k_1 is a constant. Charles' Law states that $V = k_2T$, where k_2 is a constant. Inserting V from Charles' Law into Boyle's Law results in $Pk_2T = k_1$. We can rearrange this to read $PT = \frac{k_1}{k_2}$ = a constant. Therefore, the pressure of a gas is inversely proportional to the temperature of the gas.

In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

Chapter 12

The Kinetic Molecular Theory[1]

12.1 Foundation

We assume an understanding of the atomic molecular theory postulates, including that all matter is composed of discrete particles. The elements consist of identical atoms, and compounds consist of identical molecules, which are particles containing small whole number ratios of atoms. We also assume that we have determined a complete set of relative atomic weights, allowing us to determine the molecular formula for any compound. Finally, we assume a knowledge of the **Ideal Gas Law**, and the observations from which it is derived.

12.2 Goals

Our continuing goal is to relate the properties of the atoms and molecules to the properties of the materials which they comprise. As simple examples, we compare the substances water, carbon dioxide, and nitrogen. Each of these is composed of molecules with few (two or three) atoms and low molecular weight. However, the physical properties of these substances are very different. Carbon dioxide and nitrogen are gases at room temperature, but it is well known that water is a liquid up to 100 °C. To liquefy nitrogen, we must cool it to -196 °C, so the boiling temperatures of water and nitrogen differ by about 300 °C. Water is a liquid over a rather large temperature range, freezing at 0 °C. In contrast, nitrogen is a liquid for a very narrow range of temperatures, freezing at -210 °C. Carbon dioxide poses yet another very different set of properties. At atmospheric pressure, carbon dioxide gas cannot be liquefied at all: cooling the gas to -60 °C converts it directly to solid "dry ice." As is commonly observed, warming dry ice does not produce any liquid, as the solid sublimes directly to gas.

Why should these materials, whose molecules do not seem all that different, behave so differently? What are the important characteristics of these molecules which produce these physical properties? It is important to keep in mind that these are properties of the bulk materials. At this point, it is not even clear that the concept of a molecule is useful in answering these questions about melting or boiling.

There are at least two principal questions that arise about the **Ideal Gas Law**. First, it is interesting to ask whether this law always holds true, or whether there are conditions under which the pressure of the gas cannot be calculated from $\frac{nRT}{V}$. We thus begin by considering the limitations of the validity of the **Ideal Gas Law**. We shall find that the ideal gas law is only approximately accurate and that there are variations which do depend upon the nature of the gas. Second, then, it is interesting to ask why the ideal gas law should ever hold true. In other words, why are the variations not the rule rather than the exception?

To answer these questions, we need a model which will allow us to relate the properties of bulk materials to the characteristics of individual molecules. We seek to know what happens to a gas when it is compressed into a smaller volume, and why it generates a greater resisting pressure when compressed. Perhaps most

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[1] This content is available online at <http://cnx.org/content/m12450/1.2/>.

fundamentally of all, we seek to know what happens to a substance when it is heated. What property of a gas is measured by the temperature?

12.3 Observation 1: Limitations of the Validity of the Ideal Gas Law

To design a systematic test for the validity of the **Ideal Gas Law**, we note that the value of $\frac{PV}{nRT}$, calculated from the observed values of P, V, n, and T, should always be equal to 1, exactly. Deviation of $\frac{PV}{nRT}$ from 1 indicates a violation of the **Ideal Gas Law**. We thus measure the pressure for several gases under a variety of conditions by varying n, V, and T, and we calculate the ratio $\frac{PV}{nRT}$ for these conditions.

Here (Figure 12.1: Validity of the Ideal Gas Law), the value of this ratio is plotted for several gases as a function of the "particle density" of the gas in moles, $\frac{n}{V}$. To make the analysis of this plot more convenient, the particle density is given in terms of the particle density of an ideal gas at room temperature and atmospheric pressure (*i.e.* the density of air), which is $0.04087\frac{\text{mol}}{L}$. In this figure (Figure 12.1: Validity of the Ideal Gas Law), a particle density of 10 means that the particle density of the gas is 10 times the particle density of air at room temperature. The x-axis in the figure (Figure 12.1: Validity of the Ideal Gas Law) is thus unitless.

Validity of the Ideal Gas Law

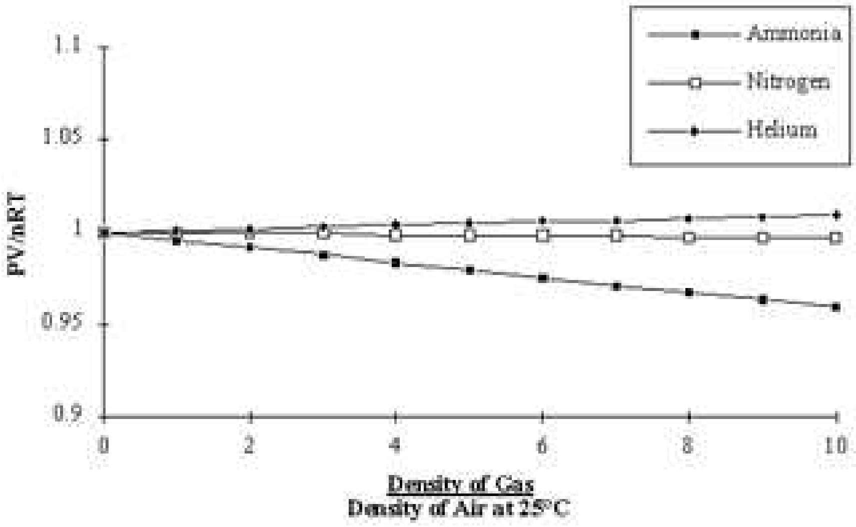

Figure 12.1

Note that $\frac{PV}{nRT}$ on the y-axis is also unitless and has value exactly 1 for an ideal gas. We observe in the data in this figure (Figure 12.1: Validity of the Ideal Gas Law) that $\frac{PV}{nRT}$ is extremely close to 1 for particle densities which are close to that of normal air. Therefore, deviations from the **Ideal Gas Law** are not expected under "normal" conditions. This is not surprising, since **Boyle's Law**, **Charles' Law**, and the **Law of Combining Volumes** were all observed under normal conditions. This figure (Figure 12.1: Validity of the Ideal Gas Law) also shows that, as the particle density increases above the normal range, the value of $\frac{PV}{nRT}$ starts to vary from 1, and the variation depends on the type of gas we are analyzing. However, even for particle densities 10 times greater than that of air at atmospheric pressure, the **Ideal Gas Law** is accurate to a few percent.

Thus, to observe any significant deviations from $PV = nRT$, we need to push the gas conditions to somewhat more extreme values. The results for such extreme conditions are shown here (Figure 12.2: Deviations from the Ideal Gas Law). Note that the densities considered are large numbers corresponding to very high pressures. Under these conditions, we find substantial deviations from the **Ideal Gas Law**. In addition, we see that the pressure of the gas (and thus $\frac{PV}{nRT}$) does depend strongly on which type of gas we are examining. Finally, this figure (Figure 12.2: Deviations from the Ideal Gas Law) shows that deviations from the **Ideal Gas Law** can generate pressures either greater than or less than that predicted by the **Ideal Gas Law**.

Deviations from the Ideal Gas Law

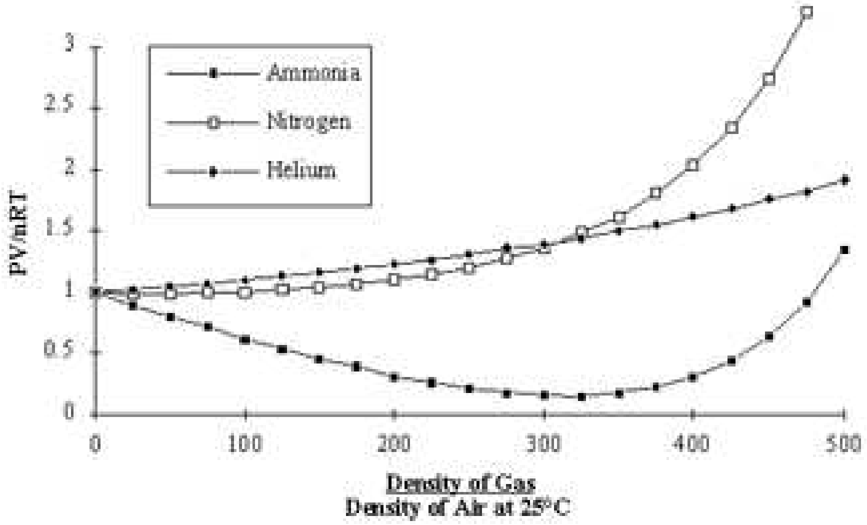

Figure 12.2

12.4 Observation 2: Density and Compressibility of Gas

For low densities for which the **Ideal Gas Law** is valid, the pressure of a gas is independent of the nature of the gas, and is therefore independent of the characteristics of the particles of that gas. We can build on this observation by considering the significance of a low particle density. Even at the high particle densities considered in this figure (Figure 12.2: Deviations from the Ideal Gas Law), all gases have low density in comparison to the densities of liquids. To illustrate, we note that 1 gram of liquid water at its boiling point has a volume very close to 1 milliliter. In comparison, this same 1 gram of water, once evaporated into steam, has a volume of over 1700 milliliters. How does this expansion by a factor of 1700 occur? It is not credible that the individual water molecules suddenly increase in size by this factor. The only plausible conclusion is that the distance between gas molecules has increased dramatically.

Therefore, it is a characteristic of a gas that the molecules are far apart from one another. In addition, the lower the density of the gas the farther apart the molecules must be, since the same number of molecules occupies a larger volume at lower density.

We reinforce this conclusion by noting that liquids and solids are virtually incompressible, whereas gases are easily compressed. This is easily understood if the molecules in a gas are very far apart from one another, in contrast to the liquid and solid where the molecules are so close as to be in contact with one another.

We add this conclusion to the observations in Figure 12.1 (Validity of the Ideal Gas Law) and Figure 12.2 (Deviations from the Ideal Gas Law) that the pressure exerted by a gas depends only on the number of particles in the gas and is independent of the type of particles in the gas, provided that the density is low enough. This requires that the gas particles be far enough apart. We conclude that the **Ideal Gas Law** holds true because there is sufficient distance between the gas particles that the identity of the gas particles becomes irrelevant.

Why should this large distance be required? If gas particle A were far enough away from gas particle B that they experience no electrical or magnetic interaction, then it would not matter what types of particles A and B were. Nor would it matter what the sizes of particles A and B were. Finally, then, we conclude from this reasoning that the validity of the ideal gas law rests of the presumption that there are no interactions of any type between gas particles.

12.5 Postulates of the Kinetic Molecular Theory

We recall at this point our purpose in these observations. Our primary concern in this study is attempting to relate the properties of individual atoms or molecules to the properties of mass quantities of the materials composed of these atoms or molecules. We now have extensive quantitative observations on some specific properties of gases, and we proceed with the task of relating these to the particles of these gases.

By taking an atomic molecular view of a gas, we can postulate that the pressure observed is a consequence of the collisions of the individual particles of the gas with the walls of the container. This presumes that the gas particles are in constant motion. The pressure is, by definition, the force applied per area, and there can be no other origin for a force on the walls of the container than that provided by the particles themselves. Furthermore, we observe easily that the pressure exerted by the gas is the same in all directions. Therefore, the gas particles must be moving equally in all directions, implying quite plausibly that the motions of the particles are random.

To calculate the force generated by these collisions, we must know something about the motions of the gas particles so that we know, for example, each particle's velocity upon impact with the wall. This is too much to ask: there are perhaps 10^{20} particles or more, and following the path of each particle is out of the question. Therefore, we seek a model which permits calculation of the pressure without this information.

Based on our observations and deductions, we take as the postulates of our model:

- A gas consists of individual particles in constant and random motion.
- The individual particles have negligible volume.
- The individual particles do not attract or repel one another in any way.
- The pressure of the gas is due entirely to the force of the collisions of the gas particles with the walls of the container.

This model is the **Kinetic Molecular Theory of Gases**. We now look to see where this model leads.

12.6 Derivation of Boyle's Law from the Kinetic Molecular Theory

To calculate the pressure generated by a gas of N particles contained in a volume V, we must calculate the force F generated per area A by collisions against the walls. To do so, we begin by determining the number of collisions of particles with the walls. The number of collisions we observe depends on how long we wait. Let's measure the pressure for a period of time $\Delta(t)$ and calculate how many collisions occur in that time period. For a particle to collide with the wall within the time $\Delta(t)$, it must start close enough to the wall to impact it in that period of time. If the particle is travelling with speed v, then the particle must be within a distance $v\Delta(t)$ of the wall to hit it. Also, if we are measuring the force exerted on the area A, the particle must hit that area to contribute to our pressure measurement.

For simplicity, we can view the situation pictorially here (Figure 12.3: Collision of a Particle with a Wall within time Δt). We assume that the particles are moving perpendicularly to the walls. (This is clearly not true. However, very importantly, this assumption is only made to simplify the mathematics of our derivation. It is not necessary to make this assumption, and the result is not affected by the assumption.) In order for a particle to hit the area A marked on the wall, it must lie within the cylinder shown, which is of length $v\Delta(t)$ and cross-sectional area A. The volume of this cylinder is $Av\Delta(t)$, so the number of particles contained in the cylinder is $(Av\Delta(t)) \times \frac{N}{V}$.

Collision of a Particle with a Wall within time Δt

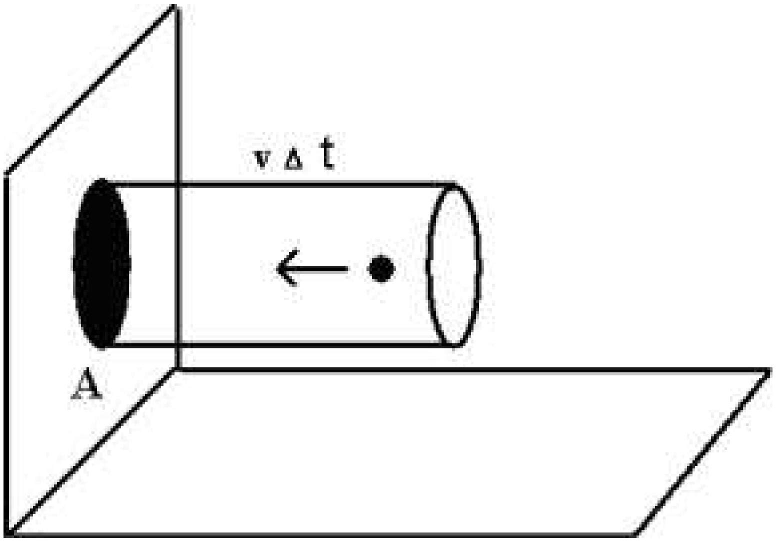

Figure 12.3

Not all of these particles collide with the wall during $\Delta(t)$, though, since most of them are not traveling in the correct direction. There are six directions for a particle to go, corresponding to plus or minus direction in x, y, or z. Therefore, on average, the fraction of particles moving in the correct direction should be $\frac{1}{6}$, assuming as we have that the motions are all random. Therefore, the number of particles which impact the wall in time $\Delta(t)$ is $(Av\Delta(t)) \times \frac{N}{6V}$.

The force generated by these collisions is calculated from Newton's equation, $F = ma$, where a is the acceleration due to the collisions. Consider first a single particle moving directly perpendicular to a wall with velocity v as in Figure 12.3 (Collision of a Particle with a Wall within time Δt). We note that, when the particle collides with the wall, the wall does not move, so the collision must generally conserve the energy of the particle. Then the particle's velocity after the collision must be $-v$, since it is now travelling in the opposite direction. Thus, the change in velocity of the particle in this one collision is $2v$. Multiplying by the number of collisions in $\Delta(t)$ and dividing by the time $\Delta(t)$, we find that the total acceleration (change in velocity per time) is $\frac{2ANv^2}{6V}$, and the force imparted on the wall due collisions is found by multiplying by the mass of the particles:

$$F = \frac{2ANmv^2}{6V} \tag{12.1}$$

To calculate the pressure, we divide by the area A, to find that

$$P = \frac{Nmv^2}{3V} \tag{12.2}$$

or, rearranged for comparison to **Boyle's Law**,

$$PV = \frac{Nmv^2}{3} \tag{12.3}$$

Since we have assumed that the particles travel with constant speed v, then the right side of this equation is a constant. Therefore the product of pressure times volume, PV, is a constant, in agreement with **Boyle's Law**. Furthermore, the product PV is proportional to the number of particles, also in agreement with the **Law of Combining Volumes**. Therefore, the model we have developed to describe an ideal gas is consistent with our experimental observations.

We can draw two very important conclusions from this derivation. First, the inverse relationship observed between pressure and volume and the independence of this relationship on the type of gas analyzed are both due to the lack of interactions between gas particles. Second, the lack of interactions is in turn due to the great distances between gas particles, a fact which will be true provided that the density of the gas is low.

12.7 Interpretation of Temperature

The absence of temperature in the above derivation is notable. The other gas properties have all been incorporated, yet we have derived an equation which omits temperature all together. The problem is that, as we discussed at length above, the temperature was somewhat arbitrarily defined. In fact, it is not precisely clear what has been measured by the temperature. We defined the temperature of a gas in terms of the volume of mercury in a glass tube in contact with the gas. It is perhaps then no wonder that such a quantity does not show up in a mechanical derivation of the gas properties.

On the other hand, the temperature does appear prominently in the **Ideal Gas Law**. Therefore, there must be a greater significance (and less arbitrariness) to the temperature than might have been expected. To discern this significance, we rewrite the last equation above in the form:

$$PV = \frac{2}{3}N\left(\frac{1}{2}mv^2\right) \tag{12.4}$$

The last quantity in parenthesis can be recognized as the kinetic energy of an individual gas particle, and $N\left(\frac{1}{2}mv^2\right)$ must be the total kinetic energy (KE) of the gas. Therefore

$$PV = \frac{2}{3}\text{KE} \tag{12.5}$$

Now we insert the **Ideal Gas Law** for PV to find that

$$\text{KE} = \frac{3}{2}nRT \tag{12.6}$$

This is an extremely important conclusion, for it reveals the answer to the question of what property is measured by the temperature. We see now that the temperature is a measure of the total kinetic energy of the gas. Thus, when we heat a gas, elevating its temperature, we are increasing the average kinetic energy of the gas particles, causing then to move, on average, more rapidly.

12.8 Analysis of Deviations from the Ideal Gas Law

We are at last in a position to understand the observations above (Section 12.3: Observation 1: Limitations of the Validity of the Ideal Gas Law) of deviations from the **Ideal Gas Law**. The most important assumption of our model of the behavior of an ideal gas is that the gas molecules do not interact. This allowed us to calculate the force imparted on the wall of the container due to a single particle collision without worrying about where the other particles were. In order for a gas to disobey the **Ideal Gas Law**, the conditions must be such that this assumption is violated.

What do the deviations from ideality tell us about the gas particles? Starting with very low density and increasing the density as in Figure 12.1 (Validity of the Ideal Gas Law), we find that, for many gases, the value of $\frac{PV}{nRT}$ falls below 1. One way to state this result is that, for a given value of V, n, and T, the pressure of the gas is less than it would have been for an ideal gas. This must be the result of the interactions of the gas particles. In order for the pressure to be reduced, the force of the collisions of the particles with the walls must be less than is predicted by our model of an ideal gas. Therefore, the effect of the interactions is to slow the particles as they approach the walls of the container. This means that an individual particle approaching a wall must experience a force acting to pull it back into the body of the gas. Hence, the gas particles must attract one another. Therefore, the effect of increasing the density of the gas is that the gas particles are confined in closer proximity to one another. At this closer range, the attractions of individual particles become significant. It should not be surprising that these attractive forces depend on what the particles are. We note in Figure 12.1 (Validity of the Ideal Gas Law) that deviation from the **Ideal Gas Law** is greater for ammonia than for nitrogen, and greater for nitrogen than for helium. Therefore, the attractive interactions of ammonia molecules are greater than those of nitrogen molecules, which are in turn greater than those of helium atoms. We analyze this conclusion is more detail below.

Continuing to increase the density of the gas, we find in Figure 12.2 (Deviations from the Ideal Gas Law) that the value of $\frac{PV}{nRT}$ begins to rise, eventually exceeding 1 and continuing to increase. Under these conditions, therefore, the pressure of the gas is greater than we would have expected from our model of non-interacting particles. What does this tell us? The gas particles are interacting in such a way as to increase the force of the collisions of the particles with the walls. This requires that the gas particles repel one another. As we move to higher density, the particles are forced into closer and closer proximity. We can conclude that gas particles at very close range experience strong repulsive forces away from one another.

Our model of the behavior of gases can be summarized as follows: at low density, the gas particles are sufficiently far apart that there are no interactions between them. In this case, the pressure of the gas is independent of the nature of the gas and agrees with the **Ideal Gas Law**. At somewhat higher densities, the particles are closer together and the interaction forces between the particles are attractive. The pressure of the gas now depends on the strength of these interactions and is lower than the value predicted by the **Ideal Gas Law**. At still higher densities, the particles are excessively close together, resulting in repulsive interaction forces. The pressure of the gas under these conditions is higher than the value predicted by the **Ideal Gas Law**.

12.9 Observation 3: Boiling Points of simple hydrides

The postulates of the **Kinetic Molecular Theory** provide us a way to understand the relationship between molecular properties and the physical properties of bulk amounts of substance. As a distinct example of such an application, we now examine the boiling points of various compounds, focusing on hydrides of sixteen elements in the main group (Groups IV through VII). These are given here (Table 12.1: Boiling Points of Hydrides of Groups IV to VII).

Boiling Points of Hydrides of Groups IV to VII

	Boiling Point (°C)
CH_4	-164
NH_3	-33
H_2O	100
HF	20
SiH_4	-111.8
PH_3	-87.7
H_2S	-60.7
HCl	-85
GeH_4	-88.5
AsH_3	-55
H_2Se	-41.5
HBr	-67
SnH_4	-52
SbH_3	-17.1
H_2Te	-2.2
HI	-35

Table 12.1

In tabular form, there are no obvious trends here, and therefore no obvious connection to the structure or bonding in the molecules. The data in the table (Table 12.1: Boiling Points of Hydrides of Groups IV to VII) are displayed in a suggestive form, however, in Figure 12.4 (Boiling Points of Main Group Hydrides), the boiling point of each hydride is plotted according to which period (row) of the periodic table the main group element belongs. For example, the Period 2 hydrides (CH_4, NH_3, H_2O, and HF) are grouped in a column to the left of the figure, followed by a column for the Period 3 hydrides (SiH_4, PH_3, H_2S, HCl), etc.

Now a few trends are more apparent. First, the lowest boiling points in each period are associated with the Group IV hydrides (CH_4, SiH_4, GeH_4, SnH_4), and the highest boiling points in each period belong to the Group VI hydrides (H_2O, H_2S, H_2Se, H_2Te). For this reason, the hydrides belonging to a single group have been connected in Figure 12.4 (Boiling Points of Main Group Hydrides).

Boiling Points of Main Group Hydrides

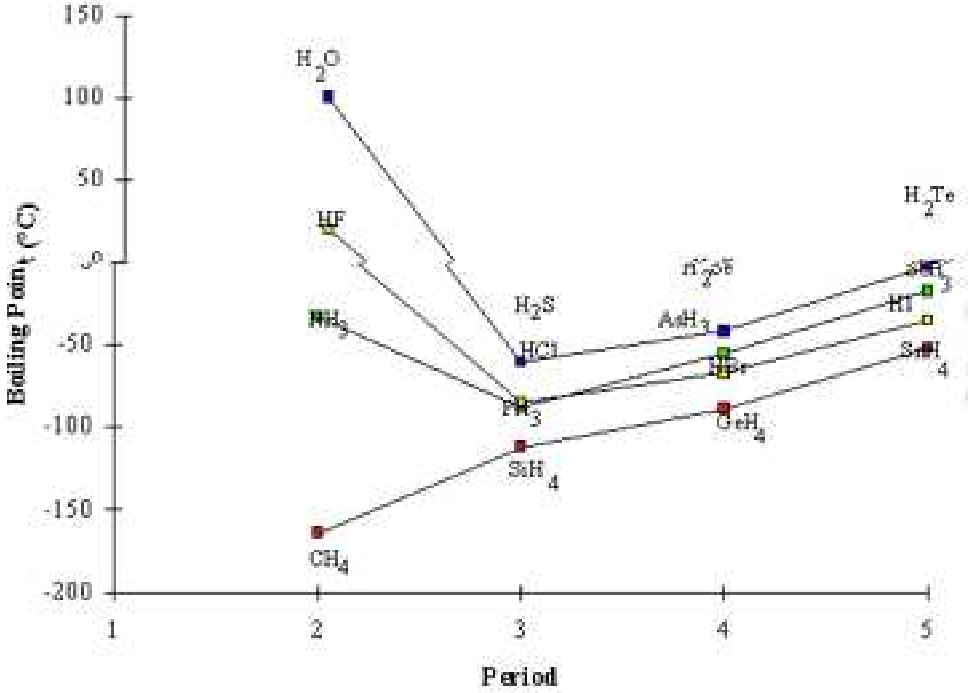

Figure 12.4

Second, we notice that, with the exceptions of NH_3, H_2O, and HF, the boiling points of the hydrides always increase in a single group as we go down the periodic table: for example, in Group IV, the boiling points increase in the order $CH_4 < SiH_4 < GeH_4 < SnH_4$. Third, we can also say that the hydrides from Period 2 appear to have unusually high boiling points **except** for CH_4, which as noted has the lowest boiling point of all.

We begin our analysis of these trends by assuming that there is a relationship between the boiling points of these compounds and the structure and bonding in their molecules. Recalling our kinetic molecular model of gases and liquids, we recognize that a primary difference between these two phases is that the strength of the interaction between the molecules in the liquid is much greater than that in the gas, due to the proximity of the molecules in the liquid. In order for a molecule to leave the liquid phase and enter into the gas phase, it must possess sufficient energy to overcome the interactions it has with other molecules in the liquid. Also recalling the kinetic molecular description, we recognize that, on average, the energies of molecules increase with increasing temperature. We can conclude from these two statements that a high boiling point implies that significant energy is required to overcome intermolecular interactions. Conversely, a substance with a low boiling point must have weak intermolecular interactions, surmountable even at low temperature.

In light of these conclusions, we can now look at Figure 12.4 (Boiling Points of Main Group Hydrides) as directly (though qualitatively) revealing the comparative strengths of intermolecular interactions of the various hydrides. For example, we can conclude that, amongst the hydrides considered here, the intermolecular interactions are greatest between H_2O molecules and weakest between CH_4 molecules. We examine the three trends in this figure, described above, in light of the strength of intermolecular forces.

First, the most dominant trend in the boiling points is that, within a single group, the boiling points of the hydrides increase as we move **down** the periodic table. This is true in all four groups in Figure 12.4 (Boiling Points of Main Group Hydrides); the only exceptions to this trend are NH_3, H_2O, and HF. We can conclude that, with notable exceptions, intermolecular interactions increase with increasing atomic number of the central atom in the molecule. This is true whether the molecules of the group considered have dipole moments (as in Groups V, VI, and VII) or not (as in Group IV). We can infer that the large intermolecular attractions for molecules with large central atoms arises from the large number of charged particles in these molecules.

This type of interaction arises from forces referred to as **London forces** or **dispersion forces**. These forces are believed to arise from the instantaneous interactions of the charged particles from one molecule with the charged particles in an adjacent molecule. Although these molecules may not be polar individually, the nuclei in one molecule may attract the electrons in a second molecule, thus inducing an instantaneous dipole in the second molecule. In turn, the second molecule induces a dipole in the first. Thus, two non-polar molecules can interact as if there were dipole-dipole attractions between them, with positive and negative charges interacting and attracting. The tendency of a molecule to have an induced dipole is called the **polarizability** of the molecule. The more charged particles there are in a molecule, the more **polarizable** a molecule is and the greater the attractions arising from dispersion forces will be.

Second, we note that, without exception, the Group IV hydrides must have the weakest intermolecular interactions in each period. As noted above, these are the only hydrides that have no dipole moment. Consequently, in general, molecules without dipole moments have weaker interactions than molecules which are polar. We must qualify this carefully, however, by noting that the nonpolar SnH_4 has a higher boiling point than the polar PH_3 and HCl. We can conclude from these comparisons that the increased polarizability of molecules with heavier atoms can offset the lack of a molecular dipole.

Third, and most importantly, we note that the intermolecular attractions involving NH_3, H_2O, and HF must be uniquely and unexpectedly large, since their boiling points are markedly out of line with those of the rest of their groups. The common feature of these molecules is that they contain small atomic number atoms which are strongly electronegative, which have lone pairs, and which are bonded to hydrogen atoms. Molecules without these features do not have unexpectedly high boiling points. We can deduce from these observations that the hydrogen atoms in each molecule are unusually strongly attracted to the lone pair electrons on the strongly electronegative atoms with the same properties in other molecules. This intermolecular attraction of a hydrogen atom to an electronegative atom is referred to as **hydrogen bonding**. It is clear from our boiling point data that hydrogen bonding interactions are much stronger than either dispersion forces or dipole-dipole attractions.

12.10 Review and Discussion Questions

Exercise 12.1

Explain the significance to the development of the kinetic molecular model of the observation that the ideal gas law works well only at low pressure.

Exercise 12.2

Explain the significance to the development of the kinetic molecular model of the observation that the pressure predicted by the ideal gas law is independent of the type of gas.

Exercise 12.3

Sketch the value of $\frac{PV}{nRT}$ as a function of density for two gases, one with strong intermolecular attractions and one with weak intermolecular attractions but strong repulsions.

Exercise 12.4

Give a brief molecular explanation for the observation that the pressure of a gas at fixed temperature increases proportionally with the density of the gas.

Exercise 12.5
Give a brief molecular explanation for the observation that the pressure of a gas confined to a fixed volume increases proportionally with the temperature of the gas.

Exercise 12.6
Give a brief molecular explanation for the observation that the volume of a balloon increases roughly proportionally with the temperature of the gas inside the balloon.

Exercise 12.7
Explain why there is a correlation between high boiling point and strong deviation from the **Ideal Gas Law**.

Exercise 12.8
Referring to Figure 12.4 (Boiling Points of Main Group Hydrides), explain why the hydride of the Group 4 element always has the lowest boiling point in each period.

Exercise 12.9
Explain why the Period 2 hydrides except CH_4 all have high boiling points, and explain why CH_4 is an exception.

Chapter 13

Phase Equilibrium and Intermolecular Interactions[1]

13.1 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.

13.2 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 no 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

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[1] This content is available online at <http://cnx.org/content/m12596/1.1/>.

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.

13.3 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 (Figure 13.1: Vapor-Liquid Phase Transition) is a straight line, which can be extrapolated to zero volume at 0K.

Vapor-Liquid Phase Transition

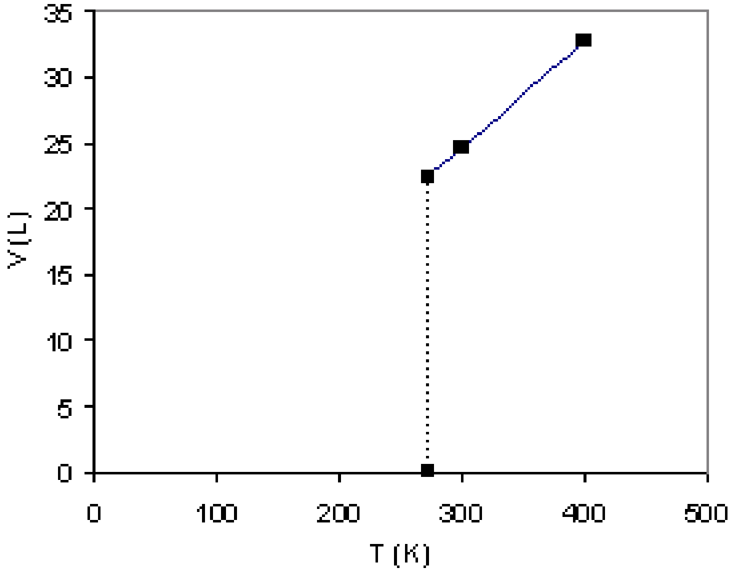

Figure 13.1

Consider, then, trying to measure the volume for lower and lower temperatures to follow the graph (Figure 13.1: Vapor-Liquid Phase Transition). To be specific, we take exactly 1.00 mol of butane C_4H_{10} at 1 atm pressure. As we lower the temperature from 400K to 300K, we observe the expected proportional decrease in the volume from 32.8L to 24.6L and this proportionality works very well for temperatures just slightly above 272.6K, where the volume is 22.4L. However, when we reach 272.6K, the volume of the butane drops very abruptly, falling to about 0.097L at temperatures just slightly below 272.6K. This is less than one-half of one percent of the previous volume! The striking change in volume is shown in the graph (Figure 13.1: Vapor-Liquid Phase Transition) as a vertical line at 272.6K.

This dramatic change in physical properties at one temperature is referred to as a **phase transition**. When cooling butane through the temperature 272.6K, 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 272.6K and then heating, we find that the butane remains entirely liquid for temperatures below 272.6K and then becomes entirely gas for temperatures above 272.6K. 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 (Section 13.4: Observation 2: Vapor pressure of a liquid).)

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 (Variation of Phase Transition with Pressure) along with the previous result for 1.00 mol. Note that the phase transition is observed to occur at exactly the same temperature, 272.6K, even though there is double the mass of butane.

Variation of Phase Transition with Pressure

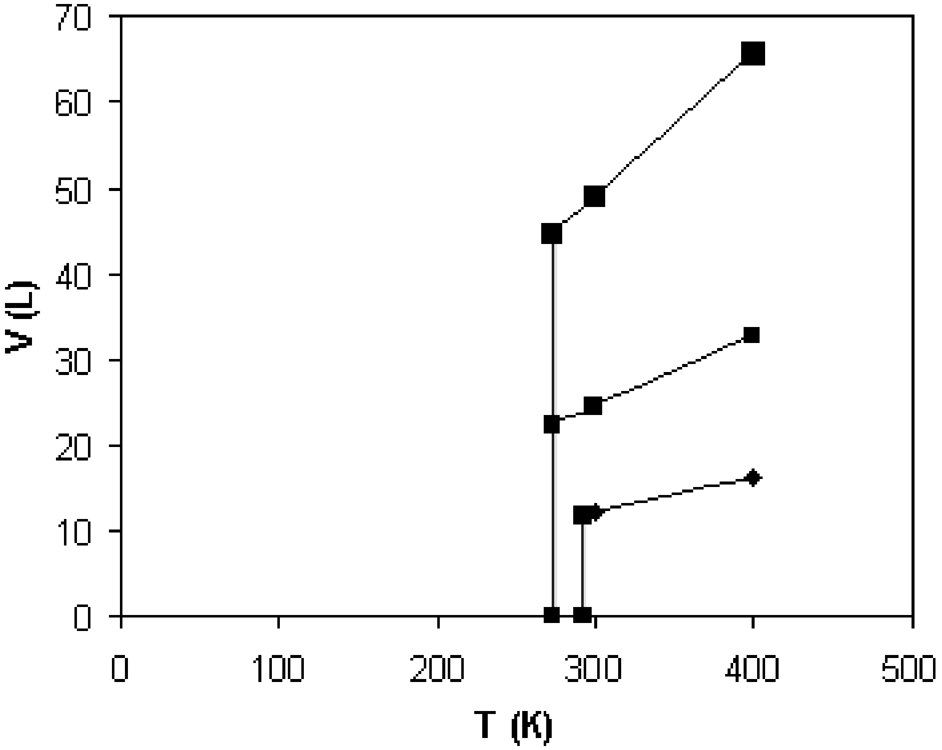

Figure 13.2

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 (Variation of Phase Transition with Pressure). 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 293.2K, over 20K higher than at the lower pressure. Therefore, the temperature of the phase transition depends on the pressure applied. We can measure the boiling point temperature of butane as a function of the applied pressure, and this result is plotted here (Figure 13.3: Boiling Point versus Pressure).

Boiling Point versus Pressure

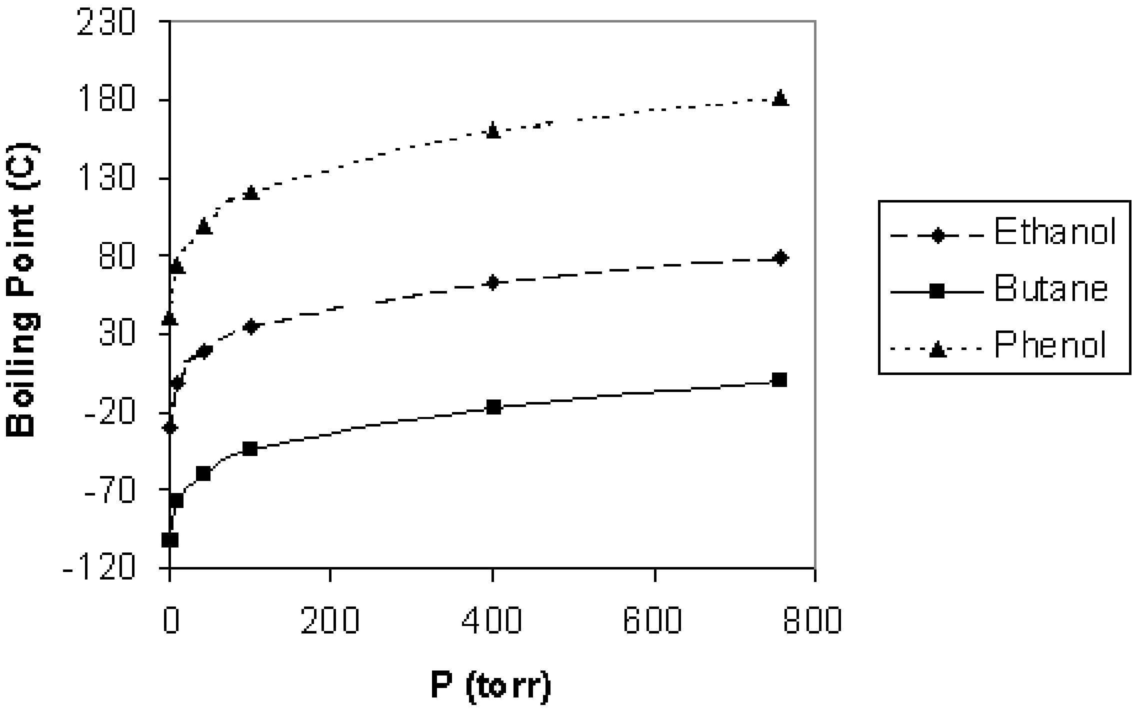

Figure 13.3

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 (Boiling Point versus Pressure), 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.

13.4 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 of 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. (Here (Figure 13.4: Measuring Vapor Pressure) is an illustration.) 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.

Measuring Vapor Pressure

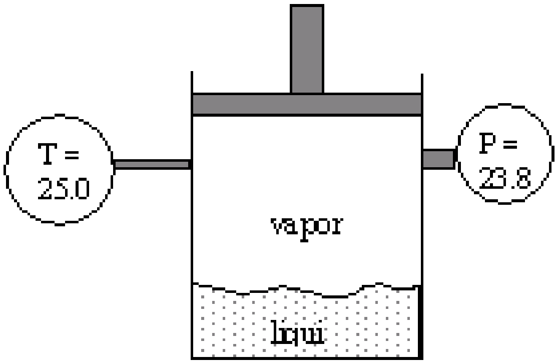

Figure 13.4

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 here (Figure 13.5: Vapor Pressures of Various Liquids). The vapor pressure for each liquid increases smoothly with the temperature, although the relationship between vapor pressure and temperature is definitely not proportional.

Vapor Pressures of Various Liquids

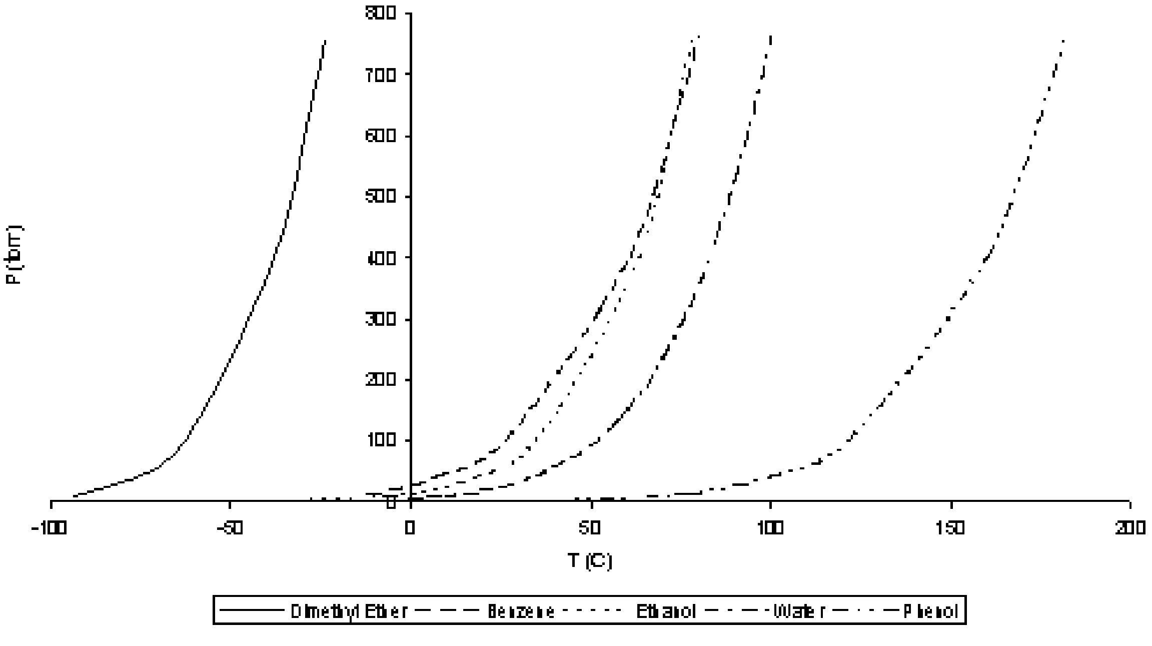

Figure 13.5

Second, Figure 13.5 (Vapor Pressures of Various Liquids) 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 (Vapor Pressures of Various Liquids), 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 as 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.

13.5 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 (Vapor Pressures of Various Liquids) in a different way. Consider the specific case of water, with vapor pressure given here (Figure 13.6: Vapor Pressure of Liquid Water). 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 (Vapor Pressure of Liquid Water) 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.

Vapor Pressure of Liquid Water

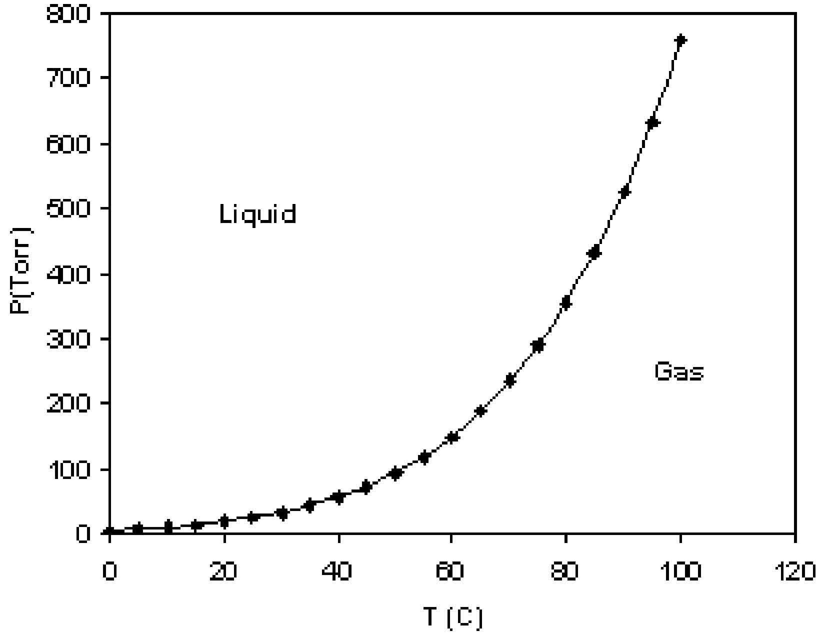

Figure 13.6

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 (Vapor Pressure of Liquid Water), we observe liquid-gas equilibrium.

What happens at temperature/pressure combinations which are not on the line in Figure 13.6 (Vapor Pressure of Liquid Water)? 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 (Vapor Pressure of Liquid Water) 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 (Vapor Pressure of Liquid Water), we refer to the graph as a **phase diagram**.

Of course, Figure 13.6 (Vapor Pressure of Liquid Water) 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 (Measuring Vapor Pressure) 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 (Vapor Pressure of Liquid Water). If we continue to lower the temperature, though, we observe an interesting transition, as shown in the more detailed Figure 13.7 (Water Phase Transitions). 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.

Water Phase Transitions

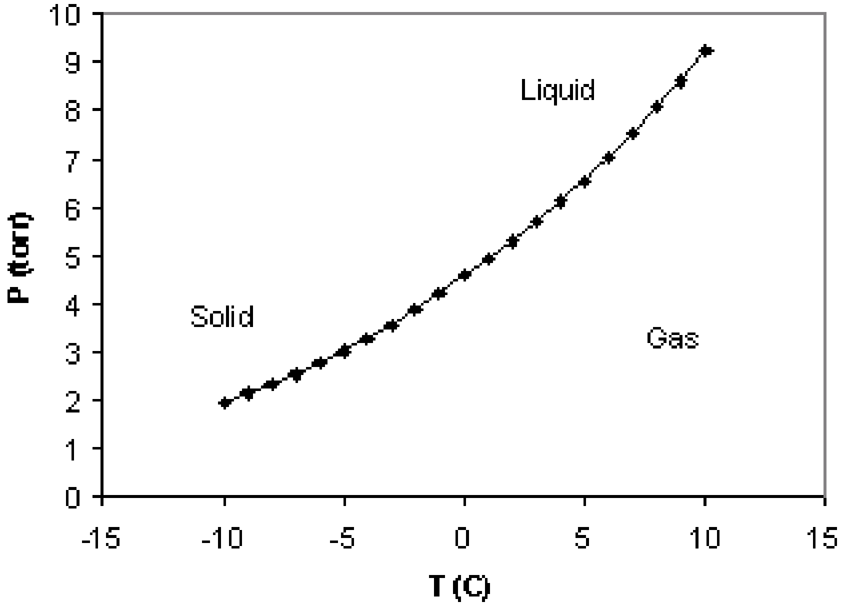

Figure 13.7

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 (Water Phase Transitions) 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 (Water Phase Transitions) 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 this (Figure 13.8: Phase Diagram of Water), where the solid-liquid line is very nearly vertical.

Phase Diagram of Water

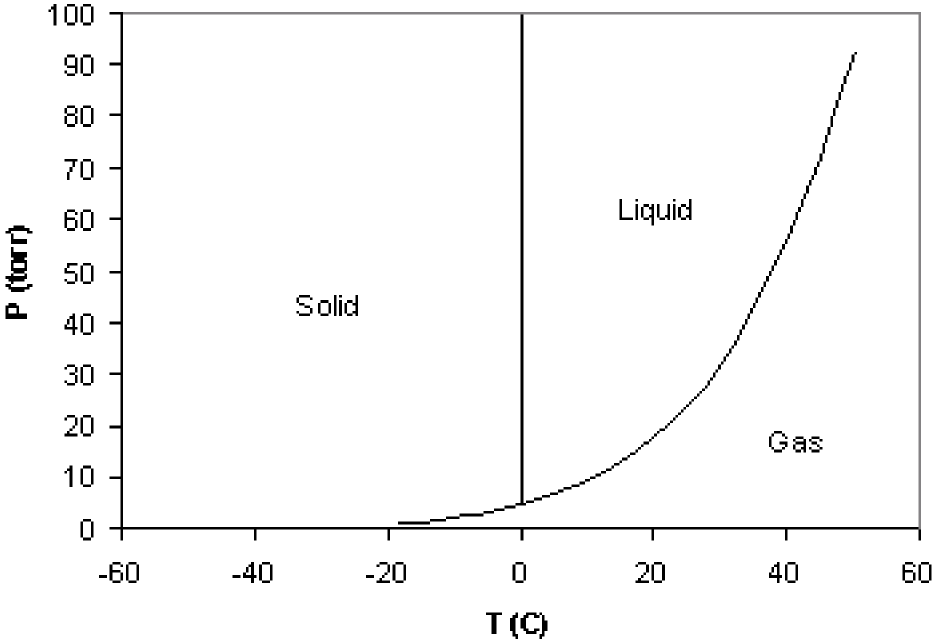

Figure 13.8

Each substance has its own unique phase diagram, corresponding to the diagram in Figure 13.8 (Phase Diagram of Water) for water.

13.6 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 (Measuring Vapor Pressure). 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.

13.7 Review and Discussion Questions

Exercise 13.1

In the phase diagram for water in Figure 13.6 (Vapor Pressure of Liquid Water), 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.

Exercise 13.2

In the phase diagram for water in Figure 13.6 (Vapor Pressure of Liquid Water), 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.

Exercise 13.3

Explain why Figure 13.6 (Vapor Pressure of Liquid Water) 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.

Exercise 13.4

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.

Exercise 13.5

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 can be in equilibrium.

Exercise 13.6

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

Exercise 13.7

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

Exercise 13.8

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

Exercise 13.9

According to Figure 13.5 (Vapor Pressures of Various Liquids) 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.

Exercise 13.10

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.

Chapter 14

Reaction Equilibrium in the Gas Phase[1]

14.1 Foundation

In beginning our study of the reactions of gases, we will assume a knowledge of the physical properties of gases as described by the **Ideal Gas Law** and an understanding of these properties as given by the postulates and conclusions of the **Kinetic Molecular Theory**. We assume that we have developed a dynamic model of phase equilibrium in terms of competing rates. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

14.2 Goals

In performing stoichiometric calculations, we assume that we can calculate the amount of product of a reaction from the amount of the reactants we start with. For example, if we burn methane gas, $CH_4\,(g)$, in excess oxygen, the reaction

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \qquad (14.1)$$

occurs, and the number of moles of $CO_2\,(g)$ produced is assumed to equal the number of moles of $CH_4\,(g)$ we start with.

From our study of phase transitions we have learned the concept of equilibrium. We observed that, in the transition from one phase to another for a substance, under certain conditions both phases are found to coexist, and we refer to this as phase equilibrium. It should not surprise us that these same concepts of equilibrium apply to chemical reactions as well. In the reaction (14.1), therefore, we should examine whether the reaction actually produces exactly one mole of CO_2 for every mole of CH_4 we start with or whether we wind up with an equilibrium mixture containing both CO_2 and CH_4. We will find that different reactions provide us with varying answers. In many cases, virtually all reactants are consumed, producing the stoichiometric amount of product. However, in many other cases, substantial amounts of reactant are still present when the reaction achieves equilibrium, and in other cases, almost no product is produced at equilibrium. Our goal will be to understand, describe and predict the reaction equilibrium.

An important corollary to this goal is to attempt to control the equilibrium. We will find that varying the conditions under which the reaction occurs can vary the amounts of reactants and products present at equilibrium. We will develop a general principle for predicting how the reaction conditions affect the amount of product produced at equilibrium.

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[1] This content is available online at <http://cnx.org/content/m12597/1.2/>.

14.3 Observation 1: Reaction equilibrium

We begin by analyzing a significant industrial chemical process, the synthesis of ammonia gas, NH_3, from nitrogen and hydrogen:

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g) \tag{14.2}$$

If we start with 1 mole of N_2 and 3 moles of H_2, the balanced equation predicts that we will produce 2 moles of NH_3. In fact, if we carry out this reaction starting with these quantities of nitrogen and hydrogen at 298K in a 100.0L reaction vessel, we observe that the number of moles of NH_3 produced is 1.91 mol. This "yield" is less than predicted by the balanced equation, but the difference is not due to a limiting reagent factor. Recall that, in stoichiometry, the limiting reagent is the one that is present in less than the ratio of moles given by the balanced equation. In this case, neither N_2 nor H_2 is limiting because they are present initially in a 1:3 ratio, exactly matching the stoichiometry. Note also that this seeming deficit in the yield is not due to any experimental error or imperfection, nor is it due to poor measurements or preparation. Rather, the observation that, at 298K, 1.91 moles rather than 2 moles are produced is completely reproducible: every measurement of this reaction at this temperature in this volume starting with 1 mole of N_2 and 3 moles of H_2 gives this result. We conclude that the reaction (14.2) achieves **reaction equilibrium** in which all three gases are present in the gas mixture. We can determine the amounts of each gas at equilibrium from the stoichiometry of the reaction. When $n_{NH_3} = 1.91\text{mol}$ are created, the number of moles of N_2 remaining at equilibrium is $n_{N_2} = 0.045\text{mol}$ and $n_{H_2} = 0.135\text{mol}$.

It is important to note that we can vary the relative amount of NH_3 produced by varying the temperature of the reaction, the volume of the vessel in which the reaction occurs, or the relative starting amounts of N_2 and H_2. We shall study and analyze this observation in detail in later sections. For now, though, we demonstrate that the concept of reaction equilibrium is general to all reactions.

Consider the reaction

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g) \tag{14.3}$$

If we begin with 1.00 mole of H_2 and 1.00 mole of I_2 at 500K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n_{HI} = 1.72\text{mol}$, leaving in the equilibrium mixture $n_{H_2} = 0.14\text{mol}$ and $n_{I_2} = 0.14\text{mol}$.

Similarly, consider the decomposition reaction

$$N_2O_4\,(g) \rightarrow 2NO_2\,(g) \tag{14.4}$$

At 298K in a 100.0L reaction flask, 1.00 mol of N_2O_4 partially decomposes to produce, at equilibrium, $n_{NO_2} = 0.64\text{mol}$ and $n_{N_2O_4} = 0.68\text{mol}$.

Some chemical reactions achieve an equilibrium that appears to be very nearly complete reaction. For example,

$$H_2\,(g) + Cl_2\,(g) \rightarrow 2HCl\,(g) \tag{14.5}$$

If we begin with 1.00 mole of H_2 and 1.00 mole of Cl_2 at 298K in a reaction vessel of fixed volume, we observe that, at equilibrium, n_{HCl} is almost exactly 2.00 mol, leaving virtually no H_2 or Cl_2. This does not mean that the reaction has not come to equilibrium. It means instead that, at equilibrium, there are essentially no reactants remaining.

In each of these cases, the amounts of reactants and products present at equilibrium vary as the conditions are varied but are completely reproducible for fixed conditions. Before making further observations that will lead to a quantitative description of the reaction equilibrium, we consider a qualitative description of equilibrium.

We begin with a dynamic equilibrium description. We know from our studies of phase transitions that equilibrium occurs when the rate of the forward process (*e.g.* evaporation) is matched by the rate of reverse process (*e.g.* condensation). Since we have now observed that gas reactions also come to equilibrium, we postulate that at equilibrium the forward reaction rate is equal to the reverse reaction rate. For example, in the reaction here (14.4), the rate of decomposition of N_2O_4 molecules at equilibrium must be exactly matched by the rate of recombination (or **dimerization**) of NO_2 molecules.

To show that the forward and reverse reactions continue to happen at equilibrium, we start with the NO_2 and N_2O_4 mixture at equilibrium and we vary the volume of the flask containing the mixture. We observe that, if we increase the volume and the reaction is allowed to come to equilibrium, the amount of NO_2 at equilibrium is larger at the expense of a smaller amount of N_2O_4. We can certainly conclude that the amounts of the gases at equilibrium depend on the reaction conditions. However, if the forward and reverse reactions stop once the equilibrium amounts of material are achieved, the molecules would not "know" that the volume of the container had increased. Since the reaction equilibrium can and does respond to a change in volume, it must be that the change in volume affects the rates of both the forward and reverse processes. This means that both reactions must be occurring at equilibrium, and that their rates must exactly match at equilibrium.

This reasoning reveals that the amounts of reactant and product present at equilibrium are determined by the rates of the forward and reverse reactions. If the rate of the forward reaction (*e.g.* decomposition of N_2O_4) is faster than the rate of the reverse reaction, then at equilibrium we have more product than reactant. If that difference in rates is very large, at equilibrium there will be much more product than reactant. Of course, the converse of these conclusions is also true. It must also be the case that the rates of these processes depends on, amongst other factors, the volume of the reaction flask, since the amounts of each gas present at equilibrium change when the volume is changed.

14.4 Observation 2: Equilibrium constants

It was noted above that the equilibrium partial pressures of the gases in a reaction vary depending upon a variety of conditions. These include changes in the initial numbers of moles of reactants and products, changes in the volume of the reaction flask, and changes in the temperature. We now study these variations quantitatively.

Consider first the reaction here (14.4). Following on our previous study of this reaction, we inject an initial amount of $N_2O_4\,(g)$ into a 100L reaction flask at 298K. Now, however, we vary the initial number of moles of $N_2O_4\,(g)$ in the flask and measure the equilibrium pressures of both the reactant and product gases. The results of a number of such studies are given here (Table 14.1: Equilibrium Partial Pressures in Decomposition Reaction).

Equilibrium Partial Pressures in Decomposition Reaction

Initial $n_{N_2O_4}$	$P_{N_2O_4}$ **(atm)**	P_{NO_2} **(atm)**
0.1	0.00764	0.033627
0.5	0.071011	0.102517
1	0.166136	0.156806
1.5	0.26735	0.198917
2	0.371791	0.234574
2.5	0.478315	0.266065
3	0.586327	0.294578
3.5	0.695472	0.320827
4	0.805517	0.345277
4.5	0.916297	0.368255
5	1.027695	0.389998

Table 14.1

We might have expected that the amount of NO_2 produced at equilibrium would increase in direct proportion to increases in the amount of N_2O_4 we begin with. Table 14.1: Equilibrium Partial Pressures in Decomposition Reaction shows that this is not the case. Note that when we increase the initial amount of N_2O_4 by a factor of 10 from 0.5 moles to 5.0 moles, the pressure of NO_2 at equilibrium increases by a factor of less than 4.

The relationship between the pressures at equilibrium and the initial amount of N_2O_4 is perhaps more easily seen in a graph of the data in Table 14.1: Equilibrium Partial Pressures in Decomposition Reaction, as shown in Figure 14.1 (Equilibrium Partial Pressures in Decomposition Reaction). There are some interesting features here. Note that, when the initial amount of N_2O_4 is less than 1 mol, the equilibrium pressure of NO_2 is greater than that of N_2O_4. These relative pressures reverse as the initial amount increases, as the N_2O_4 equilibrium pressure keeps track with the initial amount but the NO_2 pressure falls short. Clearly, the equilibrium pressure of NO_2 does not increase proportionally with the initial amount of N_2O_4. In fact, the increase is slower than proportionality, suggesting perhaps a square root relationship between the pressure of NO_2 and the initial amount of N_2O_4.

Equilibrium Partial Pressures in Decomposition Reaction

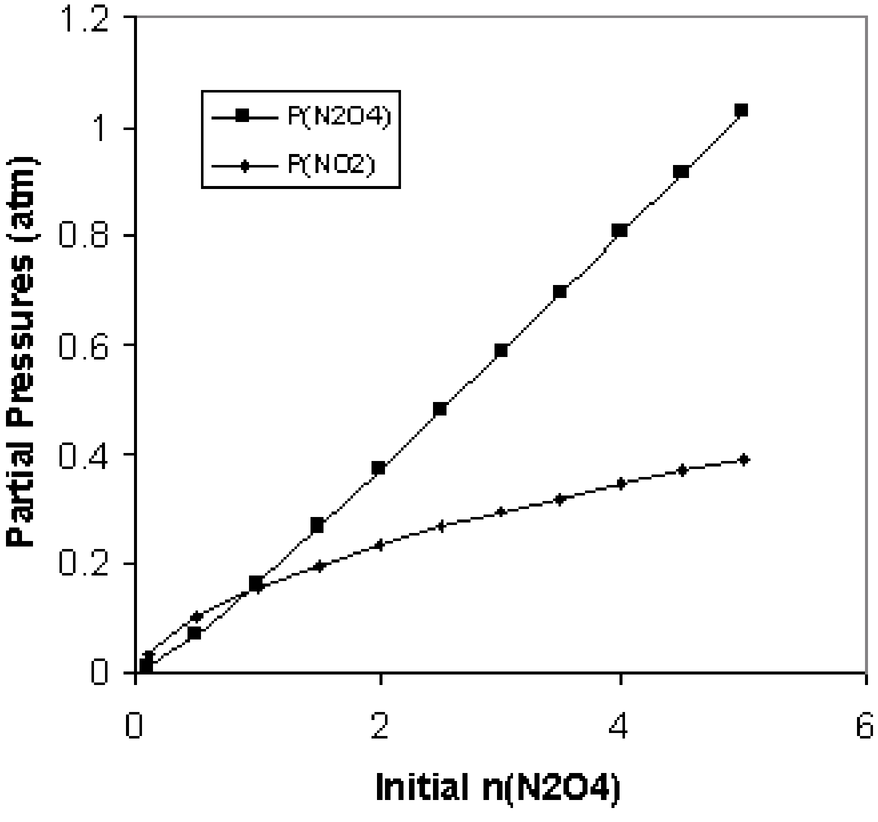

Figure 14.1

We test this in Figure 14.2 (Relationship of Pressure of Product to Initial Amount of Reactant) by plotting P_{NO_2} at equilibrium versus the square root of the initial number of moles of N_2O_4. Figure 14.2 (Relationship of Pressure of Product to Initial Amount of Reactant) makes it clear that this is not a simple proportional relationship, but it is closer. Note in Figure 14.1 (Equilibrium Partial Pressures in Decomposition Reaction) that the equilibrium pressure $P_{N_2O_4}$ increases close to proportionally with the initial amount of N_2O_4. This suggests plotting P_{NO_2} versus the square root of $P_{N_2O_4}$. This is done in Figure 14.3 (Equilibrium Partial Pressures), where we discover that there is a very simple proportional relationship between the variables plotted in this way. We have thus observed that

$$P_{NO_2} = c\sqrt{2P_{N_2O_4}} \tag{14.6}$$

where c is the slope of the graph. (14.6) can be rewritten in a standard form

$$K_p = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} \tag{14.7}$$

To test the accuracy of this equation and to find the value of K_p, we return to Table 14.1: Equilibrium Partial Pressures in Decomposition Reaction and add another column in which we calculate the value of K_p for each of the data points. Table 14.2: Equilibrium Partial Pressures in Decomposition Reaction makes it clear that the "constant" in (14.7) truly is independent of both the initial conditions and the equilibrium partial pressure of either one of the reactant or product. We thus refer to the constant K_p in (14.7) as the **reaction equilibrium constant**.

Relationship of Pressure of Product to Initial Amount of Reactant

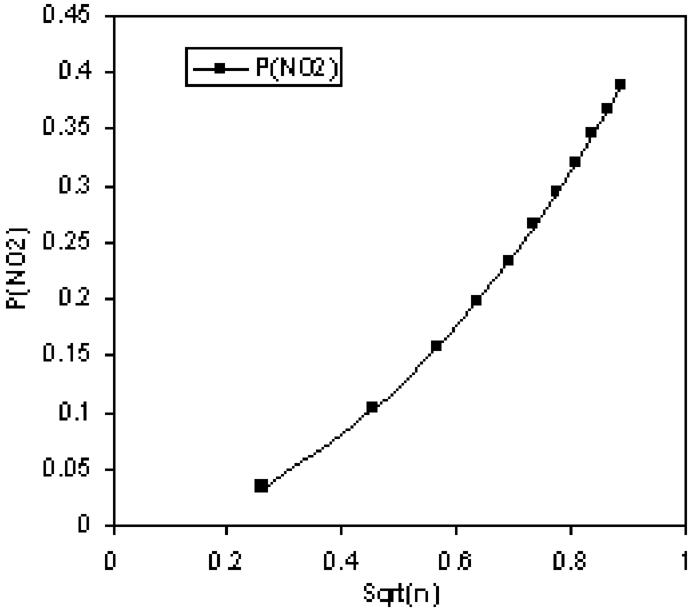

Figure 14.2

Equilibrium Partial Pressures

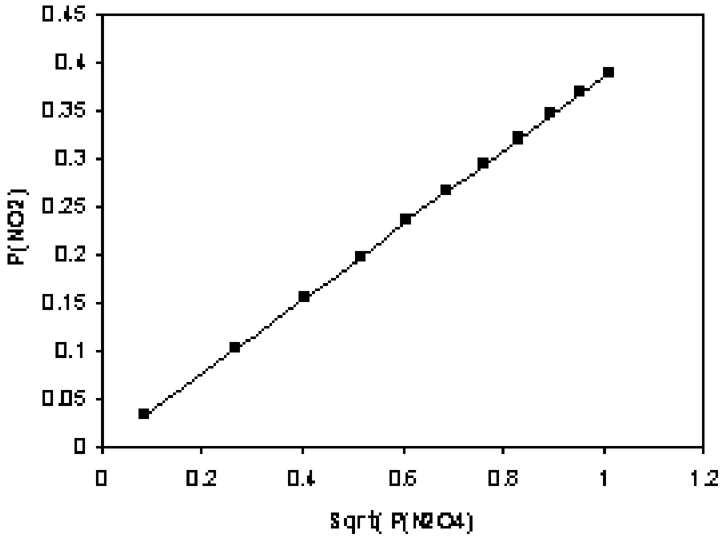

Figure 14.3

Equilibrium Partial Pressures in Decomposition Reaction

Initial $n_{N_2O_4}$	$P_{N_2O_4}$ **(atm)**	P_{NO_2} **(atm)**	K_p
0.1	0.00764	0.0336	0.148
0.5	0.0710	0.102	0.148
1	0.166	0.156	0.148
1.5	0.267	0.198	0.148
2	0.371	0.234	0.148
2.5	0.478	0.266	0.148
3	0.586	0.294	0.148
3.5	0.695	0.320	0.148
4	0.805	0.345	0.148
4.5	0.916	0.368	0.148
5	1.027	0.389	0.148

Table 14.2

It is very interesting to note the functional form of the equilibrium constant. The product NO_2 pressure appears in the numerator, and the exponent 2 on the pressure is the stoichiometric coefficient on NO_2 in the balanced chemical equation. The reactant N_2O_4 pressure appears in the denominator, and the exponent 1 on the pressure is the stoichiometric coefficient on N_2O_4 in the chemical equation.

We now investigate whether other reactions have equilibrium constants and whether the form of this equilibrium constant is a happy coincidence or a general observation. We return to the reaction for the synthesis of ammonia (14.2).

In a previous section (Section 14.2: Goals), we considered only the equilibrium produced when 1 mole of N_2 is reacted with 3 moles of H_2. We now consider a range of possible initial values of these amounts, with the resultant equilibrium partial pressures given in Table 14.3: Equilibrium Partial Pressures of the Synthesis of Ammonia. In addition, anticipating the possibility of an equilibrium constant, we have calculated the ratio of partial pressures given by:

$$K_p = \frac{{P_{NH_3}}^2}{P_{N_2}{P_{H_2}}^3} \tag{14.8}$$

In Table 14.3: Equilibrium Partial Pressures of the Synthesis of Ammonia, the equilibrium partial pressures of the gases are in a very wide variety, including whether the final pressures are greater for reactants or products. However, from the data in Table 14.3: Equilibrium Partial Pressures of the Synthesis of Ammonia, it is clear that, despite these variations, K_p in (14.8) is essentially a constant for all of the initial conditions examined and is thus the **reaction equilibrium constant** for this reaction (14.2).

Equilibrium Partial Pressures of the Synthesis of Ammonia

V (L)	n_{N_2}	n_{H_2}	P_{N_2}	P_{H_2}	P_{NH_3}	K_p
10	1	3	0.0342	0.1027	4.82	6.2×10^5
10	0.1	0.3	0.0107	0.0322	0.467	6.0×10^5
100	0.1	0.3	0.00323	0.00968	0.0425	6.1×10^5
100	3	3	0.492	0.00880	0.483	6.1×10^5
100	1	3	0.0107	0.0322	0.467	6.0×10^5
1000	1.5	1.5	0.0255	0.00315	0.0223	6.2×10^5

Table 14.3

Studies of many chemical reactions of gases result in the same observations. Each reaction equilibrium can be described by an equilibrium constant in which the partial pressures of the products, each raised to their corresponding stoichiometric coefficient, are multiplied together in the numerator, and the partial pressures of the reactants, each raised to their corresponding stoichiometric coefficient, are multiplied together in the denominator. For historical reasons, this general observation is sometimes referred to as the **Law of Mass Action**.

14.5 Observation 3: Temperature Dependence of the Reaction Equilibrium

We have previously observed that phase equilibrium, and in particular vapor pressure, depend on the temperature, but we have not yet studied the variation of reaction equilibrium with temperature. We focus our initial study on this reaction (14.3) and we measure the equilibrium partial pressures at a variety of temperatures. From these measurements, we can compile the data showing the temperature dependence of the equilibrium constant K_p for this reaction in Table 14.4: Equilibrium Constant for the Synthesis of HI.

Equilibrium Constant for the Synthesis of HI

T (K)	K_p
500	6.25×10^{-3}
550	8.81×10^{-3}
650	1.49×10^{-2}
700	1.84×10^{-2}
720	1.98×10^{-2}

Table 14.4

Note that the equilibrium constant increases dramatically with temperature. As a result, at equilibrium, the pressure of HI must also increase dramatically as the temperature is increased.

These data do not seem to have a simple relationship between K_p and temperature. We must appeal to arguments based on Thermodynamics, from which it is possible to show that the equilibrium constant should vary with temperature according to the following equation:

$$\ln(K_p) = -\frac{\Delta\left(H^{\circ}\right)}{RT} + \frac{\Delta\left(S^{\circ}\right)}{R} \tag{14.9}$$

If $\Delta\left(H^{\circ}\right)$ and $\Delta\left(S^{\circ}\right)$ do not depend strongly on the temperature, then this equation would predict a simple straight line relationship between $\ln(K_p)$ and $\frac{1}{T}$. In addition, the slope of this line should be $-\frac{\Delta\left(H^{\circ}\right)}{R}$. We test this possibility with the graph in Figure 14.4 (Inverse of Temperature vs. Natural Log of Equilibrium Constant).

Inverse of Temperature vs. Natural Log of Equilibrium Constant

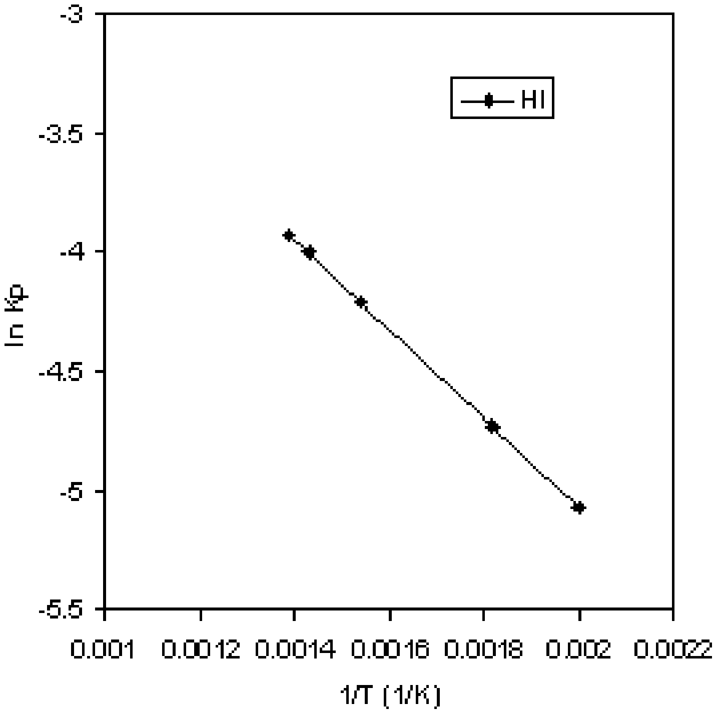

Figure 14.4

In fact, we do observe a straight line through the data. In this case, the line has a negative slope. Note carefully that this means that K_p is **increasing** with temperature. The negative slope via (14.9) means that $-\frac{\Delta\left(H^{\circ}\right)}{R}$ must be negative, and indeed for this reaction (14.3) in this temperature range, $\Delta\left(H^{\circ}\right) = 15.6\frac{\text{kJ}}{\text{mol}}$. This value matches well with the slope of the line in Figure 14.4 (Inverse of Temperature vs. Natural Log of Equilibrium Constant).

Given the validity of (14.9) in describing the temperature dependence of the equilibrium constant, we can also predict that an exothermic reaction with $\Delta\left(H^{\circ}\right) < 0$ should have a positive slope in the graph of $\ln\left(K_p\right)$ versus $\frac{1}{T}$, and thus the equilibrium constant should **decrease** with increasing temperature. A good example of an exothermic reaction is the synthesis of ammonia (14.2) for which $\Delta\left(H^{\circ}\right) = -99.2\frac{\text{kJ}}{\text{mol}}$. Equilibrium constant data are given in Table 14.5: Equilibrium Constant for the Synthesis of Ammonia. Note that, as predicted, the equilibrium constant for this exothermic reaction decreases rapidly with increasing temperature. The data from Table 14.5: Equilibrium Constant for the Synthesis of Ammonia is shown in Figure 14.5 (Inverse of Temperature vs. Natural Log of Equilibrium Constant), clearly showing the contrast between the endothermic reaction and the exothermic reaction. The slope of the graph is positive for the exothermic reaction and negative for the endothermic reaction. From (14.9), this is a general result for all reactions.

Equilibrium Constant for the Synthesis of Ammonia

T (K)	K_p
250	7×10^8
298	6×10^5
350	2×10^3
400	36

Table 14.5

Inverse of Temperature vs. Natural Log of Equilibrium Constant

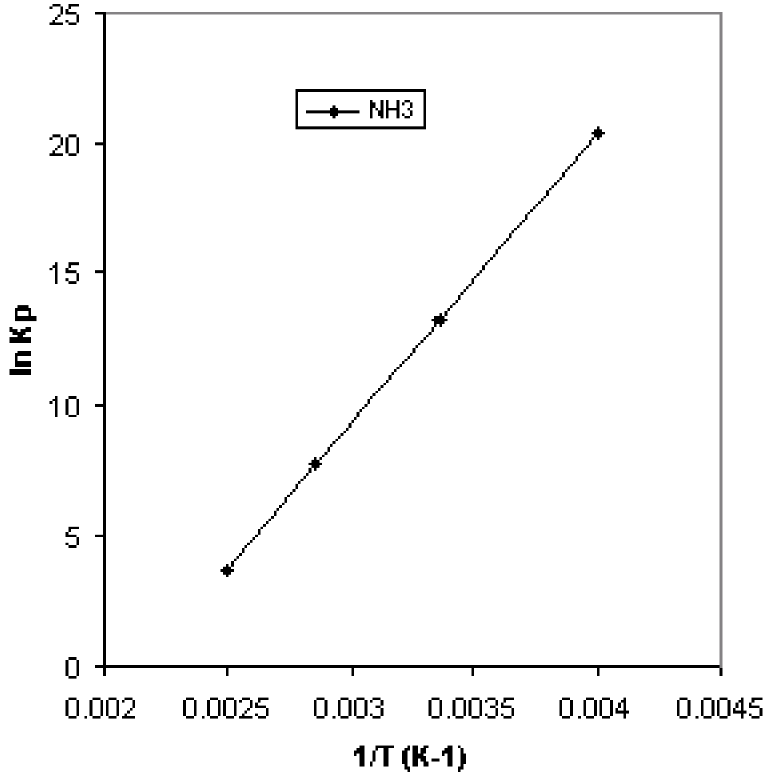

Figure 14.5

14.6 Observation 4: Changes in Equilibrium and Le Châtelier's Principle

One of our goals at the outset was to determine whether it is possible to control the equilibrium which occurs during a gas reaction. We might want to force a reaction to produce as much of the products as possible. In the alternative, if there are unwanted by-products of a reaction, we might want conditions which minimize the product. We have observed that the amount of product varies with the quantities of initial materials and with changes in the temperature. Our goal is a systematic understanding of these variations.

A look back at Table 14.1: Equilibrium Partial Pressures in Decomposition Reaction and Table 14.2: Equilibrium Partial Pressures in Decomposition Reaction shows that the equilibrium pressure of the product of the reaction increases with increasing the initial quantity of reaction. This seems quite intuitive. Less intuitive is the variation of the equilibrium pressure of the product of this reaction (14.2) with variation in the volume of the container, as shown in Table 14.3: Equilibrium Partial Pressures of the Synthesis of Ammonia. Note that the pressure of NH_3 decreases by more than a factor of ten when the volume is increased by a factor of ten. This means that, at equilibrium, there are fewer moles of NH_3 produced when the reaction occurs in a larger volume.

To understand this effect, we rewrite the equilibrium constant in (14.8) to explicit show the volume of the container. This is done by applying **Dalton's Law of Partial Pressures**, so that each partial pressure is given by the Ideal Gas Law:

$$\begin{aligned} K_p &= \frac{{n_{NH_3}}^2\left(\frac{RT}{V}\right)^2}{n_{N_2}\frac{RT}{V}{n_{H_2}}^3\left(\frac{RT}{V}\right)^3} \\ &= \frac{{n_{NH_3}}^2}{n_{N_2}{n_{H_2}}^3\left(\frac{RT}{V}\right)^2} \end{aligned} \tag{14.10}$$

Therefore,

$$K_p\left(\frac{RT}{V}\right)^2 = \frac{{n_{NH_3}}^2}{n_{N_2}{n_{H_2}}^3} \tag{14.11}$$

This form of the equation makes it clear that, when the volume increases, the left side of the equation decreases. This means that the right side of the equation must decrease also, and in turn, n_{NH_3} must decrease while n_{N_2} and n_{H_2}must increase. The equilibrium is thus shifted from products to reactants when the volume increases for this reaction (14.2).

The effect of changing the volume must be considered for each specific reaction, because the effect depends on the stoichiometry of the reaction. One way to determine the consequence of a change in volume is to rewrite the equilibrium constant as we have done in (14.11).

Finally, we consider changes in temperature. We note that K_p increases with T for endothermic reactions and decreases with T for exothermic reactions. As such, the products are increasingly favored with increasing temperature when the reaction is endothermic, and the reactants are increasingly favored with increasing temperature when the reaction is exothermic. On reflection, we note that when the reaction is exothermic, the reverse reaction is endothermic. Putting these statements together, we can say that the reaction equilibrium always shifts in the direction of the endothermic reaction when the temperature is increased.

All of these observations can be collected into a single unifying concept known as **Le Châtelier's Principle**.

Rule 14.1: Le Châtelier's Principle

When a reaction at equilibrium is stressed by a change in conditions, the equilibrium will be reestablished in such a way as to counter the stress.

This statement is best understood by reflection on the types of "stresses" we have considered in this section. When a reactant is added to a system at equilibrium, the reaction responds by consuming some of that added reactant as it establishes a new equilibrium. This offsets some of the stress of the increase in reactant. When the temperature is raised for a reaction at equilibrium, this adds thermal energy. The system shifts the equilibrium in the endothermic direction, thus absorbing some of the added thermal energy, countering the stress.

The most challenging of the three types of stress considered in this section is the change in volume. By increasing the volume containing a gas phase reaction at equilibrium, we reduce the partial pressures of all gases present and thus reduce the total pressure. Recall that the response of this reaction (14.2) to the volume increase was to create more of the reactants at the expense of the products. One consequence of this shift is that more gas molecules are created, and this increases the total pressure in the reaction flask. Thus, the reaction responds to the stress of the volume increase by partially offsetting the pressure decrease with an increase in the number of moles of gas at equilibrium.

Le Châtelier's principle is a useful mnemonic for predicting how we might increase or decrease the amount of product at equilibrium by changing the conditions of the reaction. From this principle, we can predict whether the reaction should occur at high temperature or low temperature, and whether it should occur at high pressure or low pressure.

14.7 Review and Discussion Questions

Exercise 14.1
In the data given for equilibrium of this reaction (14.3), there is no volume given. Show that changing the volume for the reaction does not change the number of moles of reactants and products present at equilibrium, *i.e.* changing the volume does not shift the equilibrium.

Exercise 14.2
For this reaction (14.4) the number of moles of NO_2 at equilibrium increases if we increase the volume in which the reaction is contained. Explain why this must be true in terms of dynamic equilibrium, give a reason why the rates of the forward and reverse reactions might be affected differently by changes in the volume.

Exercise 14.3
We could balance (14.2) by writing

$$2N_2\,(g) + 6H_2\,(g) \rightarrow 4NH_3\,(g) \tag{14.12}$$

Write the form of the equilibrium constant for the reaction balanced as in (14.12). What is the value of the equilibrium constant? (Refer to Table 14.3: Equilibrium Partial Pressures of the Synthesis of Ammonia.) Of course, the pressures at equilibrium do not depend on whether the reaction is balanced as in (14.2) or as in (14.12). Explain why this is true, even though the equilibrium constant can be written differently and have a different value.

Exercise 14.4
Show that the equilibrium constant K_p in (14.8) for this reaction (14.2) can be written in terms of the concentrations or particle densities, *e.g.* $[N_2] = \frac{n_{N_2}}{V}$, instead of the partial pressures. In this form, we call the equilibrium constant K_c. Find the relationship between K_p and K_c, and calculate the value of K_c.

Exercise 14.5
For each of these reactions, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.

14.7.1

$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$

14.7.2

$O_3\,(g) + NO\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$

14.7.3

$2O_3\left(g\right) \rightarrow 3O_2\left(g\right)$

Exercise 14.6

Plot the data in Table 14.4: Equilibrium Constant for the Synthesis of HI on a graph showing K_p on the y-axis and T on the x-axis. The shape of this graph is reminiscent of the graph of another physical property as a function of increasing temperature. Identify that property, and suggest a reason why the shapes of the graphs might be similar.

Exercise 14.7

Using Le Châtelier's principle, predict whether the specified "stress" will produce an increase or a decrease in the amount of product observed at equilibrium for the reaction:

$$2H_2\left(g\right) + CO\left(g\right) \rightarrow CH_3OH\left(g\right) \tag{14.13}$$

$$\Delta\left(H^{\circ}\right) = -91\frac{\text{kJ}}{\text{mol}}$$

14.7.1

Volume of container is increased.

14.7.2

Helium is added to container.

14.7.3

Temperature of container is raised.

14.7.4

Hydrogen is added to container.

14.7.5

CH_3OH is extracted from container as it is formed.

Chapter 15

Acid-Base Equilibrium[1]

15.1 Foundation

We have developed an understanding of **equilibrium** involving phase transitions and involving reactions entirely in the gas phase. We will assume an understanding of the principles of dynamic equilibrium, reaction equilibrium constants, and **Le Châtelier's Principle**. To understand application of these principles to reactions in solution, we will now assume a definition of certain classes of substances as being either acids or bases. An acid is a substance whose molecules donate positive hydrogen ions (protons) to other molecules or ions. When dissolved in pure water, acid molecules will transfer a hydrogen ion to a water molecule or to a cluster of several water molecules. This increases the concentration of H^+ ions in the solution. A base is a substance whose molecules accept hydrogen ions from other molecules. When dissolved in pure water, base molecules will accept a hydrogen ion from a water molecule, leaving behind an increased concentration of OH^- ions in the solution. To understand what determines acid-base behavior, we will assume an understanding of the bonding, structure, and properties of individual molecules.

15.2 Goals

Acids and bases are very common substances whose properties vary greatly. Many acids are known to be quite corrosive, with the ability to dissolve solid metals or burn flesh. Many other acids, however, are not only benign but vital to the processes of life. Far from destroying biological molecules, they carry out reactions critical for organisms. Similarly, many bases are caustic cleansers while many others are medications to calm indigestion pains.

In this concept study, we will develop an understanding of the characteristics of molecules which make them either acids or bases. We will examine measurements about the relative strengths of acids and bases, and we will use these to develop a quantitative understanding of the relative strengths of acids and bases. From this, we can develop a qualitative understanding of the properties of molecules which determine whether a molecule is a strong acid or a weak acid, a strong base or a weak base. This understanding is valuable in predicting the outcomes of reactions, based on the relative quantitative strengths of acids and bases. These reactions are commonly referred to as neutralization reactions. A surprisingly large number of reactions, particularly in organic chemistry, can be understood as transfer of hydrogen ions from acid molecules to base molecules.

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[1] This content is available online at <http://cnx.org/content/m12591/1.3/>.

15.3 Observation 1: Strong Acids and Weak Acids

From the definition of an acid given in the Foundation, a typical acid can be written as HA, representing the hydrogen ion which will be donated and the rest of the molecule which will remain as a negative ion after the donation. The typical reaction of an acid in aqueous solution reacting with water can be written as

$$HA\,(\mathrm{aq}) + H_2O\,(l) \rightarrow H_3O^+\,(\mathrm{aq}) + A^-\,(\mathrm{aq}) \tag{15.1}$$

In this reaction, $HA\,(\mathrm{aq})$ represents an acid molecule dissolved in aqueous solution. $H_3O^+\,(\mathrm{aq})$ is a notation to indicate that the donated proton has been dissolved in solution. Observations indicate that the proton is associated with several water molecules in a cluster, rather than attached to a single molecule. H_3O^+ is a simplified notation to represent this result. Similarly, the $A^-\,(\mathrm{aq})$ ion is solvated by several water molecules. (15.1) is referred to as **acid ionization**.

(15.1) implies that a 0.1M solution of the acid HA in water should produce H_3O^+ ions in solution with a concentration of 0.1M. In fact, the concentration of H_3O^+ ions, $[H_3O^+]$, can be measured by a variety of techniques. Chemists commonly use a measure of the H_3O^+ ion concentration called the pH, defined by:

$$\mathrm{pH} = -\log\left[H_3O^+\right]$$

We now observe the concentration $[H_3O^+]$ produced by dissolving a variety of acids in solution at a concentration of 0.1M, and the results are tabulated in Table 15.1: H3O+ pH for 0.1M Acid Solutions.

H3O+ pH for 0.1M Acid Solutions

Acid	$[H_3O^+]$ **(M)**	**pH**
H_2SO_4	0.1	1
HNO_3	0.1	1
HCl	0.1	1
HBr	0.1	1
HI	0.1	1
$HClO_4$	0.1	1
$HClO_3$	0.1	1
HNO_2	6.2×10^{-3}	2.2
HCN	7×10^{-6}	5.1
HIO	1×10^{-6}	5.8
HF	5.5×10^{-3}	2.3
$HOCN$	5.5×10^{-3}	2.3
$HClO_2$	2.8×10^{-2}	1.6
CH_3COOH (acetic acid)	1.3×10^{-3}	2.9
CH_3CH_2COOH (propionic acid)	1.1×10^{-3}	2.9

Table 15.1

Note that there are several acids listed for which $[H_3O^+] = 0.1M$, and pH = 1. This shows that, for these acids, the acid ionization is complete: essentially every acid molecule is ionized in the solution according to (15.1). However, there are other acids listed for which $[H_3O^+]$ is considerably less than 0.1M and the pH is considerably greater than 1. For each of these acids, therefore, not all of the acid molecules ionize according to (15.1). In fact, it is clear in Table 15.1: H3O+ pH for 0.1M Acid Solutions that in these acids the vast majority of the acid molecules do not ionize, and only a small percentage does ionize.

From these observations, we distinguish two classes of acids: **strong acids** and **weak acids**. Strong acids are those for which nearly 100% of the acid molecules ionize, whereas weak acids are those for which only a small percentage of molecules ionize. There are seven strong acids listed in Table 15.1: H3O+ pH for 0.1M Acid Solutions. From many observations, it is possible to determine that these seven acids are the only commonly observed strong acids. The vast majority of all substances with acidic properties are weak acids. We seek to characterize weak acid ionization quantitatively and to determine what the differences in molecular properties are between strong acids and weak acids.

15.4 Observation 2: Percent Ionization in Weak Acids

Table 15.1: H3O+ pH for 0.1M Acid Solutions shows that the pH of 0.1M acid solutions varies from one weak acid to another. If we dissolve 0.1 moles of acid in a 1.0L solution, the fraction of those acid molecules which will ionize varies from weak acid to weak acid. For a few weak acids, using the data in Table 15.1: H3O+ pH for 0.1M Acid Solutions we calculate the percentage of ionized acid molecules in 0.1M acid solutions in Table 15.2: Percent Ionization of 0.1M Acid Solutions.

Percent Ionization of 0.1M Acid Solutions

Acid	$[H_3O^+]$ **(M)**	**% ionization**
HNO_2	6.2×10^{-3}	6.2%
HCN	7×10^{-6}	0.007%
HIO	1×10^{-6}	0.001%
HF	5.5×10^{-3}	5.5%
$HOCN$	5.5×10^{-3}	5.5%
$HClO_2$	2.8×10^{-2}	28.2%
CH_3COOH (acetic acid)	1.3×10^{-3}	1.3%
CH_3CH_2COOH (propionic acid)	1.1×10^{-3}	1.1%

Table 15.2

We might be tempted to conclude from Table 15.2: Percent Ionization of 0.1M Acid Solutions that we can characterize the strength of each acid by the percent ionization of acid molecules in solution. However, before doing so, we observe the pH of a single acid, nitrous acid, in solution as a function of the concentration of the acid.

$$HNO_2\,(\text{aq}) + H_2O\,(l) \rightarrow H_3O^+\,(\text{aq}) + NO_2^-\,(\text{aq}) \tag{15.2}$$

In this case, "concentration of the acid" refers to the number of moles of acid that we dissolved per liter of water. Our observations are listed in Table 15.3: % Ionization of Nitrous Acid, which gives $[H_3O^+]$, pH, and percent ionization as a function of nitrous acid concentration.

% Ionization of Nitrous Acid

c_0 **(M)**	$[H_3O^+]$	**pH**	**% Ionization**
0.50	1.7×10^{-2}	1.8	3.3%
0.20	1.0×10^{-2}	2.0	5.1%
0.10	7.0×10^{-3}	2.2	7.0%
0.050	4.8×10^{-3}	2.3	9.7%
0.020	2.9×10^{-3}	2.5	14.7%
0.010	2.0×10^{-3}	2.7	20.0%
0.005	1.3×10^{-3}	2.9	26.7%
0.001	4.9×10^{-4}	3.3	49.1%
0.0005	3.0×10^{-4}	3.5	60.8%

Table 15.3

Surprisingly, perhaps, the percent ionization varies considerably as a function of the concentration of the nitrous acid. We recall that this means that the fraction of molecules which ionize, according to (15.2), depends on how many acid molecules there are per liter of solution. Since some but not all of the acid molecules are ionized, this means that nitrous acid molecules are present in solution at the same time as the negative nitrite ions and the positive hydrogen ions. Recalling our observation of equilibrium in gas phase reactions, we can conclude that (15.2) achieves equilibrium for each concentration of the nitrous acid.

Since we know that gas phase reactions come to equilibrium under conditions determined by the equilibrium constant, we might speculate that the same is true of reactions in aqueous solution, including acid ionization. We therefore define an analogy to the gas phase reaction equilibrium constant. In this case, we would not be interested in the pressures of the components, since the reactants and products are all in solution. Instead, we try a function composed of the equilibrium concentrations:

$$K = \frac{[H_3O^+]\left[NO_2^-\right]}{[HNO_2] > [H_2O]} \tag{15.3}$$

The concentrations at equilibrium can be calculated from the data in Table 15.3: % Ionization of Nitrous Acid for nitrous acid. $[H_3O^+]$ is listed and $\left[NO_2^-\right] = [H_3O^+]$. Furthermore, if c_0 is the initial concentration of the acid defined by the number of moles of acid dissolved in solution per liter of solution, then $[HA] = c_0 - [H_3O^+]$. Note that the contribution of $[H_2O\,(l)]$ to the value of the function K is simply a constant. This is because the "concentration" of water in the solution is simply the molar density of water, $\frac{n_{H_2O}}{V} = 55.5M$, which is not affected by the presence or absence of solute. All of the relevant concentrations, along with the function in (15.3) are calculated and tabulated in Table 15.4: Equilibrium Concentrations and K for Nitrous Acid.

Equilibrium Concentrations and K for Nitrous Acid

c_0 **(M)**	$[H_3O^+]$	$[NO_2^-]$	$[HNO_2]$	K
0.50	1.7×10^{-2}	1.7×10^{-2}	0.48	1.0×10^{-5}
0.20	1.0×10^{-2}	1.0×10^{-2}	0.19	9.9×10^{-6}
0.10	7.0×10^{-3}	7.0×10^{-3}	9.3×10^{-2}	9.6×10^{-6}
0.050	4.8×10^{-3}	4.8×10^{-3}	4.5×10^{-2}	9.4×10^{-6}
0.020	2.9×10^{-3}	2.9×10^{-3}	4.5×10^{-2}	9.4×10^{-6}
0.010	2.0×10^{-3}	2.0×10^{-3}	8.0×10^{-3}	8.9×10^{-6}
0.005	1.3×10^{-3}	1.3×10^{-3}	3.6×10^{-3}	8.8×10^{-6}
0.001	4.9×10^{-4}	4.9×10^{-4}	5.1×10^{-4}	8.5×10^{-6}
0.0005	3.0×10^{-4}	3.0×10^{-4}	2.0×10^{-4}	8.5×10^{-6}

Table 15.4

We note that the function K in (15.3) is approximately, though only approximately, the same for all conditions analyzed in Table 15.3: % Ionization of Nitrous Acid. Variation of the concentration by a factor of 1000 produces a change in K of only 10% to 15%. Hence, we can regard the function K as a constant which approximately describes the acid ionization equilibrium for nitrous acid. By convention, chemists omit the constant concentration of water from the equilibrium expression, resulting in the **acid ionization equilibrium constant**, K_a, defined as:

$$K_a = \frac{[H_3O^+]\,[NO_2^-]}{[HNO_2]} \tag{15.4}$$

From an average of the data in Table 15.4: Equilibrium Concentrations and K for Nitrous Acid, we can calculate that, at 25 °C for nitrous acid, $K_a = 5 \times 10^{-4}$. Acid ionization constants for the other weak acids in Table 15.2: Percent Ionization of 0.1M Acid Solutions are listed in Table 15.5: Weak Acid Ionization Constants, Ka and pKa.

Weak Acid Ionization Constants, Ka and pKa

Acid	K_a	**p**K_a
HNO_2	5×10^{-4}	3.3
HCN	4.9×10^{-10}	9.3
HIO	2.3×10^{-11}	10.6
HF	3.5×10^{-4}	3.4
$HOCN$	3.5×10^{-4}	3.4
$HClO_2$	1.1×10^{-2}	2.0
CH_3COOH (acetic acid)	1.7×10^{-5}	4.8
CH_3CH_2COOH (propionic acid)	1.4×10^{-5}	4.9

Table 15.5

We make two final notes about the results in Table 15.5: Weak Acid Ionization Constants, Ka and pKa. First, it is clear the larger the value of K_a, the stronger the acid. That is, when K_a is a larger number, the percent ionization of the acid is larger, and vice versa. Second, the values of K_a very over many orders of magnitude. As such, it is often convenient to define the quanity pK_a, analogous to pH, for purposes of comparing acid strengths:

$$pK_a = -\log K_a \tag{15.5}$$

The value of pK_a for each acid is also listed in Table 15.5: Weak Acid Ionization Constants, Ka and pKa. Note that a small value of pK_a implies a large value of K_a and thus a stronger acid. Weaker acids have larger values of pK_a. K_a and pK_a thus give a simple quantitative comparison of the strength of weak acids.

15.5 Observation 3: Autoionization of Water

Since we have the ability to measure pH for acid solutions, we can measure pH for pure water as well. It might seem that this would make no sense, as we would expect $[H_3O^+]$ to equal zero exactly in pure water. Surprisingly, this is incorrect: a measurement on pure water at 25 °C yields pH = 7, so that $[H_3O^+] = 1.0 \times 10^{-7} M$. There can be only one possible source for these ions: water molecules. The process

$$H_2O\,(l) + H_2O\,(l) \rightarrow H_3O^+\,(\text{aq}) + OH^-\,(\text{aq}) \tag{15.6}$$

is referred to as the **autoionization** of water. Note that, in this reaction, some water molecules behave as acid, donating protons, while other water molecules behave as base, accepting protons.

Since at equilibrium $[H_3O^+] = 1.0 \times 10^{-7} M$, it must also be true that $[OH^-] = 1.0 \times 10^{-7} M$. We can write the equilibrium constant for (15.6), following our previous convention of omitting the pure water from the expression, and we find that, at 25 °C,

$$\begin{aligned} K_w &= [H_3O^+]\,[OH^-] \\ &= 1.0 \times 10^{-14} M \end{aligned} \tag{15.7}$$

(In this case, the subscript "w" refers to "water".)

(15.6) occurs in pure water but must also occur when ions are dissolved in aqueous solutions. This includes the presence of acids ionized in solution. For example, we consider a solution of 0.1M acetic acid. Measurements show that, in this solution $[H_3O^+] = 1.3 \times 10^{-3} M$ and $[OH^-] = 7.7 \times 10^{-12} M$. We note two things from this observation: first, the value of $[OH^-]$ is considerably less than in pure water; second, the autoionization equilibrium constant remains the same at 1.0×10^{-14}. From these notes, we can conclude that the autoionization equilibrium of water occurs in acid solution, but the extent of autoionization is suppressed by the presence of the acid in solution.

We consider a final note on the autoionization of water. The pH of pure water is 7 at 25 °C. Adding any acid to pure water, no matter how weak the acid, must increase $[H_3O^+]$, thus producing a pH below 7. As such, we can conclude that, for all acid solutions, pH is less than 7, or on the other hand, any solution with pH less than 7 is acidic.

15.6 Observation 4: Base Ionization, Neutralization and Hydrolysis of Salts

We have not yet examined the behavior of base molecules in solution, nor have we compared the relative strengths of bases. We have defined a base molecule as one which accepts a positive hydrogen ion from another molecule. One of the most common examples is ammonia, NH_3. When ammonia is dissolved in aqueous solution, the following reaction occurs:

$$NH_3\,(\text{aq}) + H_2O\,(l) \rightarrow NH_4^+\,(\text{aq}) + OH^-\,(\text{aq}) \tag{15.8}$$

Due to the lone pair of electrons on the highly electronegative N atom, NH_3 molecules will readily attach a free hydrogen ion forming the ammonium ion NH_4^+. When we measure the concentration of OH^- for various initial concentration of NH_3 in water, we observe the results in Table 15.6: Equilibrium Concentrations and Kb for Ammonia. We should anticipate that a base ionization equilibrium constant might exist comparable to the acid ionization equilibrium constant, and in Table 15.6: Equilibrium Concentrations and Kb for Ammonia, we have also calculated the value of the function K_b defined as:

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} \tag{15.9}$$

Equilibrium Concentrations and Kb for Ammonia

c_0 **(M)**	$[OH^-]$	K_b	**pH**
0.50	3.2×10^{-3}	2.0×10^{-5}	11.5
0.20	2.0×10^{-3}	2.0×10^{-5}	11.3
0.10	1.4×10^{-3}	2.0×10^{-5}	11.1
0.050	9.7×10^{-4}	1.9×10^{-5}	11.0
0.020	6.0×10^{-4}	1.9×10^{-5}	10.8
0.010	4.2×10^{-4}	1.9×10^{-5}	10.6
0.005	3.0×10^{-4}	1.9×10^{-5}	10.5
0.001	1.3×10^{-4}	1.8×10^{-5}	10.1
0.0005	8.7×10^{-5}	1.8×10^{-5}	9.9

Table 15.6

Given that we have dissolved a base in pure water, we might be surprised to discover the presence of positive hydrogen ions, H_3O^+, in solution, but a measurement of the pH for each of the solutions reveals small amounts. The pH for each solution is also listed in Table 15.6: Equilibrium Concentrations and Kb for Ammonia. The source of these H_3O^+ ions must be the autoionization of water. Note, however, that in each case in basic solution, the concentration of H_3O^+ ions is less than that in pure water. Hence, the presence of the base in solution has suppressed the autoionization. Because of this, in each case the pH of a basic solution is greater than 7.

Base ionization is therefore quite analogous to acid ionization observed earlier. We now consider a comparison of the strength of an acid to the strength of a base. To do so, we consider a class of reactions called "neutralization reactions" which occur when we mix an acid solution with a base solution. Since the acid donates protons and the base accepts protons, we might expect, when mixing acid and base, to achieve a solution which is no longer acidic or basic. For example, if we mix together equal volumes of 0.1M HCl (aq) and 0.1M $NaOH$ (aq), the following reaction occurs:

$$HCl\,(\text{aq}) + NaOH\,(\text{aq}) \rightarrow Na^+\,(\text{aq}) + Cl^-\,(\text{aq}) + H_2O\,(l) \tag{15.10}$$

The resultant solution is simply a salt solution with $NaCl$ dissolved in water. This solution has neither acidic nor basic properties, and the pH is 7; hence the acid and base have neutralized each other. In this case, we have mixed together a strong acid with a strong base. Since both are strong and since we mixed equal molar quantities of each, the neutralization reaction is essentially complete.

We next consider mixing together a weak acid solution with a strong base solution, again with equal molar quantities of acid and base. As an example, we mix 100ml of 0.1M acetic acid (HA) solution with

100ml of 0.1M sodium hydroxide. In this discussion, we will abbreviate the acetic acid molecular formula CH_3COOH as HA and the acetate ion CH_3COO^- as A^-. The reaction of HA and $NaOH$ is:

$$HA\,(\text{aq}) + NaOH\,(\text{aq}) \rightarrow Na^+\,(\text{aq}) + A^-\,(\text{aq}) + H_2O\,(l) \tag{15.11}$$

A^- (aq) is the acetate ion in solution, formed when an acetic acid molecule donates the positive hydrogen ion. We have thus created a salt solution again, in this case of sodium acetate in water. Note that the volume of the combined solution is 200ml, so the concentration of sodium acetate (NaA) in solution is 0.050M.

Unlike our previous $NaCl$ salt solution, a measurement in this case reveals that the pH of the product salt solution is 9.4, so the solution is basic. Thus, mixing equal molar quantities of strong base with weak acid produces a basic solution. In essence, the weak acid does not fully neutralize the strong base. To understand this, we examine the behavior of sodium acetate in solution. Since the pH is greater than 7, then there is an excess of OH^- ions in solution relative to pure water. These ions must have come from the reaction of sodium acetate with the water. Therefore, the negative acetate ions in solution must behave as a base, accepting positive hydrogen ions:

$$A^-\,(\text{aq}) + H_2O\,(\text{aq}) \rightarrow HA\,(\text{aq}) + OH^-\,(l) \tag{15.12}$$

The reaction of an ion with water to form either an acid or a base solution is referred to as **hydrolysis**. From this example, the salt of a weak acid behaves as a base in water, resulting in a pH greater than 7.

To understand the extent to which the hydrolysis of the negative ion occurs, we need to know the equilibrium constant for this reaction. This turns out to be determined by the acid ionization constant for HA. To see this, we write the equilibrium constant for the hydrolysis of A^- as

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} \tag{15.13}$$

Multiplying numerator and denominator by $[H_3O^+]$, we find that

$$\begin{aligned} K_h &= \frac{[HA][OH^-]}{[A^-]}\frac{[H_3O^+]}{[H_3O^+]} \\ &= \frac{K_w}{K_a} \end{aligned} \tag{15.14}$$

Therefore, for the hydrolysis of acetate ions in solution, $K_h = 5.8 \times 10^{-10}$. This is fairly small, so the acetate ion is a very weak base.

15.7 Observation 5: Acid strength and molecular properties

We now have a fairly complete quantitative description of acid-base equilibrium. To complete our understanding of acid-base equilibrium, we need a predictive model which relates acid strength or base strength to molecular properties. In general, we expect that the strength of an acid is related either to the relative ease by which it can donate a hydrogen ion or by the relative stability of the remaining negative ion formed after the departure of the hydrogen ion.

To begin, we note that there are three basic categories of acids which we have examined in this study. First, there are simple **binary acids**: HF; HCl; HBr; HI. Second, there are acids formed from main group elements combined with one or more oxygen atoms, such H_2SO_4 or HNO_3. These are called **oxyacids**. Third, there are the **carboxylic acids**, organic molecules which contain the carboxylic functional group in Figure 15.1 (Carboxylic Functional Group).

Carboxylic Functional Group

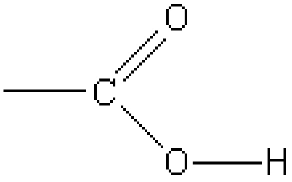


Figure 15.1

We consider first the simple binary acids. HCl, HBr, and HI are all strong acids, whereas HF is a weak acid. In comparing the experimental values of pK_a values in Table 15.7: H-X Bond Strengths and pKa, we note that the acid strength increases in the order $HF < HCl < HBr < HI$. This means that the hydrogen ion can more readily separate from the covalent bond with the halogen atom (X) as we move down the periodic table. This is reasonable, because the strength of the H-X bond also decreases as we move down the periodic table, as shown in Table 15.7: H-X Bond Strengths and pKa.

H-X Bond Strengths and pKa

	pK_a	**Bond Energy** ($\frac{\text{kJ}}{\text{mol}}$)
HF	3.1	567.7
HCl	-6.0	431.6
HBr	-9.0	365.9
HI	-9.5	298.0

Table 15.7

The decreasing strength of the H-X bond is primarily due to the increase is the size of the X atom as we move down the periodic table. We conclude that one factor which influences acidity is the strength of the H-X bond: a weaker bond produces a stronger acid, and vice versa.

In the acids in the other two categories, the hydrogen atom which ionizes is attached directly to an oxygen atom. Thus, to understand acidity in these molecules, we must examine what the oxygen atom is in turn bonded to. It is very interesting to note that, in examining compounds like R-O-H, where R is an atom or group of atoms, we can get either acidic or basic properties. For examples, $NaOH$ is a strong base, whereas $HOCl$ is a weak acid. This means that, when $NaOH$ ionizes in solution, the Na-O linkage ionizes, whereas when $HOCl$ ionizes in solution, the H-O bond ionizes.

To understand this behavior, we compare the strength of the simple oxyacids HOI, $HOBr$, and $HOCl$. The pK_a's for these acids are found experimentally to be, respectively, 10.6, 8.6, and 7.5. The acid strength for HOX increases as we move up the periodic table in the halogen group. This means that the H-O bond ionizes more readily when the oxygen atom is bonded to a more electronegative atom.

We can add to this observation by comparing the strengths of the acids $HOCl$, $HOClO$, $HOClO_2$, and $HOClO_3$. (Note that the molecular formulae are more commonly written as $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$. We have written them instead to emphasize the molecular structure.) The pK_a's of these acids are, respectively, 7.5, 2.0, -2.7, and -8.0. In each case, the molecule with more oxygen atoms on the central Cl atom is the stronger acid: $HOClO$ is more acidic than $HOCl$, *etc.* A similar result is found in comparing the oxyacids of nitrogen. $HONO_2$, nitric acid, is one of the strong acids, whereas $HONO$, nitrous acid, is a weak acid. Since oxygen atoms are very strongly electronegative, these trends add to our observation that increasing electronegativity of the attached atoms increases the ionization of the O-H bond.

Why would electronegativity play a role in acid strength? There are two conclusions we might draw. First, a greater electronegativity of the atom or atoms attached to the H-O in the oxyacid apparently results in a weaker H-O bond, which is thus more readily ionized. We know that an electronegative atom polarizes bonds by drawing the electrons in the molecule towards it. In this case, the Cl in $HOCl$ and the Br in $HOBr$ must polarize the H-O bond, weakening it and facilitating the ionization of the hydrogen. In comparing $HOCl$ to $HOClO$, the added oxygen atom must increase the polarization of the H-O bond, thus weakening the bond further and increasing the extent of ionization.

A second conclusion has to do with the ion created by the acid ionization. The negative ion produced has a surplus electron, and the relative energy of this ion will depend on how readily that extra electron is attracted to the atoms of ion. The more electronegative those atoms are, the stronger is the attraction. Therefore, the OCl^- ion can more readily accommodate the negative charge than can the OBr^- ion. And the $OClO^-$ ion can more readily accommodate the negative charge than can the OCl^- ion.

We conclude that the presence of strongly electronegative atoms in an acid increases the polarization of the H-O bond, thus facilitating ionization of the acid, and increases the attraction of the extra electron to the negative ion, thus stabilizing the negative ion. Both of these factors increase the acid strength. Chemists commonly use both of these conclusions in understanding and predicting relative acid strength.

The relative acidity of carbon compounds is a major subject of organic chemistry, which we can only visit briefly here. In each of the carboxylic acids, the H-O group is attached to a carbonyl C=O group, which is in turn bonded to other atoms. The comparison we observe here is between carboxylic acid molecules, denoted as $RCOOH$, and other organic molecules containing the H-O group, such as alcohols denoted as ROH. (R is simply an atom or group of atoms attached to the functional group.) The former are obviously acids whereas the latter group contains molecules which are generally extremely weak acids. One interesting comparison is for the acid and alcohol when R is the benzene ring, C_6H_5. Benzoic acid, C_6H_5COOH, has $pK_a = 4.2$, whereas phenol, C_6H_5OH, has $pK_a = 9.9$. Thus, the presence of the doubly bonded oxygen atom on the carbon atom adjacent to the O-H clearly increases the acidity of the molecule, and thus increases ionization of the O-H bond.

This observation is quite reasonable in the context of our previous conclusion. Adding an electronegative oxygen atom in near proximity to the O-H bond both increases the polarization of the O-H bond and stabilizes the negative ion produced by the acid ionization. In addition to the electronegativity effect, carboxylate anions, $RCOO^-$, exhibit resonance stabilization, as seen in Figure 15.2.

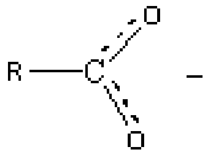


Figure 15.2

The resonance results in a sharing of the negative charge over several atoms, thus stabilizing the negative ion. This is a major contributing factor in the acidity of carboxylic acids versus alcohols.

15.8 Review and Discussion Questions

Exercise 15.1
Strong acids have a higher percent ionization than do weak acids. Why don't we use percent ionization as a measure of acid strength, rather than K_a?

Exercise 15.2
Using the data in Table 15.4: Equilibrium Concentrations and K for Nitrous Acid for nitrous acid, plot $[H_3O^+]$ versus c_0, the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. On a second graph, plot $[H_3O^+]^2$ versus c_0, the initial concentration of the acid, and versus $[HNO_2]$ the equilibrium concentration of the acid. Which of these results gives a straight line? Using the equilibrium constant expression, explain your answer.

Exercise 15.3
Using Le Châtelier's principle, explain why the concentration of $[OH^-]$ is much lower in acidic solution than it is in neutral solution.

Exercise 15.4
We considered mixing a strong base with a weak acid, but we did not consider mixing a strong acid with a weak acid. Consider mixing 0.1M HNO_3 and 0.1M HNO_2. Predict the pH of the solution and the percent ionization of the nitrous acid. Rationalize your prediction using Le Châtelier's principle.

Exercise 15.5
Imagine taking a 0.5M solution of nitrous acid and slowing adding water to it. Looking at Table 15.3: % Ionization of Nitrous Acid, we see that, as the concentration of nitrous acid decreases, the percent ionization increases. By contrast, $[H_3O^+]$ decreases. Rationalize these results using Le Châtelier's principle.

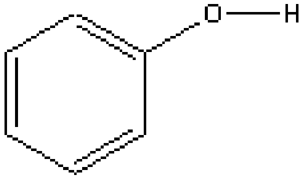
Exercise 15.6
We observed that mixing a strong acid and a strong base, in equal amounts and concentrations, produces a neutral solution, and that mixing a strong base with a weak acid, in equal amounts and concentrations, produces a basic solution. Imagine mixing a weak acid and a weak base, in equal amounts and concentrations. Predict whether the resulting solution will be acidic, basic, or neutral, and explain your prediction.

Exercise 15.7
Using the electronegativity arguments presented above (Section 15.7: Observation 5: Acid strength and molecular properties), explain why, in general, compounds like M-O-H are bases rather than acids, when M is a metal atom. Predict the relationship between the properties of the metal atom M and the strength of the base MOH.

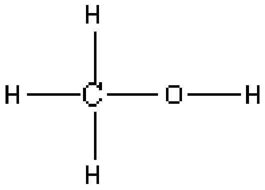
Exercise 15.8
Ionization of sulfuric acid H_2SO_4 produces HSO_4^-, which is also an acid. However, HSO_4^- is a much weaker acid than H_2SO_4. Using the conclusions from above (Section 15.7: Observation 5: Acid strength and molecular properties), explain why HSO_4^- is a much weaker acid.

Exercise 15.9
Predict and explain the relative acid strengths of H_2S and HCl. Predict and explain the relative acid strengths of H_3PO_4 and $H_3\mathrm{As}O_4$.

Exercise 15.10
Using arguments from above (Section 15.7: Observation 5: Acid strength and molecular properties), predict and explain the relative acidity of phenol (Figure 15.3(a): Phenol) and methanol (Figure 15.3(b): Methanol).



(a) Phenol



(b) Methanol

Figure 15.3

Chapter 16

Reaction Rates[1]

16.1 Foundation

We will assume an understanding of the postulates of the **Kinetic Molecular Theory** and of the energetics of chemical reactions. We will also assume an understanding of phase equilibrium and reaction equilibrium, including the temperature dependence of equilibrium constants.

16.2 Goals

We have carefully examined the observation that chemical reactions come to equilibrium. Depending on the reaction, the equilibrium conditions can be such that there is a mixture of reactants and products, or virtually all products, or virtually all reactants. We have not considered the time scale for the reaction to achieve these conditions, however. In many cases, the speed of the reaction might be of more interest than the final equilibrium conditions of the reaction. Some reactions proceed so slowly towards equilibrium as to appear not to occur at all. For example, metallic iron will eventually oxidize in the presence of aqueous salt solutions, but the time is sufficiently long for this process that we can reasonably expect to build a boat out of iron. On the other hand, some reactions may be so rapid as to pose a hazard. For example, hydrogen gas will react with oxygen gas so rapidly as to cause an explosion. In addition, the time scale for a reaction can depend very strongly on the amounts of reactants and their temperature.

In this concept development study, we seek an understanding of the rates of chemical reactions. We will define and measure reaction rates and develop a quantitative analysis of the dependence of the reaction rates on the conditions of the reaction, including concentration of reactants and temperature. This quantitative analysis will provide us insight into the process of a chemical reaction and thus lead us to develop a model to provide an understanding of the significance of reactant concentration and temperature.

We will find that many reactions proceed quite simply, with reactant molecules colliding and exchanging atoms. In other cases, we will find that the process of reaction can be quite complicated, involving many molecular collisions and rearrangements leading from reactant molecules to product molecules. The rate of the chemical reaction is determined by these steps.

16.3 Observation 1: Reaction Rates

We begin by considering a fairly simple reaction on a rather elegant molecule. One oxidized form of buckminsterfullerene C_{60} is $C_{60}O_3$, with a three oxygen bridge as shown in Figure 16.1 (Oxidized Buckminsterfullerene).

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[1] This content is available online at <http://cnx.org/content/m12728/1.2/>.

Oxidized Buckminsterfullerene

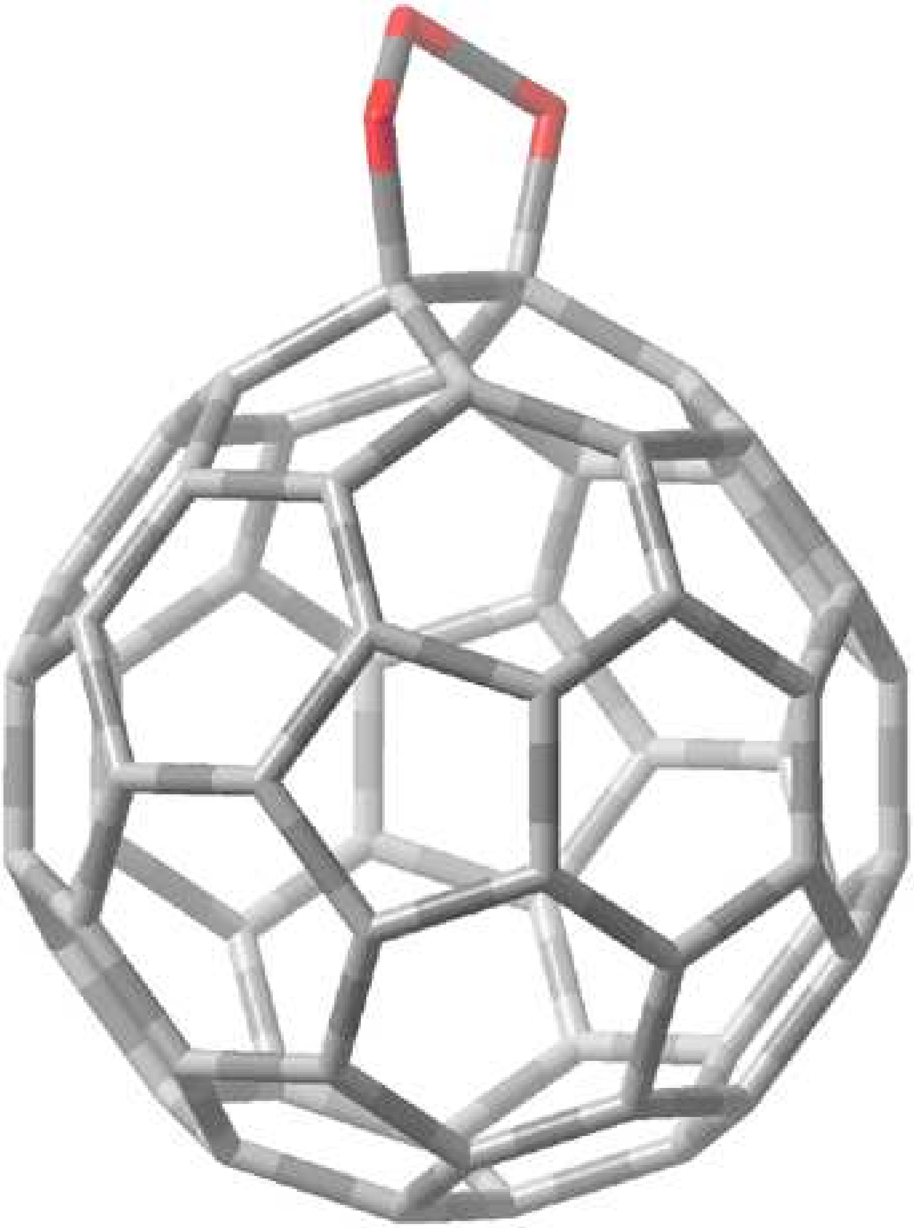


Figure 16.1

$C_{60}O_3$ is prepared from C_{60} dissolved in toluene solution at temperatures of $0\,^{\circ}C$ or below. When the solution is warmed, $C_{60}O_3$ decomposes, releasing O_2 and creating $C_{60}O$ in a reaction which goes essentially to completion. We can actually watch this process happen in time by measuring the amount of light of a specific frequency absorbed by the $C_{60}O_3$ molecules, called the **absorbance**. The absorbance is proportional to the concentration of the $C_{60}O_3$ in the toluene solution, so observing the absorbance as a function of time is essentially the same as observing the concentration as a function of time. One such set of data is given in Table 16.1: Oxidized Buckminsterfullerene Absorbance during Thermal Decomposition at 23 °C, and is shown in the graph in Figure 16.2 (Oxidized Buckminsterfullerene Absorbance).

Oxidized Buckminsterfullerene Absorbance during Thermal Decomposition at 23 °C

time (minutes)	$C_{60}O_3$ **absorbance**
3	0.04241
9	0.03634
15	0.03121
21	0.02680
27	0.02311
33	0.01992
39	0.01721
45	0.01484
51	0.01286
57	0.01106
63	0.00955
69	0.00827
75	0.00710
81	0.00616
87	0.00534
93	0.00461
99	0.00395

Table 16.1

Oxidized Buckminsterfullerene Absorbance

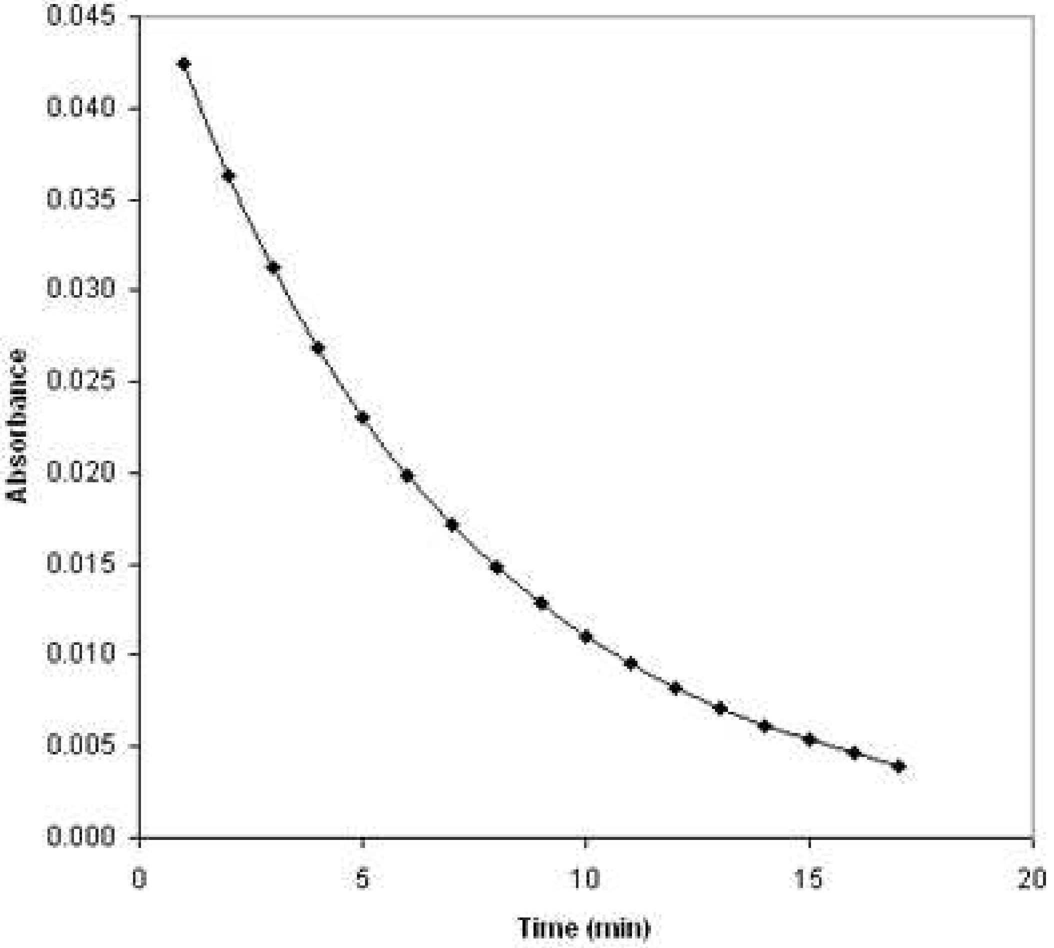


Figure 16.2

The rate at which the decomposition reaction is occurring is clearly related to the rate of change of the concentration $[C_{60}O_3]$, which is proportional to the slope of the graph in Figure 16.2 (Oxidized Buckminsterfullerene Absorbance). Therefore, we define the rate of this reaction as

$$\text{Rate} = -\frac{d\left[C_{60}O_3\right]}{dt} \simeq -\frac{\Delta\left(\left[C_{60}O_3\right]\right)}{\Delta\left(t\right)} \tag{16.1}$$

We want the rate of reaction to be positive, since the reaction is proceeding forward. However, because we are measuring the rate of disappearance of the reactant in this case, that rate is negative. We include a negative sign in this definition of rate so that the rate in (16.1) is a positive number. Note also that the slope of the graph in Figure 16.2 (Oxidized Buckminsterfullerene Absorbance) should be taken as the derivative of the graph, since the graph is not a straight line. We will approximate that derivative by estimating the slope at each time in the data, taking the change in the absorbance of the $C_{60}O_3$ divided by the change in time at each time step. The rate, calculated in this way, is plotted as a function of time in Figure 16.3 (Rate of Decomposition).

Rate of Decomposition

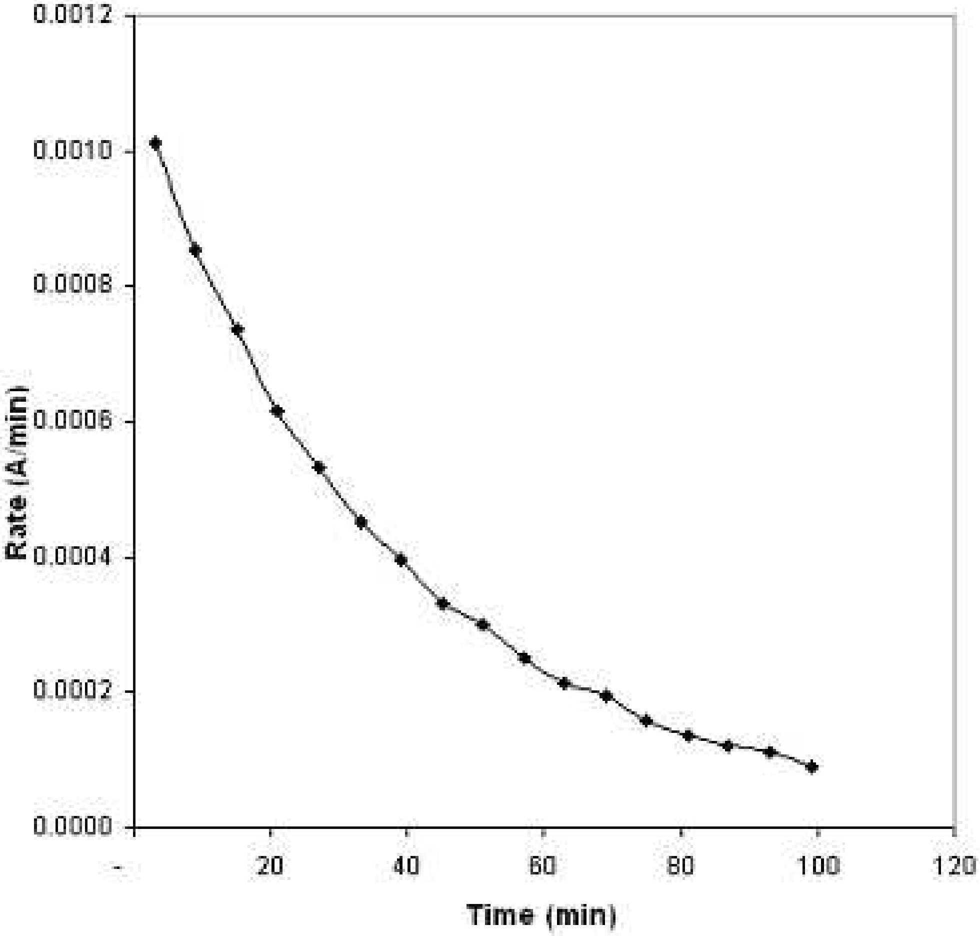
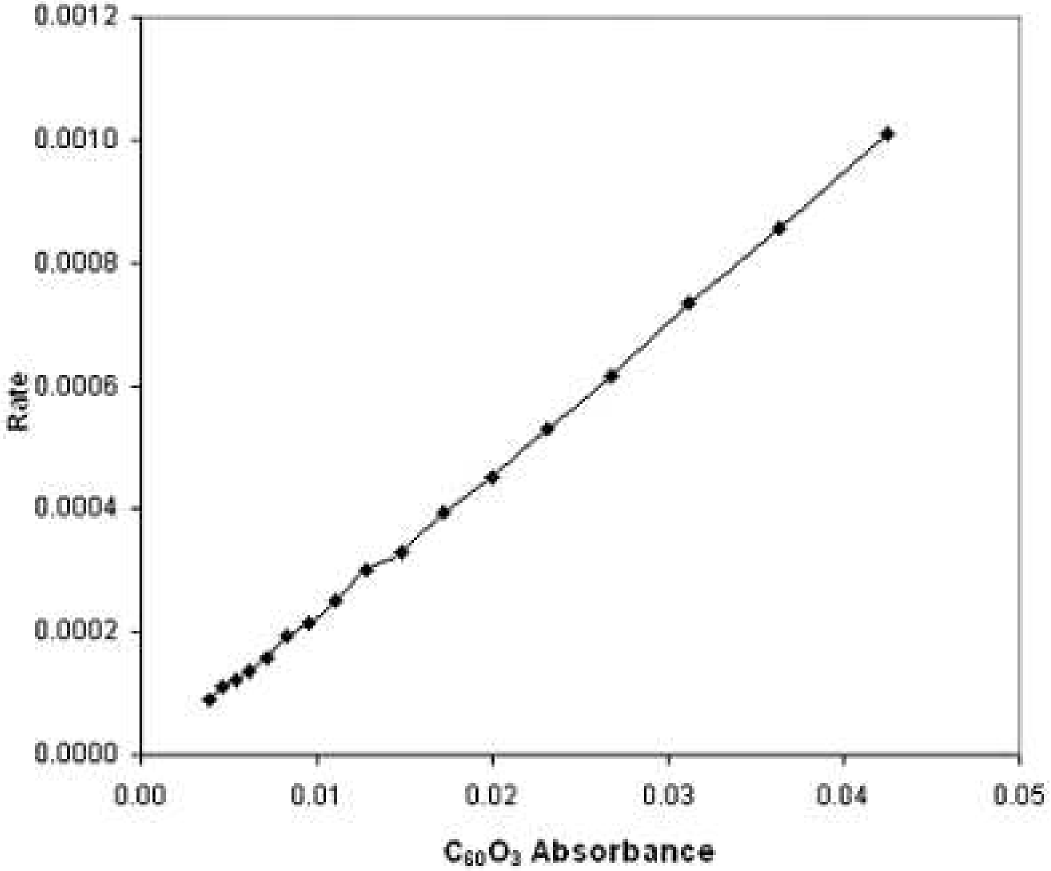


Figure 16.3

It is clear that the slope of the graph in Figure 16.2 (Oxidized Buckminsterfullerene Absorbance) changes over the course of time. Correspondingly, Figure 16.3 (Rate of Decomposition) shows that the rate of the reaction decreases as the reaction proceeds. The reaction is at first very fast but then slows considerably as the reactant $C_{60}O_3$ is depleted.

The shape of the graph for rate versus time (Figure 16.3 (Rate of Decomposition)) is very similar to the shape of the graph for concentration versus time (Figure 16.2 (Oxidized Buckminsterfullerene Absorbance)). This suggests that the rate of the reaction is related to the concentration of $C_{60}O_3$ at each time. Therefore, in Figure 16.4 (Rate versus Concentration), we plot the rate of the reaction, defined in (16.1) and shown in Figure 16.3 (Rate of Decomposition), versus the absorbance of the $C_{60}O_3$.



Rate versus Concentration

Figure 16.4

We find that there is a very simple proportional relationship between the rate of the reaction and the concentration of the reactant. Therefore, we can write

$$\begin{aligned} \text{Rate} &= -\frac{d[C_{60}O_3]}{dt} \\ &= k\,[C_{60}O_3] \end{aligned} \tag{16.2}$$

where k is a proportionality constant. This equation shows that, early in the reaction when $[C_{60}O_3]$ is large, the reaction proceeds rapidly, and that as $C_{60}O_3$ is consumed, the reaction slows down. (16.2) is an example of a **rate law**, expressing the relationship between the rate of a reaction and the concentrations of the reactant or reactants. Rate laws are expressions of the relationship between experimentally observed rates and concentrations.

As a second example of a reaction rate, we consider the dimerization reaction of butadiene gas, $CH_2{=}CH\text{-}CH{=}CH_2$. Two butadiene molecules can combine to form vinylcyclohexene, shown in Figure 16.5 (Dimerization of Butadiene to Vinylcyclohexene).

Dimerization of Butadiene to Vinylcyclohexene

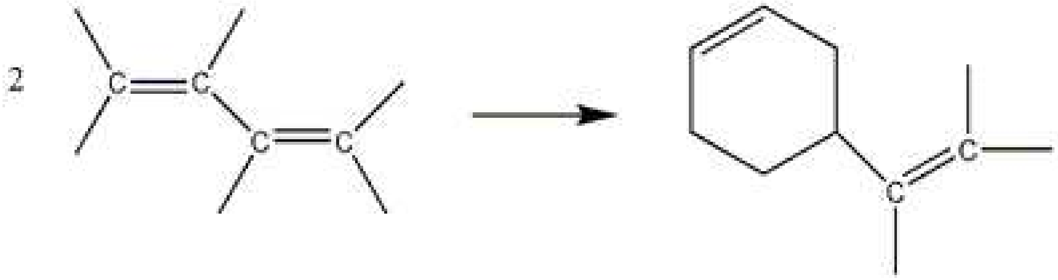


Figure 16.5

Table 16.2: Dimerization of Butadiene at 250 °C provides experimental data on the gas phase concentration of butadiene $[C_4H_6]$ as a function of time at $T = 250\,°C$.

Dimerization of Butadiene at 250 °C

Time (s)	$[C_4H_6]$ **(M)**	**Rate (M/s)**	$\frac{\text{Rate}}{[C_4H_6]}$	$\frac{\text{Rate}}{[C_4H_6]^2}$
0	0.0917	9.48×10^{-6}	1.03×10^{-4}	1.13×10^{-3}
500	0.0870	8.55×10^{-6}	9.84×10^{-5}	1.13×10^{-3}
1000	0.0827	7.75×10^{-6}	9.37×10^{-5}	1.13×10^{-3}
1500	0.0788	7.05×10^{-6}	8.95×10^{-5}	1.14×10^{-3}
2000	0.0753	6.45×10^{-6}	8.57×10^{-5}	1.14×10^{-3}
2500	0.0720	5.92×10^{-6}	8.22×10^{-5}	1.14×10^{-3}
3000	0.0691	5.45×10^{-6}	7.90×10^{-5}	1.14×10^{-3}
3500	0.0664	5.04×10^{-6}	7.60×10^{-5}	1.14×10^{-3}
4000	0.0638	4.67×10^{-6}	7.32×10^{-5}	1.15×10^{-3}

Table 16.2

We can estimate the rate of reaction at each time step as in (16.1), and these data are presented in Table 16.2: Dimerization of Butadiene at 250 °C as well. Again we see that the rate of reaction decreases as the concentration of butadiene decreases. This suggests that the rate is given by an expression like (16.2). To test this, we calculate $\frac{\text{Rate}}{[C_4H_6]}$ in Table 16.2: Dimerization of Butadiene at 250 °C for each time step. We note that this is **not** a constant, so (16.2) does not describe the relationship between the rate of reaction and the concentration of butadiene. Instead we calculate $\frac{\text{Rate}}{[C_4H_6]^2}$ in Table 16.2: Dimerization of Butadiene at 250 °C. We discover that this ratio is a constant throughout the reaction. Therefore, the relationship between the rate of the reaction and the concentration of the reactant in this case is given by

$$\begin{aligned} \text{Rate} &= -\frac{d[C_4H_6]}{dt} \\ &= k[C_4H_6]^2 \end{aligned} \qquad (16.3)$$

which is the rate law for the reaction in Figure 16.5 (Dimerization of Butadiene to Vinylcyclohexene). This is a very interesting result when compared to (16.2). In both cases, the results demonstrate that the rate of reaction depends on the concentration of the reactant. However, we now also know that the way in which the rate varies with the concentration depends on what the reaction is. Each reaction has its own rate law, observed experimentally.

16.4 Observation 2: Rate Laws and the Order of Reaction

We would like to understand what determines the specific dependence of the reaction rate on concentration in each reaction. In the first case considered above, the rate depends on the concentration of the reactant to the first power. We refer to this as a **first order reaction**. In the second case above, the rate depends on the concentration of the reactant to the second power, so this is called a **second order reaction**. There are also **third order reactions**, and even **zeroth order reactions** whose rates do not depend on the amount of the reactant. We need more observations of rate laws for different reactions.

The approach used in the previous section (Section 16.3: Observation 1: Reaction Rates) to determine a reaction's rate law is fairly clumsy and at this point difficult to apply. We consider here a more systematic approach. First, consider the decomposition of $N_2O_5\,(g)$.

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

We can create an initial concentration of N_2O_5 in a flask and measure the rate at which the N_2O_5 first decomposes. We can then create a different initial concentration of N_2O_5 and measure the new rate at which the N_2O_5 decomposes. By comparing these rates, we can find the order of the decomposition reaction. The rate law for decomposition of $N_2O_5\,(g)$ is of the general form:

$$\text{Rate} = k[N_2O_5]^m \tag{16.4}$$

so we need to determine the exponent m. For example, at $25\,°C$ we observe that the rate of decomposition is $1.4 \times 10^{-3}\frac{M}{s}$ when the concentration of N_2O_5 is $0.020M$. If instead we begin we $[N_2O_5] = 0.010M$, we observe that the rate of decomposition is $7.0 \times 10^{-4}\frac{M}{s}$. We can compare the rate from the first measurement Rate (1) to the rate from the second measurement Rate (2). From (16.4), we can write that

$$\begin{aligned} \frac{\text{Rate(1)}}{\text{Rate(2)}} &= \frac{k{[N_2O_5]_1}^m}{k{[N_2O_5]_2}^m} \\ &= \frac{1.4\times10^{-3}\frac{M}{s}}{7.0\times10^{-4}\frac{M}{s}} \\ &= \frac{k(0.020M)^m}{k(0.010M)^m} \end{aligned} \tag{16.5}$$

This can be simplified on both sides of the equation to give

$$2.0 = 2.0^m$$

Clearly, then $m = 1$, and the decomposition is a first order reaction. We can also then find the first order rate constant k for this reaction by simply plugging in one of the initial rate measurements to (16.4). We find that $k = 0.070s^{-1}$.

This approach to finding reaction order is called the method of initial rates, since it relies on fixing the concentration at specific initial values and measuring the initial rate associated with each concentration.

So far we have considered only reactions which have a single reactant. Consider a second example of the method of initial rates involving the reaction of hydrogen gas and iodine gas:

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g) \tag{16.6}$$

In this case, we expect to find that the rate of the reaction depends on the concentrations for both reactants. As such, we need more initial rate observations to determine the rate law. In Table 16.3: Hydrogen Gas and Iodine Gas Initial Rate Data at 700K, observations are reported for the initial rate for three sets of initial concentrations of H_2 and I_2.

Hydrogen Gas and Iodine Gas Initial Rate Data at 700K

Experiment	$[H_2]_0$ **(M)**	$[I_2]_0$ **(M)**	**Rate (M/sec)**
1	0.10	0.10	3.00×10^{-4}
2	0.20	0.10	6.00×10^{-4}
3	0.20	0.20	1.19×10^{-3}

Table 16.3

Following the same process we used in the N_2O_5 example, we write the general rate law for the reaction as

$$\text{Rate} = k[H_2]^n[I_2]^m \tag{16.7}$$

By comparing experiment 1 to experiment 2, we can write

$$\begin{aligned} \frac{\text{Rate}(1)}{\text{Rate}(2)} &= \frac{k{[H_2]_1}^n{[I_2]_1}^m}{k{[H_2]_2}^n{[I_2]_2}^m} \\ &= \frac{3.00\times10^{-4}\frac{M}{s}}{6.00\times10^{-4}\frac{M}{s}} \\ &= \frac{k(0.10M)^m(0.10M)^n}{k(0.20M)^m(0.10M)^n} \end{aligned} \tag{16.8}$$

This simplifies to

$$0.50 = 0.50^m 1.00^n$$

from which it is clear that $m = 1$. Similarly, we can find that $n = 1$. The reaction is therefore first order in each reactant and is second order overall.

$$\text{Rate} = k\,[H_2]\,[I_2] \tag{16.9}$$

Once we know the rate law, we can use any of the data from Table 16.3: Hydrogen Gas and Iodine Gas Initial Rate Data at 700K to determine the rate constant, simply by plugging in concentrations and rate into (16.9). We find that $k = 3.00 \times 10^{-2} \times \frac{1}{Ms}$.

This procedure can be applied to any number of reactions. The challenge is preparing the initial conditions and measuring the initial change in concentration precisely versus time. Table 16.4: Rate Laws for Various Reactions provides an overview of the rate laws for several reactions. A variety of reaction orders are observed, and they cannot be easily correlated with the stoichiometry of the reaction.

Rate Laws for Various Reactions

Reaction	**Rate Law**
$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$	$\text{Rate} = k[NO]^2\,[O_2]$
$2NO\,(g) + 2H_2\,(g) \rightarrow 2N_2\,(g) + 2H_2O\,(g)$	$\text{Rate} = k[NO]^2\,[H_2]$
$2ICl\,(g) + H_2\,(g) \rightarrow 2HCl\,(g) + I_2\,(g)$	$\text{Rate} = k\,[ICl]\,[H_2]$
$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$	$\text{Rate} = k\,[N_2O_5]$
$2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$	$\text{Rate} = k\,[NO_2]\,[F_2]$
$2H_2O_2\,(\text{aq}) \rightarrow 2H_2O\,(l) + O_2\,(g)$	$\text{Rate} = k\,[H_2O_2]$
$H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g)$	$\text{Rate} = k\,[H_2]\,[Br_2]^{\frac{1}{2}}$
$O_3\,(g) + Cl\,(g) \rightarrow O_2\,(g) + ClO\,(g)$	$\text{Rate} = k\,[O_3]\,[Cl]$

Table 16.4

16.5 Concentrations as a Function of Time and the Reaction Half-life

Once we know the rate law for a reaction, we should be able to predict how fast a reaction will proceed. From this, we should also be able to predict how much reactant remains or how much product has been produced at any given time in the reaction. We will focus on the reactions with a single reactant to illustrate these ideas.

Consider a first order reaction like $A \rightarrow$ products, for which the rate law must be

$$\begin{aligned} \text{Rate} &= -\tfrac{d[A]}{dt} \\ &= k\,[A] \end{aligned} \tag{16.10}$$

From Calculus, it is possible to use (16.10) to find the function $[A]\,(t)$ which tells us the concentration $[A]$ as a function of time. The result is

$$[A] = [A]_0 e^{-(kt)} \tag{16.11}$$

or equivalently

$$\ln\left([A]\right) = \ln\left([A]_0\right) - kt \tag{16.12}$$

(16.12) reveals that, if a reaction is first order, we can plot $\ln([A])$ versus time and get a straight line with slope equal to $-k$. Moreover, if we know the rate constant and the initial concentration, we can predict the concentration at any time during the reaction.

An interesting point in the reaction is the time at which exactly half of the original concentration of A has been consumed. We call this time the **half life** of the reaction and denote it as $t_{\frac{1}{2}}$. At that time, $[A] = \frac{1}{2}[A]_0$. From (16.12) and using the properties of logarithms, we find that, for a first order reaction

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} \tag{16.13}$$

This equation tells us that the half-life of a first order reaction does not depend on how much material we start with. It takes exactly the same amount of time for the reaction to proceed from all of the starting material to half of the starting material as it does to proceed from half of the starting material to one-fourth of the starting material. In each case, we halve the remaining material in a time equal to the constant half-life in (16.13).

These conclusions are only valid for first order reactions. Consider then a second order reaction, such as the butadiene dimerization discussed above (p. 164). The general second order reaction $A \rightarrow$ products has the rate law

$$\begin{aligned} \text{Rate} &= -\tfrac{d[A]}{dt} \\ &= k[A]^2 \end{aligned} \tag{16.14}$$

Again, we can use Calculus to find the function $[A]\,(t)$ from (16.14). The result is most easily written as

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k\,(t) \tag{16.15}$$

Note that, as t increases, $\frac{1}{[A]}$ increases, so $[A]$ decreases. (16.15) reveals that, for a reaction which is second order in the reactant A, we can plot $\frac{1}{[A]}$ as a function of time to get a straight line with slope equal to k. Again, if we know the rate constant and the initial concentration, we can find the concentration $[A]$ at any time of interest during the reaction.

The half-life of a second order reaction differs from the half-life of a first order reaction. From (16.15), if we take $[A] = \frac{1}{2}[A]_0$, we get

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \tag{16.16}$$

This shows that, unlike a first order reaction, the half-life for a second order reaction depends on how much material we start with. From (16.16), the more concentrated the reactant is, the shorter the half-life.

16.6 Observation 3: Temperature Dependence of Reaction Rates

It is a common observation that reactions tend to proceed more rapidly with increasing temperature. Similarly, cooling reactants can have the effect of slowing a reaction to a near halt. How is this change in rate reflected in the rate law equation, *e.g.* (16.9)? One possibility is that there is a slight dependence on temperature of the concentrations, since volumes do vary with temperature. However, this is insufficient to account for the dramatic changes in rate typically observed. Therefore, the temperature dependence of reaction rate is primarily found in the rate constant, k.

Consider for example the reaction of hydrogen gas with iodine gas at high temperatures, as given in (16.6). The rate constant of this reaction at each temperature can be found using the method of initial rates, as discussed above, and we find in Table 16.5: Rate Constant for Hydrogen Gas and Iodine Gas that the rate constant increases dramatically as the temperature increases.

Rate Constant for Hydrogen Gas and Iodine Gas

T (K)	**k** $\left(\frac{1}{Ms}\right)$
667	6.80×10^{-3}
675	9.87×10^{-3}
700	3.00×10^{-2}
725	8.43×10^{-2}
750	2.21×10^{-1}
775	5.46×10^{-1}
800	1.27

Table 16.5

As shown in Figure 16.6 (Rate Constant), the rate constant appears to increase exponentially with temperature. After a little experimentation with the data, we find in Figure 16.7 (Rate Constant) that there is a simple linear relationship between $\ln(k)$ and $\frac{1}{T}$.

Rate Constant

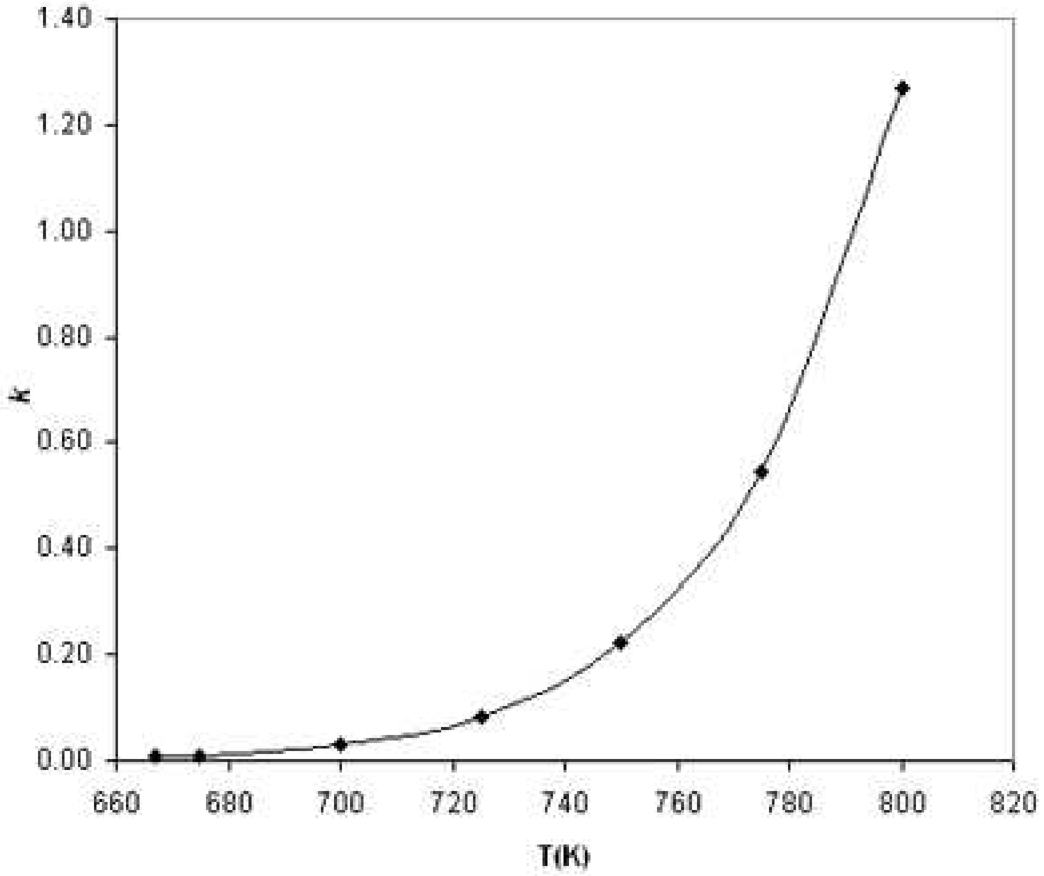


Figure 16.6

Rate Constant

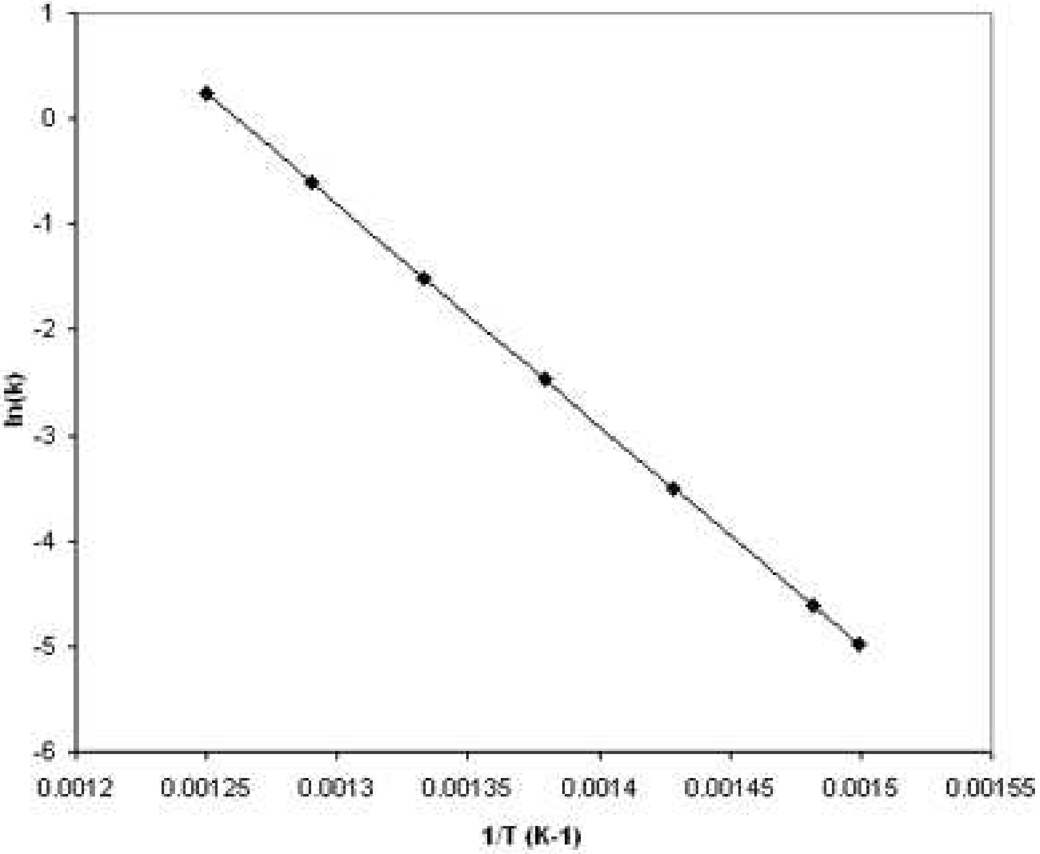


Figure 16.7

From Figure 16.7 (Rate Constant), we can see that the data in Table 16.4: Rate Laws for Various Reactions fit the equation

$$\ln(k) = a\frac{1}{T} + b \tag{16.17}$$

where a and b are constant for this reaction. It turns out that, for our purposes, all reactions have rate constants which fit (16.17), but with different constants a and b for each reaction. Figure 16.7 (Rate Constant) is referred to as an **Arrhenius plot**, after Svante Arrhenius.

It is very important to note that the form of (16.17) and the appearance of Figure 16.7 (Rate Constant) are both the same as the equations and graphs for the temperature dependence of the equilibrium constant for an endothermic reaction. This suggests a model to account for the temperature dependence of the rate constant, based on the energetics of the reaction. In particular, it appears that the reaction rate is related to the amount of energy required for the reaction to occur. We will develop this further in the next section.

16.7 Collision Model for Reaction Rates

At this point, we have only observed the dependence of reaction rates on concentration of reactants and on temperature, and we have fit these data to equations called rate laws. Although this is very convenient, it does not provide us insight into why a particular reaction has a specific rate law or why the temperature dependence should obey (16.17). Nor does it provide any physical insights into the order of the reaction or the meaning of the constants a and b in (16.17).

We begin by asking why the reaction rate should depend on the concentration of the reactants. To answer this, we consider a simple reaction between two molecules in which atoms are transferred between the molecules during the reaction. For example, a reaction important in the decomposition of ozone O_3 by aerosols is

$$O_3\,(g) + Cl\,(g) \rightarrow O_2\,(g) + ClO\,(g)$$

What must happen for a reaction to occur between an O_3 molecule and a Cl atom? Obviously, for these two particles to react, they must come into close proximity to one another so that an O atom can be transferred from one to the other. In general, two molecules cannot trade atoms to produce new product molecules unless they are close enough together for the atoms of the two molecules to interact. This requires a collision between molecules.

The rate of collisions depends on the concentrations of the reactants, since the more molecules there are in a confined space, the more likely they are to run into each other. To write this relationship in an equation, we can think in terms of probability, and we consider the reaction above. The probability for an O_3 molecule to be near a specific point increases with the number of O_3 molecules, and therefore increases with the concentration of O_3 molecules. The probability for a Cl atom to be near that specific point is also proportional to the concentration of Cl atoms. Therefore, the probability for an O_3 molecule and a Cl atom to be in close proximity to the same specific point at the same time is proportional to the $[O_3]$ times $[Cl]$.

It is important to remember that not all collisions between O_3 molecules and Cl atoms will result in a reaction. There are other factors to consider including how the molecules approach one another. The atoms may not be positioned properly to exchange between molecules, in which case the molecules will simply bounce off of one another without reacting. For example, if the Cl atom approaches the center O atom of the O_3 molecule, that O atom will not transfer. Another factor is energy associated with the reaction. Clearly, though, a collision must occur for the reaction to occur, and therefore there rate of the reaction can be no faster than the rate of collisions between the reactant molecules.

Therefore, we can say that, in a **bimolecular reaction**, where two molecules collide and react, the rate of the reaction will be proportional to the product of the concentrations of the reactants. For the reaction of O_3 with Cl, the rate must therefore be proportional to $[O_3]\,[Cl]$, and we observe this in the experimental rate law in Table 16.4: Rate Laws for Various Reactions. Thus, it appears that we can understand the rate law by understanding the collisions which must occur for the reaction to take place.

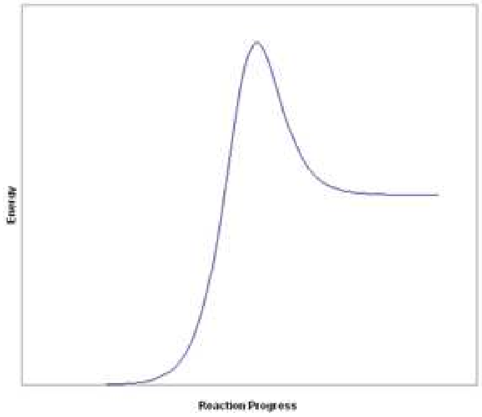
We also need our model to account for the temperature dependence of the rate constant. As noted at the end of the last section (p. 171), the temperature dependence of the rate constant in (16.17) is the same as the temperature dependence of the equilibrium constant for an endothermic reaction. This suggests that the temperature dependence is due to an energetic factor required for the reaction to occur. However, we find experimentally that (16.17) describes the rate constant temperature dependence regardless of whether the reaction is endothermic or exothermic. Therefore, whatever the energetic factor is that is required for the reaction to occur, it is not just the endothermicity of the reaction. It must be that all reactions, regardless of the overall change in energy, require energy to occur.

A model to account for this is the concept of **activation energy**. For a reaction to occur, at least some bonds in the reactant molecule must be broken, so that atoms can rearrange and new bonds can be created. At the time of collision, bonds are stretched and broken as new bonds are made. Breaking these bonds and rearranging the atoms during the collision requires the input of energy. The minimum amount of energy required for the reaction to occur is called the activation energy, E_a. This is illustrated in Figure 16.8 (Reaction Energy), showing conceptually how the energy of the reactants varies as the reaction proceeds. In Figure 16.8(a) (Endothermic Reaction), the energy is low early in the reaction, when the molecules are still arranged as reactants. As the molecules approach and begin to rearrange, the energy rises sharply, rising to a maximum in the middle of the reaction. This sharp rise in energy is the activation energy, as illustrated. After the middle of the reaction has passed and the molecules are arranged more as products than reactants, the energy begins to fall again. However, the energy does not fall to its original value, so this is an endothermic reaction.

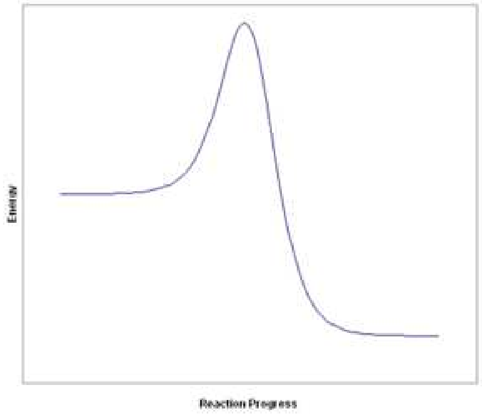
Figure 16.8(b) (Exothermic Reaction) shows the analogous situation for an exothermic reaction. Again, as the reactants approach one another, the energy rises as the atoms begin to rearrange. At the middle of the collision, the energy maximizes and then falls as the product molecules form. In an exothermic reaction, the product energy is lower than the reactant energy.

Figure 16.8 (Reaction Energy) thus shows that an energy barrier must be surmounted for the reaction to occur, regardless of whether the energy of the products is greater than (Figure 16.8(a) (Endothermic Reaction)) or less than (Figure 16.8(b) (Exothermic Reaction)) the energy of the reactants. This barrier accounts for the temperature dependence of the reaction rate. We know from the kinetic molecular theory that as temperature increases the average energy of the molecules in a sample increases. Therefore, as temperature increases, the fraction of molecules with sufficient energy to surmount the reaction activation barrier increases.

Reaction Energy



(a) Endothermic Reaction



(b) Exothermic Reaction

Figure 16.8

Although we will not show it here, kinetic molecular theory shows that the fraction of molecules with energy greater than E_a at temperature T is proportional to $e^{-\frac{E_a}{RT}}$. This means that the reaction rate and therefore also the rate constant must be proportional to $e^{-\frac{E_a}{RT}}$. Therefore we can write

$$k\left(T\right) = Ae^{-\frac{E_a}{RT}} \tag{16.18}$$

where A is a proportionality constant. If we take the logarithm of both sides of (16.18), we find that

$$\ln\left(k\left(T\right)\right) = -\frac{E_a}{RT} + \ln\left(A\right) \tag{16.19}$$

This equation matches the experimentally observed (16.17). We recall that a graph of $\ln\left(k\right)$ versus $\frac{1}{T}$ is observed to be linear. Now we can see that the slope of that graph is equal to $-\frac{E_a}{R}$.

As a final note on (16.19), the constant A must have some physical significant. We have accounted for the probability of collision between two molecules and we have accounted for the energetic requirement for a successful reactive collision. We have not accounted for the probability that a collision will have the appropriate orientation of reactant molecules during the collision. Moreover, not every collision which occurs with proper orientation and sufficient energy will actually result in a reaction. There are other random factors relating to the internal structure of each molecule at the instant of collision. The factor A takes account for all of these factors, and is essentially the probability that a collision with sufficient energy for reaction will indeed lead to reaction. A is commonly called the **frequency factor**.

16.8 Observation 4: Rate Laws for More Complicated Reaction Processes

Our collision model in the previous section accounts for the concentration and temperature dependence of the reaction rate, as expressed by the rate law. The concentration dependence arises from calculating the probability of the reactant molecules being in the same vicinity at the same instant. Therefore, we should be able to predict the rate law for any reaction by simply multiplying together the concentrations of all reactant molecules in the balanced stoichiometric equation. The order of the reaction should therefore be simply related to the stoichiometric coefficients in the reaction. However, Table 16.4: Rate Laws for Various Reactions shows that this is incorrect for many reactions.

Consider for example the apparently simple reaction

$$2ICl\,(g) + H_2\,(g) \rightarrow 2HCl\,(g) + I_2\,(g) \tag{16.20}$$

Based on the collision model, we would assume that the reaction occurs by $2ICl$ molecules colliding with a single H_2 molecule. The probability for such a collision should be proportional to $[ICl]^2\,[H_2]$. However, experimentally we observe (see Table 16.4: Rate Laws for Various Reactions) that the rate law for this reaction is

$$\text{Rate} = k\,[ICl]\,[H_2] \tag{16.21}$$

As a second example, consider the reaction

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g) \tag{16.22}$$

It would seem reasonable to assume that this reaction occurs as a single collision in which an oxygen atom is exchanged between the two molecules. However, the experimentally observed rate law for this reaction is

$$\text{Rate} = k[NO_2]^2 \tag{16.23}$$

In this case, the $[CO]$ concentration does not affect the rate of the reaction at all, and the $[NO_2]$ concentration is squared. These examples demonstrate that the rate law for a reaction cannot be predicted from the stoichiometric coefficients and therefore that the collision model does not account for the rate of the reaction. There must be something seriously incomplete with the collision model.

The key assumption of the collision model is that the reaction occurs by a single collision. Since this assumption leads to incorrect predictions of rate laws in some cases, the assumption must be invalid in at least those cases. It may well be that reactions require more than a single collision to occur, even in reactions involving just two types of molecules as in (16.22). Moreover, if more than two molecules are involved as in (16.20), the chance of a single collision involving all of the reactive molecules becomes very small. We conclude that many reactions, including those in (16.20) and (16.22), must occur as a result of several collisions occurring in sequence, rather than a single collision. The rate of the chemical reaction must be determined by the rates of the individual steps in the reaction.

Each step in a complex reaction is a single collision, often referred to as an **elementary process**. In single collision process step, our collision model should correctly predict the rate of that step. The sequence of such elementary processes leading to the overall reaction is referred to as the **reaction mechanism**. Determining the mechanism for a reaction can require gaining substantially more information than simply the rate data we have considered here. However, we can gain some progress just from the rate law.

Consider for example the reaction in (16.22) described by the rate law in (16.23). Since the rate law involved $[NO_2]^2$, one step in the reaction mechanism must involve the collision of two NO_2 molecules. Furthermore, this step must determine the rate of the overall reaction. Why would that be? In any multi-step process, if one step is considerably slower than all of the other steps, the rate of the multi-step process is determined entirely by that slowest step, because the overall process cannot go any faster than the slowest step. It does not matter how rapidly the rapid steps occur. Therefore, the slowest step in a multi-step process is thus called the **rate determining** or **rate limiting** step.

This argument suggests that the reaction in (16.22) proceeds via a slow step in which two NO_2 molecules collide, followed by at least one other rapid step leading to the products. A possible mechanism is therefore

Step 1

$$NO_2 + NO_2 \rightarrow NO_3 + NO \tag{16.24}$$

Step 2

$$NO_3 + CO \rightarrow NO_2 + CO_2 \tag{16.25}$$

If Step 1 (16.24: Step 1) is much slower than Step 2 (16.25: Step 2), the rate of the reaction is entirely determined by the rate of Step 1 (16.24: Step 1). From our collision model, the rate law for Step 1 (16.24: Step 1) must be Rate = $k[NO_2]^2$, which is consistent with the experimentally observed rate law for the overall reaction. This suggests that the mechanism in (16.24) (Step 1) and (16.25) (Step 2) is the correct description of the reaction process for (16.22), with the first step as the rate determining step.

There are a few important notes about the mechanism. First, one product of the reaction is produced in the first step, and the other is produced in the second step. Therefore, the mechanism does lead to the overall reaction, consuming the correct amount of reactant and producing the correct amount of reactant. Second, the first reaction produces a new molecule, NO_3, which is neither a reactant nor a product. The second step then consumes that molecule, and NO_3 therefore does not appear in the overall reaction, (16.22). As such, NO_3 is called a **reaction intermediate**. Intermediates play important roles in the rates of many reactions.

If the first step in a mechanism is rate determining as in this case, it is easy to find the rate law for the overall expression from the mechanism. If the second step or later steps are rate determining, determining the rate law is slightly more involved. The process for finding the rate law in such a case is illustrated in Exercise 16.11.

16.9 Review and Discussion Questions

Exercise 16.1
When $C_{60}O_3$ in toluene solution decomposes, O_2 is released leaving $C_{60}O_3$ in solution.

16.9.1

Based on the data in Figure 16.2 (Oxidized Buckminsterfullerene Absorbance) and Figure 16.3 (Rate of Decomposition), plot the concentration of $C_{60}O$ as a function of time.

16.9.2

How would you define the rate of the reaction in terms of the slope of the graph from above (Section 16.9.1)? How is the rate of appearance of $C_{60}O$ related to the rate of disappearance of $C_{60}O_3$? Based on this, plot the rate of appearance of $C_{60}O$ as a function of time.

Exercise 16.2
The reaction $2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$ was found in this study to have rate law given by Rate $= k\,[N_2O_5]$ with $k = 0.070s^{-1}$.

16.9.1

How is the rate of appearance of NO_2 related to the rate of disappearance of N_2O_5? Which rate is larger?

16.9.2

Based on the rate law and rate constant, sketch a plot of $[N_2O_5]$, $[NO_2]$, and $[O_2]$ versus time all on the same graph.

Exercise 16.3
For which of the reactions listed in Table 16.4: Rate Laws for Various Reactions can you be certain that the reaction does not occur as a single step collision? Explain your reasoning.

Exercise 16.4
Consider two decomposition reactions for two hypothetical materials, A and B. The decomposition of A is found to be first order, and the decomposition of B is found to be second order.

16.9.1

Assuming that the two reactions have the same rate constant at the same temperature, sketch $[A]$ and $[B]$ versus time on the same graph for the same initial conditions, *i.e.* $[A]_0 = [B]_0$.

16.9.2

Compare the half-lives of the two reactions. Under what conditions will the half-life of B be less than the half-life of A? Under what conditions will the half-life of B be greater than the half-life of A?

Exercise 16.5
A graph of the logarithm of the equilibrium constant for a reaction versus $\frac{1}{T}$ is linear but can have either a negative slope or a positive slope, depending on the reaction, as was observed here (Chapter 14). However, the graph of the logarithm of the rate constant for a reaction versus $\frac{1}{T}$ has a negative slope for essentially every reaction. Using equilibrium arguments, explain why the graph for the rate constant must have a negative slope.

Exercise 16.6
Using (16.18) and the data in Table 16.5: Rate Constant for Hydrogen Gas and Iodine Gas, determine the activation energy for the reaction $H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$.

Exercise 16.7
We found that the rate law for the reaction $H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$ is Rate $= k\,[H_2]\,[I_2]$. Therefore, the reaction is **second order** overall but **first order** in H_2. Imagine that we start with $[H_2]_0 = [I_2]_0$ and we measure $[H_2]$ versus time. Will a graph of $\ln([H_2])$ versus time be linear or will a graph of $\frac{1}{[H_2]}$ versus time be linear? Explain your reasoning.

Exercise 16.8
As a rough estimate, chemists often assume a **rule of thumb** that the rate of any reaction will double when the temperature is increased by $10\,°C$.

16.9.1

What does this suggest about the activation energies of reactions?

16.9.2

Using (16.18), calculate the activation energy of a reaction whose rate doubles when the temperature is raised from $25\,^{\circ}C$ to $35\,^{\circ}C$.

16.9.3

Does this rule of thumb estimate depend on the temperature range? To find out, calculate the factor by which the rate constant increases when the temperature is raised from $100\,^{\circ}C$ to $110\,^{\circ}C$, assuming the same activation energy you found above (Section 16.9.2). Does the rate double in this case?

Exercise 16.9

Consider a very simple hypothetical reaction $A + B \leftrightarrow 2C$ which comes to equilibrium.

16.9.1

At equilibrium, what must be the relationship between the rate of the forward reaction, $A+B \rightarrow 2C$ and the reverse reaction $2C \rightarrow A + B$?

16.9.2

Assume that both the forward and reverse reactions are elementary processes occurring by a single collision. What is the rate law for the forward reaction? What is the rate law for the reverse reaction?

16.9.3

Using the previous results from here (Section 16.9.1) and here (Section 16.9.2), show that the equilibrium constant for this reaction can be calculated from $K_c = \frac{k_f}{k_r}$, where k_f is the rate constant for the forward reaction and k_r is the rate constant for the reverse reaction.

Exercise 16.10

Consider a very simple hypothetical reaction $A + B \leftrightarrow C + D$. By examining Figure 16.8 (Reaction Energy), provide and explain the relationship between the activation energy in the forward direction, $E_{a,f}$, and in the reverse direction, $E_{a,r}$. Does this relationship depend on whether the reaction is endothermic (Figure 16.8(a) (Endothermic Reaction)) or exothermic (Figure 16.8(b) (Exothermic Reaction))? Explain.

Exercise 16.11

For the reaction $H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$, the rate law is Rate $= k\,[H_2]\,[I_2]$. Although this suggests that the reaction is a one-step elementary process, there is evidence that the reaction occurs in two steps, and the second step is the rate determining step:

Step 1

$$I_2 \leftrightarrow 2I \tag{16.26}$$

Step 2

$$H_2 + 2I \rightarrow 2HI \tag{16.27}$$

Where Step 1 (16.26: Step 1) is fast and Step2 (16.27: Step 2) is slow.

16.9.1

If the both the forward and reverse reactions in Step 1 (16.26: Step 1) are much faster than Step2 (16.27: Step 2), explain why Step 1 (16.26: Step 1) can be considered to be at equilibrium.

16.9.2

What is the rate law for the rate determining step?

16.9.3

Since the rate law above (Section 16.9.2) depends on the concentration of an intermediate I, we need to find that intermediate. Calculate $[I]$ from Step 1 (16.26: Step 1), assuming that Step1 (16.26: Step 1) is at equilibrium.

16.9.4

Substitute $[I]$ from above (Section 16.9.3) into the rate law found previously (Section 16.9.2) to find the overall rate law for the reaction. Is this result consistent with the experimental observation?

Chapter 17

Equilibrium and the Second Law of Thermodynamics[1]

17.1 Foundation

We have observed and defined phase transitions and phase equilibrium. We have also observed equilibrium in a variety of reaction systems. We will assume an understanding of the postulates of the **Kinetic Molecular Theory** and of the energetics of chemical reactions.

17.2 Goals

We have developed an understanding of the concept of equilibrium, both for phase equilibrium and reaction equilibrium. As an illustration, at normal atmospheric pressure, we expect to find H_2O in solid form below 0 °C, in liquid form below 100 °C, and in gaseous form above 100 °C. What changes as we move from low temperature to high temperature cause these transitions in which phase is observed? Viewed differently, if a sample of gaseous water at 120 °C is cooled to below 100 °C, virtually all of the water vapor spontaneously condenses to form the liquid:

$$H_2O\,(g) \rightarrow H_2O\,(l) \text{ spontaneous below } 100\,^{\circ}\mathrm{C}$$

By contrast, very little of liquid water at 80 °C spontaneously converts to gaseous water:

$$H_2O\,(l) \rightarrow H_2O\,(g) \text{ not spontaneous below } 100\,^{\circ}\mathrm{C}$$

We can thus rephrase our question as, what determines which processes are spontaneous and which are not? What factors determine what phase is "stable"?

As we know, at certain temperatures and pressures, more than one phase can be stable. For example, at 1 atm pressure and 0 °C,

$$H_2O\,(s) \leftrightarrow H_2O\,(l) \, \text{equilibrium at } 0\,^{\circ}\mathrm{C}$$

Small variations in the amount of heat applied or extracted to the liquid-solid equilibrium cause shifts towards liquid or solid without changing the temperature of the two phases at equilibrium. Therefore, when the two phases are at equilibrium, neither direction of the phase transition is spontaneous at 0 °C. We therefore need to understand what factors determine when two or more phases can co-exist at equilibrium.

This analysis leaves unanswered a series of questions regarding the differences between liquids and gases. The concept of a gas phase or a liquid phase is not a characteristic of an individual molecule. In fact, it does

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[1] This content is available online at <http://cnx.org/content/m12593/1.4/>.

not make any sense to refer to the "phase" of an individual molecule. The phase is a collective property of large numbers of molecules. Although we can discuss the importance of molecular properties regarding liquid and gas phases, we have not discussed the factors which determine whether the gas phase or the liquid phase is most stable at a given temperature and pressure.

These same questions can be applied to reaction equilibrium. When a mixture of reactants and products is not at equilibrium, the reaction will occur spontaneously in one direction or the other until the reaction achieves equilibrium. What determines the direction of spontaneity? What is the driving force towards equilibrium? How does the system **know** that equilibrium has been achieved? Our goal will be to understand the driving forces behind spontaneous processes and the determination of the equilibrium point, both for phase equilibrium and reaction equilibrium.

17.3 Observation 1: Spontaneous Mixing

We begin by examining common characteristics of spontaneous processes, and for simplicity, we focus on processes not involving phase transitions or chemical reactions. A very clear example of such a process is mixing. Imagine putting a drop of blue ink in a glass of water. At first, the blue dye in the ink is highly concentrated. Therefore, the molecules of the dye are closely congregated. Slowly but steadily, the dye begins to diffuse throughout the entire glass of water, so that eventually the water appears as a uniform blue color. This occurs more readily with agitation or stirring but occurs spontaneously even without such effort. Careful measurements show that this process occurs without a change in temperature, so there is no energy input or released during the mixing.

We conclude that, although there is no energetic advantage to the dye molecules dispersing themselves, they do so spontaneously. Furthermore, this process is **irreversible** in the sense that, without considerable effort on our part, the dye molecules will never return to form a single localized drop. We now seek an understanding of how and why this mixing occurs.

Consider the following rather abstract model for the dye molecules in the water. For the glass, we take a row of ten small boxes, each one of which represents a possible location for a molecule, either of water or of dye. For the molecules, we take marbles, clear for water and blue for ink. Each box will accommodate only a single marble, since two molecules cannot be in the same place as the same time. Since we see a drop of dye when the molecules are congregated, we model a "drop" as three blue marbles in consecutive boxes. Notice that there are only eight ways to have a "drop" of dye, assuming that the three dye "molecules" are indistinguishable from one another. Two possibilities are shown in Figure 17.1(a) and Figure 17.1(b). It is not difficult to find the other six.

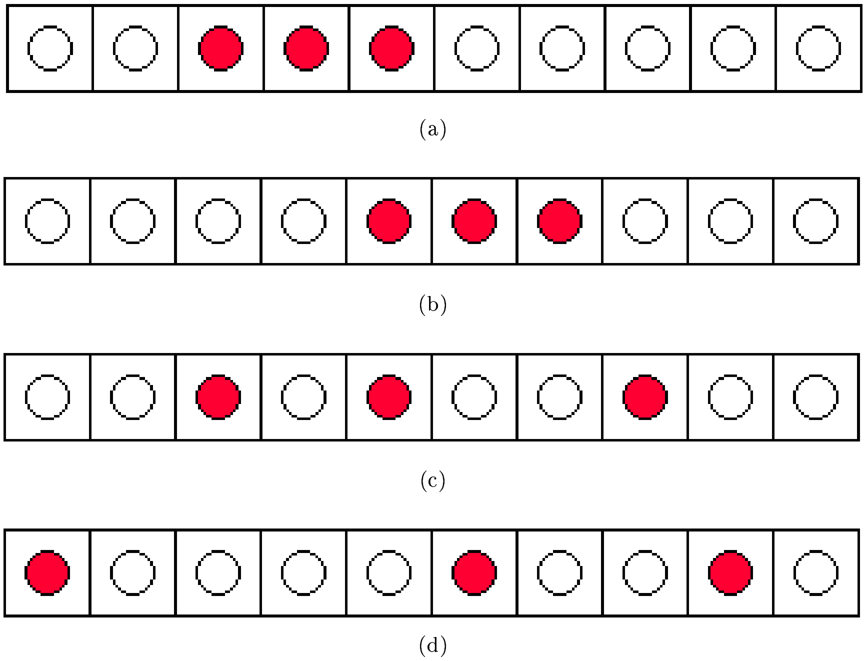

Figure 17.1: (a) An unmixed state. (b) Another unmixed state. (c) A mixed state. (d) Another mixed state.

By contrast, there are many more ways to arrange the dye molecules so that they do not form a drop, *i.e.*, so that the three molecules are not together. Two possibilities are shown in Figure 17.1(c) and Figure 17.1(d). The total number of such possibilities is 112. (The total number of all possible arrangements can be calculated as follows: there are 10 possible locations for the first blue marble, 9 for the second, and 8 for the third. This gives 720 possible arrangements, but many of these are identical, since the marbles are indistinguishable. The number of duplicates for each arrangement is 6, calculated from three choices for the first marble, two for the second, and one for the third. The total number of non-identical arrangements of the molecules is $\frac{720}{6} = 120$.) We conclude that, if we randomly place the 3 marbles in the tray of 10 boxes, the chances are only 8 out of 120 (or 1 out of 15) of observing a drop of ink.

Now, in a real experiment, there are many, many times more ink molecules and many, many times more possible positions for each molecule. To see how this comes into play, consider a row of 500 boxes and 5 blue marbles. (The **mole fraction** of ink is thus 0.01.) The total number of distinct configurations of the blue marbles in these boxes is approximately 2×10^{11}. The number of these configurations which have all five ink marbles together in a drop is 496. If the arrangements are sampled randomly, the chances of observing a drop of ink with all five molecules together are thus about one in 500 million. The possibilities are remote even for observing a partial "droplet" consisting of fewer than all five dye molecules. The chance for four of the molecules to be found together is about one in 800,000. Even if we define a droplet to be only three molecules together, the chances of observing one are less than one in 1600.

We could, with some difficulty, calculate the probability for observing a drop of ink when there are 10^{23} molecules. However, it is reasonably deduced from our small calculations that the probability is essentially zero for the ink molecules, randomly distributed into the water molecules, to be found together. We conclude from this that the reason why we observe ink to disperse in water is that the probability is infinitesimally small for randomly distributed dye molecules to be congregated in a drop.

Interestingly, however, when we set up the real ink and water experiment, we did not randomly distribute the ink molecules. Rather, we began initially with a drop of ink in which the dye molecules were already congregated. We know that, according to our kinetic theory, the molecules are in constant random motion. Therefore, they must be constantly rearranging themselves. Since these random motions do not energetically favor any one arrangement over any other one arrangement, we can assume that all possible arrangements are equally probable. Since most of the arrangements do not correspond to a drop of ink, then **most of the time** we will not observe a drop. In the case above with five blue marbles in 500 boxes, we expect to see a drop only once in every 500 million times we look at the "glass". In a real glass of water with a real drop of ink, the chances are very much smaller than this.

We draw two very important conclusions from our model. First, the random motions of molecules make every possible arrangement of these molecules equally probable. Second, mixing occurs spontaneously simply because there are vastly many more arrangements which are mixed than which are not. The first conclusion tells us "how" mixing occurs, and the second tells us "why." On the basis of these observations, we deduce the following preliminary generalization: a spontaneous process occurs because it produces the most probable final state.

17.4 Probability and Entropy

There is a subtlety in our conclusion to be considered in more detail. We have concluded that all possible arrangements of molecules are equally probable. We have further concluded that mixing occurs because the final mixed state is overwhelmingly probable. Placed together, these statements appear to be openly contradictory. To see why they are not, we must analyze the statements carefully. By an "arrangement" of the molecules, we mean a specification of the location of each and every molecule. We have assumed that, due to random molecular motion, each such arrangement is equally probable. In what sense, then, is the final state "overwhelmingly probable"?

Recall the system illustrated in Figure 17.1 (Arrangement of Three Ink Molecules), where we placed three identical blue marbles into ten spaces. We calculated before that there are 120 unique ways to do this. If we ask for the probability of the arrangement in Figure 17.1(a), the answer is thus $\frac{1}{120}$. This is also the probability for each of the other possible arrangements, according to our model. However, if we now ask instead for the probability of observing a "mixed" state (with no drop), the answer is $\frac{112}{120}$, whereas the probability of observing an "unmixed" state (with a drop) is only $\frac{8}{120}$. Clearly, the probabilities are not the same when considering the less specific characteristics "mixed" and "unmixed".

In chemistry we are virtually never concerned with **microscopic** details, such as the locations of specific individual molecules. Rather, we are interested in more general characteristics, such as whether a system is mixed or not, or what the temperature or pressure is. These properties of interest to us are **macroscopic**. As such, we refer to a specific arrangement of the molecules as a **microstate**, and each general state (mixed or unmixed, for example) as a **macrostate**. All microstates have the same probability of occurring, according to our model. As such, the macrostates have widely differing probabilities.

We come to an important result: the probability of observing a particular macrostate (*e.g.*, a mixed state) is proportional to the number of microstates with that macroscopic property. For example, from Figure 17.1 (Arrangement of Three Ink Molecules), there are 112 arrangements (microstates) with the "mixed" macroscopic property. As we have discussed, the probability of observing a mixed state is $\frac{112}{120}$, which is obviously proportional to 112. Thus, one way to measure the relative probability of a particular macrostate is by the number of microstates W corresponding to that macrostate. W stands for "ways", *i.e.*, there are 112 "ways" to get a mixed state in Figure 17.1 (Arrangement of Three Ink Molecules).

Now we recall our conclusion that a spontaneous process always produces the outcome with greatest probability. Since W measures this probability for any substance or system of interest, we could predict, using W, whether the process leading from a given initial state to a given final state was spontaneous by simply comparing probabilities for the initial and final states. For reasons described below, we instead define a function of W,

$$S\left(W\right)=k\ln\left(W\right) \tag{17.1}$$

called the **entropy**, which can be used to make such predictions about spontaneity. (The k is a proportionality constant which gives S appropriate units for our calculations.) Notice that the more microstates there are, the greater the entropy is. Therefore, a macrostate with a high probability (*e.g.* a mixed state) has a large entropy. We now modify our previous deduction to say that a spontaneous process produces the final state of greatest entropy. (Following modifications added below, this statement forms the **Second Law of Thermodynamics**.)

It would seem that we could use W for our calculations and that the definition of the new function S is unnecessary. However, the following reasoning shows that W is not a convenient function for calculations. We consider two identical glasses of water at the same temperature. We expect that the value of any physical property for the water in two glasses is twice the value of that property for a single glass. For example, if the enthalpy of the water in each glass is H_1, then it follows that the total enthalpy of the water in the two glasses together is $H_{\text{total}}=2H_1$. Thus, the enthalpy of a system is proportional to the quantity of material in the system: if we double the amount of water, we double the enthalpy. In direct contrast, we consider the calculation involving W for these two glasses of water. The number of microstates of the macroscopic state of one glass of water is W_1, and likewise the number of microstates in the second glass of water is W_1. However, if we combine the two glasses of water, the number of microstates of the total system is found from the product $W_{\text{total}}=W_1\times W_1$, which does not equal $2W_1$. In other words, W is not proportional to the quantity of material in the system. This is inconvenient, since the value of W thus depends on whether the two systems are combined or not. (If it is not clear that we should multiply the W values, consider the simple example of rolling dice. The number of states for a single die is 6, but for two dice the number is $6\times6=36$, not $6+6=12$.)

We therefore need a new function $S\left(W\right)$, so that, when we combine the two glasses of water, $S_{\text{total}}=S_1+S_1$. Since $S_{\text{total}}=S\left(W_{\text{total}}\right)$, $S_1=S\left(W_1\right)$, and $W_{\text{total}}=W_1\times W_1$, then our new function S must satisfy the equation

$$S\left(W_1\times W_1\right)=S\left(W_1\right)+S\left(W_1\right)$$

The only function S which will satisfy this equation is the logarithm function, which has the property that $\ln\left(x\times y\right)=\ln\left(x\right)+\ln\left(y\right)$. We conclude that an appropriate state function which measures the number of microstates in a particular macrostate is (17.1).

17.5 Observation 2: Absolute Entropies

It is possible, though exceedingly difficult, to calculate the entropy of any system under any conditions of interest from the equation $S=k\ln\left(W\right)$. It is also possible, using more advanced theoretical thermodynamics, to determine S experimentally by measuring heat capacities and enthalpies of phase transitions. Values of S determined experimentally, often referred to as "absolute" entropies, have been tabulated for many materials at many temperatures, and a few examples are given in Table 17.1: Absolute Entropies of Specific Substances. We treat these values as observations and attempt to understand these in the context of (17.1).

Absolute Entropies of Specific Substances

	T (°C)	**S ($\frac{J}{\text{mol}\,^\circ\text{C}}$)**
$H_2O\,(g)$	25	188.8
$H_2O\,(l)$	25	69.9
$H_2O\,(l)$	0	63.3
$H_2O\,(s)$	0	41.3
$NH_3\,(g)$	25	192.4
$HN_3\,(l)$	25	140.6
$HN_3\,(g)$	25	239.0
$O_2\,(g)$	25	205.1
$O_2\,(g)$	50	207.4
$O_2\,(g)$	100	211.7
$CO\,(g)$	25	197.7
$CO\,(g)$	50	200.0
$CO_2\,(g)$	24	213.7
$CO_2\,(g)$	50	216.9
$Br_2\,(l)$	25	152.2
$Br_2\,(g)$	25	245.5
$I_2\,(s)$	25	116.1
$I_2\,(g)$	25	260.7
$CaF_2\,(s)$	25	68.9
$CaCl_2\,(s)$	25	104.6
$CaBr_2\,(s)$	25	130
$C_8H_{18}\,(s)$	25	361.1

Table 17.1

There are several interesting generalities observed in Table 17.1: Absolute Entropies of Specific Substances. First, in comparing the entropy of the gaseous form of a substance to either its liquid or solid form at the same temperature, we find that the gas always has a substantially greater entropy. This is easy to understand from (17.1): the molecules in the gas phase occupy a very much larger volume. There are very many more possible locations for each gas molecule and thus very many more arrangements of the molecules in the gas. It is intuitively clear that W should be larger for a gas, and therefore the entropy of a gas is greater than that of the corresponding liquid or solid.

Second, we observe that the entropy of a liquid is always greater than that of the corresponding solid. This is understandable from our kinetic molecular view of liquids and solids. Although the molecules in the liquid occupy a comparable volume to that of the molecules in the solid, each molecule in the liquid is free to move throughout this entire volume. The molecules in the solid are relatively fixed in location. Therefore, the number of arrangements of molecules in the liquid is significantly greater than that in the solid, so the liquid has greater entropy by (17.1).

Third, the entropy of a substance increases with increasing temperature. The temperature is, of course, a measure of the average kinetic energy of the molecules. In a solid or liquid, then, increasing the temperature increases the total kinetic energy available to the molecules. The greater the energy, the more ways there are to distribute this energy amongst the molecules. Although we have previously only referred to the range of positions for a molecule as affecting W, the range of energies available for each molecule similarly affects W. As a result, as we increase the total energy of a substance, we increase W and thus the entropy.

Fourth, the entropy of a substance whose molecules contain many atoms is greater than that of a substance composed of smaller molecules. The more atoms there are in a molecule, the more ways there are to arrange those atoms. With greater internal flexibility, W is larger when there are more atoms, so the entropy is greater.

Fifth, the entropy of a substance with a high molecular weight is greater than that of substance with a low molecular weight. This result is a harder to understand, as it arises from the distribution of the momenta of the molecules rather than the positions and energies of the molecules. It is intuitively clear that the number of arrangements of the molecules is **not** affected by the mass of the molecules. However, even at the same temperature, the range of momenta available for a heavier molecule is greater than for a lighter one. To see why, recall that the momentum of a molecule is $p = mv$ and the kinetic energy is $\mathrm{KE} = \frac{mv^2}{2} = \frac{p^2}{2m}$. Therefore, the maximum momentum available at a fixed total kinetic energy KE is $p = \sqrt{2m\mathrm{KE}}$. Since this is larger for larger mass molecules, the range of momenta is greater for heavier particles, thus increasing W and the entropy.

17.6 Observation 3: Condensation and Freezing

We have concluded from our observations of spontaneous mixing that a spontaneous process always produces the final state of greatest probability. A few simple observations reveal that our deduction needs some thoughtful refinement. For example, we have observed that the entropy of liquid water is greater than that of solid water. This makes sense in the context of (17.1), since the kinetic theory indicates that liquid water has a greater value of W. Nevertheless, we observe that liquid water spontaneously freezes at temperatures below $0\,^{\circ}\mathrm{C}$. This process clearly displays a decrease in entropy and therefore evidently a shift from a more probable state to a less probable state. This appears to contradict directly our conclusion.

Similarly, we expect to find condensation of water droplets from steam when steam is cooled. On days of high humidity, water spontaneously liquefies from the air on cold surfaces such as the outside of a glass of ice water or the window of an air conditioned building. In these cases, the transition from gas to liquid is clearly from a higher entropy phase to a lower entropy phase, which does not seem to follow our reasoning thus far.

Our previous conclusions concerning entropy and probability increases were compelling, however, and we should be reluctant to abandon them. What we have failed to take into consideration is that these phase transitions involve changes of energy and thus heat flow. Condensation of gas to liquid and freezing of liquid to solid both involve evolution of heat. This heat flow is of consequence because our observations also revealed that the entropy of a substance can be increased significantly by heating. One way to preserve our conclusions about spontaneity and entropy is to place a condition on their validity: a spontaneous process produces the final state of greatest probability and entropy **provided that** the process does not involve evolution of heat. This is an unsatisfying result, however, since most physical and chemical processes involve heat transfer. As an alternative, we can force the process not to evolve heat by **isolating** the system undergoing the process: no heat can be released if there is no sink to receive the heat, and no heat can be absorbed if there is no source of heat. Therefore, we conclude from our observations that a spontaneous process **in an isolated system** produces the final state of greatest probability and entropy. This is one statement of the **Second Law of Thermodynamics**.

17.7 Free Energy

How can the Second Law be applied to a process in a system that is not isolated? One way to view the lessons of the previous observations is as follows: in analyzing a process to understand why it is or is not spontaneous, we must consider both the change in entropy of the system undergoing the process **and** the effect of the heat released or absorbed during the process on the entropy of the surroundings. Although we cannot prove it here, the entropy increase of a substance due to heat q at temperature T is given by $\Delta(S) = \frac{q}{T}$. From another study (Chapter 10), we can calculate the heat transfer for a process occurring under constant pressure from the enthalpy change, $\Delta(H)$. By conservation of energy, the heat flow into the surroundings must be $-\Delta(H)$. Therefore, the increase in the entropy of the surroundings due to heat transfer must be $\Delta(S_{\text{surr}}) = -\frac{\Delta(H)}{T}$. Notice that, if the reaction is exothermic, $\Delta(H) < 0$ so $\Delta(S_{\text{surr}}) > 0$.

According to our statement of the Second Law, a spontaneous process in an isolated system is always accompanied by an increase in the entropy of the system. If we want to apply this statement to a non-isolated system, we must include the surroundings in our entropy calculation. We can say then that, for a spontaneous process,

$$\Delta(S_{\text{total}}) = \Delta(S_{\text{sys}}) + \Delta(S_{\text{surr}}) > 0$$

Since $\Delta(S_{\text{surr}}) = -\frac{\Delta(H)}{T}$, then we can write that $\Delta(S) - \frac{\Delta(H)}{T} > 0$. This is easily rewritten to state that, for a spontaneous process:

$$\Delta(H) - T\Delta(S) < 0 \tag{17.2}$$

(17.2) is really just a different form of the Second Law of Thermodynamics. However, this form has the advantage that it takes into account the effects on both the system undergoing the process and the surroundings. Thus, this new form can be applied to non-isolated systems.

(17.2) reveals why the temperature affects the spontaneity of processes. Recall that the condensation of water vapor occurs spontaneously at temperature below 100 °C but not above. Condensation is an exothermic process; to see this, consider that the reverse process, evaporation, obviously requires heat input. Therefore $\Delta(H) < 0$ for condensation. However, condensation clearly results in a decrease in entropy, therefore $\Delta(S) < 0$ also. Examining (17.2), we can conclude that $\Delta(H) - T\Delta(S) < 0$ will be less than zero for condensation only if the temperature is not too high. At high temperature, the term $-\Delta(S)$, which is positive, becomes larger than $\Delta(H)$, so $\Delta(H) - T\Delta(S) > 0$ for condensation at high temperature. Therefore, condensation only occurs at lower temperatures.

Because of the considerable practical utility of (17.2) in predicting the spontaneity of physical and chemical processes, it is desirable to simplify the calculation of the quantity on the left side of the inequality. One way to do this is to define a new quantity $G = H - TS$, called the **free energy**. If we calculate from this definition the change in the free energy which occurs during a process at constant temperature, we get

$$\Delta(G) = G_{\text{final}} - G_{\text{initial}} = H_{\text{final}} - TS_{\text{final}} - (H_{\text{initial}} - TS_{\text{initial}}) = \Delta(H) - T\Delta(S)$$

and therefore a simplified statement of the Second Law of Thermodynamics in (17.2) is that

$$\Delta(G) < 0 \tag{17.3}$$

for any spontaneous process. Thus, in any spontaneous process, the free energy of the system decreases. Note that G is a state function, since it is defined in terms of H, T, and S, all of which are state functions. Since G is a state function, then $\Delta(G)$ can be calculated along any convenient path. As such, the methods used to calculate $\Delta(H)$ in another study (Chapter 10) can be used just as well to calculate $\Delta(G)$.

17.8 Thermodynamic Description of Phase Equilibrium

As we recall, the entropy of vapor is much greater than the entropy of the corresponding amount of liquid. A look back at Table 17.1: Absolute Entropies of Specific Substances shows that, at 25 °C, the entropy of one mole of liquid water is $69.9\frac{J}{K}$, whereas the entropy of one mole of water vapor is $188.8\frac{J}{K}$. Our first thought, based on our understanding of spontaneous processes and entropy, might well be that a mole of liquid water at 25 °C should spontaneously convert into a mole of water vapor, since this process would greatly increase the entropy of the water. We know, however, that this does not happen. Liquid water will exist in a closed container at 25 °C without spontaneously converting entirely to vapor. What have we left out?

The answer, based on our discussion of free energy, is the energy associated with evaporation. The conversion of one mole of liquid water into one mole of water vapor results in absorption of 44.0kJ of energy from the surroundings. Recall that this loss of energy from the surroundings results in a significant decrease in entropy of the surroundings. We can calculate the amount of entropy decrease in the surroundings from $\Delta\left(S_{\text{surr}}\right)=-\frac{\Delta(H)}{T}$. At 25 °C, this gives $\Delta\left(S_{\text{surr}}\right)=\frac{-44.0\text{kJ}}{298.15K}=-147.57\frac{J}{K}$ for a single mole. This entropy decrease is greater than the entropy increase of the water, $188.8\frac{J}{K}-69.9\frac{J}{K}=118.9\frac{J}{K}$. Therefore, the entropy of the universe **decreases** when one mole of liquid water converts to one mole of water vapor at 25 °C.

We can repeat this calculation in terms of the free energy change:

$$\Delta(G)=\Delta(H)-T\Delta(S)$$

$$\Delta(G)=44000\frac{J}{\text{mol}}-(298.15K)\left(118.9\frac{J}{K\text{mol}}\right)$$

$$\Delta(G)=8.55\frac{\text{kJ}}{\text{mol}}>0$$

Since the free energy increases in the transformation of one mole of liquid water to one mole of water vapor, we predict that the transformation will not occur spontaneously. This is something of a relief, because we have correctly predicted that the mole of liquid water is stable at 25 °C relative to the mole of water vapor.

We are still faced with our perplexing question, however. Why does any water evaporate at 25 °C? How can this be a spontaneous process?

The answer is that we have to be careful about interpreting our prediction. The entropy of one mole of water vapor at 25 °C **and 1.00 atm pressure** is $188.8\frac{J}{K}$. We should clarify our prediction to say that one mole of liquid water will not spontaneously evaporate to form one mole of water vapor at 25 °C and 1.00 atm pressure. This prediction is in agreement with our observation, because we have found that the water vapor formed spontaneously above liquid water at 25 °C has pressure 23.8 torr, well below 1.00 atm.

Assuming that our reasoning is correct, then the spontaneous evaporation of water at 25 °C when **no** water vapor is present initially must have $\Delta(G)<0$. And, indeed, as water vapor forms and the pressure of the water vapor increases, evaporation must continue as long as $\Delta(G)<0$. Eventually, evaporation stops in a closed system when we reach the vapor pressure, so we must reach a point where $\Delta(G)$ is no longer less than zero, that is, evaporation stops when $\Delta(G)=0$. This is the point where we have equilibrium between liquid and vapor.

We can actually determine the conditions under which this is true. Since $\Delta(G)=\Delta(H)-T\Delta(S)$, then when $\Delta(G)=0$, $\Delta(H)=T\Delta(S)$. We already know that $\Delta(H)=44.0$kJ for the evaporation of one mole of water. Therefore, the pressure of water vapor at which $\Delta(G)=0$ at 25 °C is the pressure at which $\Delta(S)=\frac{\Delta(H)}{T}=147.6\frac{J}{K}$ for a single mole of water evaporating. This is larger than the value of $\Delta(S)$ for one mole and 1.00 atm pressure of water vapor, which as we calculated was $118.9\frac{J}{K}$. Evidently, $\Delta(S)$ for evaporation changes as the pressure of the water vapor changes. We therefore need to understand why the entropy of the water vapor depends on the pressure of the water vapor.

Recall that 1 mole of water vapor occupies a much smaller volume at 1.00 atm of pressure than it does at the considerably lower vapor pressure of 23.8 torr. In the larger volume at lower pressure, the water molecules have a much larger space to move in, and therefore the number of microstates for the water molecules must be larger in a larger volume. Therefore, the entropy of one mole of water vapor is larger in a larger volume at lower pressure. The entropy change for evaporation of one mole of water is thus greater when the evaporation occurs to a lower pressure. With a greater entropy change to offset the entropy loss of the surroundings, it is possible for the evaporation to be spontaneous at lower pressure. And this is exactly what we observe.

To find out how much the entropy of a gas changes as we decrease the pressure, we assume that the number of microstates W for the gas molecule is proportional to the volume V. This would make sense, because the larger the volume, the more places there are for the molecules to be. Since the entropy is given by $S = k\ln(W)$, then S must also be proportional to $\ln(V)$. Therefore, we can say that

$$\begin{aligned} S(V_2) - S(V_1) &= R\ln(V_2) - R\ln(V_1) \\ &= R\ln\left(\frac{V_2}{V_1}\right) \end{aligned} \tag{17.4}$$

We are interested in the variation of S with pressure, and we remember from Boyle's law that, for a fixed temperature, volume is inversely related to pressure. Thus, we find that

$$\begin{aligned} S(P_2) - S(P_1) &= R\ln\left(\frac{P_1}{P_2}\right) \\ &= -\left(R\ln\left(\frac{P_2}{P_1}\right)\right) \end{aligned} \tag{17.5}$$

For water vapor, we know that the entropy at 1.00 atm pressure is $188.8\frac{J}{K}$ for one mole. We can use this and the equation above to determine the entropy at any other pressure. For a pressure of 23.8torr = 0.0313atm, this equation gives that S(23.8torr)) is $217.6\frac{J}{K}$ for one mole of water vapor. Therefore, at this pressure, the $\Delta(S)$ for evaporation of one mole of water vapor is $217.6\frac{J}{K} - 69.9\frac{J}{K} = 147.6\frac{J}{K}$. We can use this to calculate that for evaporation of one mole of water at 25 °C and water vapor pressure of 23.8 torr is $\Delta(G) = \Delta(H) - T\Delta(S) = 44.0\text{kJ} - (298.15K)\left(147.6\frac{J}{K}\right) = 0.00\text{kJ}$. This is the condition we expected for equilibrium.

We can conclude that the evaporation of water when no vapor is present initially is a spontaneous process with $\Delta(G) < 0$, and the evaporation continues until the water vapor has reached its the equilibrium vapor pressure, at which point $\Delta(G) = 0$.

17.9 Thermodynamic description of reaction equilibrium

Having developed a thermodynamic understanding of phase equilibrium, it proves to be even more useful to examine the thermodynamic description of reaction equilibrium to understand why the reactants and products come to equilibrium at the specific values that are observed.

Recall that $\Delta(G) = \Delta(H) - T\Delta(S) < 0$ for a spontaneous process, and $\Delta(G) = \Delta(H) - T\Delta(S) = 0$ at equilibrium. From these relations, we would predict that most (but not all) exothermic processes with $\Delta(H) < 0$ are spontaneous, because all such processes increase the entropy of the surroundings when they occur. Similarly, we would predict that most (but not all) processes with $\Delta(S) > 0$ are spontaneous.

We try applying these conclusions to synthesis of ammonia

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \tag{17.6}$$

at 298K, for which we find that $\Delta\left(S^\circ\right) = -198\frac{J}{\text{mol}K}$. Note that $\Delta\left(S^\circ\right) < 0$ because the reaction reduces the total number of gas molecules during ammonia synthesis, thus reducing W, the number of ways of arranging the atoms in these molecules. $\Delta\left(S^\circ\right) < 0$ suggests that (17.6) should not occur at all. However, $\Delta\left(H^\circ\right) = -92.2\frac{\text{kJ}}{\text{mol}}$. Overall, we find that $\Delta\left(G^\circ\right) = -33.0\frac{\text{kJ}}{\text{mol}}$ at 298K, which according to (17.3) suggests that (17.6) is spontaneous.

Given this analysis, we are now pressed to ask, if (17.6) is predicted to be spontaneous, why does the reaction come to equilibrium without fully consuming all of the reactants? The answer lies in a more careful examination of the values given: $\Delta\left(S^\circ\right)$, $\Delta\left(H^\circ\right)$, and $\Delta\left(G^\circ\right)$ are the values for this reaction **at standard conditions**, which means that all of the gases in the reactants and products are taken to be at 1 atm pressure. Thus, the fact that $\Delta\left(G^\circ\right) < 0$ for (17.6) at standard conditions means that, if all three gases are present at 1 atm pressure, the reaction will spontaneously produce an increase in the amount of NH_3. Note that this will reduce the pressure of the N_2 and H_2 and increase the pressure of the NH_3. This changes the value of $\Delta(S)$ and thus of $\Delta(G)$, because as we already know the entropies of all three gases depend on their pressures. As the pressure of NH_3 increases, its entropy decreases, and as the pressures of the reactants gases decrease, their entropies increase. The result is that $\Delta(S)$ becomes increasingly negative. The reaction creates more NH_3 until the value of $\Delta(S)$ is sufficiently negative that $\Delta(G) = \Delta(H) - T\Delta(S) = 0$.

From this analysis, we can say by looking at $\Delta\left(S^{\circ}\right)$, $\Delta\left(H^{\circ}\right)$, and $\Delta\left(G^{\circ}\right)$ that, since $\Delta\left(G^{\circ}\right) < 0$ for (17.6), reaction equilibrium results in production of more product and less reactant than at standard conditions. Moreover, the more negative $\Delta\left(G^{\circ}\right)$ is, the more strongly favored are the products over the reactants at equilibrium. By contrast, the more positive $\Delta\left(G^{\circ}\right)$ is, the more strongly favored are the reactants over the products at equilibrium.

17.10 Thermodynamic Description of the Equilibrium Constant

Thermodynamics can also provide a quantitative understanding of the equilibrium constant. Recall that the condition for equilibrium is that $\Delta(G) = 0$. As noted before, $\Delta(G)$ depends on the pressures of the gases in the reaction mixture, because $\Delta(S)$ depends on these pressures. Though we will not prove it here, it can be shown by application of (17.5) to a reaction that the relationship between $\Delta(G)$ and the pressures of the gases is given by the following equation:

$$\Delta(G) = \Delta\left(G^{\circ}\right) + RT\ln(Q) \tag{17.7}$$

(Recall again that the superscript ° refers to standard pressure of 1 atm. $\Delta\left(G^{\circ}\right)$ is the difference between the free energies of the products and reactants when all gases are at 1 atm pressure.) In this equation, Q is a quotient of partial pressures of the gases in the reaction mixture. In this quotient, each product gas appears in the numerator with an exponent equal to its stoichiometic coefficient, and each reactant gas appears in the denominator also with its corresponding exponent. For example, for the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \tag{17.8}$$

$$Q = \frac{{P_{HI}}^2}{P_{H_2}P_{I_2}} \tag{17.9}$$

It is important to note that the partial pressures in Q need not be the equilibrium partial pressures. However, if the pressures in Q are the equilibrium partial pressures, then Q has the same value as K_p, the equilibrium constant, by definition. Moreover, if the pressures are at equilibrium, we know that $\Delta(G) = 0$. If we look back at (17.7), we can conclude that

$$\Delta\left(G^{\circ}\right) = -\left(RT\ln\left(K_p\right)\right) \tag{17.10}$$

This is an exceptionally important relationship, because it relates two very different observations. To understand this significance, consider first the case where $\Delta\left(G^{\circ}\right) < 0$. We have previously reasoned that, in this case, the reaction equilibrium will favor the products. From (17.10) we can note that, if $\Delta\left(G^{\circ}\right) < 0$, it must be that $K_p > 1$. Furthermore, if $\Delta\left(G^{\circ}\right)$ is a large negative number, K_p is a very large number. By contrast, if $\Delta\left(G^{\circ}\right)$ is a large positive number, K_p will be a very small (though positive) number much less than 1. In this case, the reactants will be strongly favored at equilibrium.

Note that the thermodynamic description of equilibrium and the dynamic description of equilibrium are complementary. Both predict the same equilibrium. In general, the thermodynamic arguments give us an understanding of the conditions under which equilibrium occurs, and the dynamic arguments help us understand how the equilibrium conditions are achieved.

17.11 Review and Discussion Questions

Exercise 17.1

Each possible sequence of the 52 cards in a deck is equally probable. However, when you shuffle a deck and then examine the sequence, the deck is never ordered. Explain why in terms of microstates, macrostates, and entropy.

Exercise 17.2

Assess the validity of the statement, "In all spontaneous processes, the system moves toward a state of lowest energy." Correct any errors you identify.

Exercise 17.3

In each case, determine whether spontaneity is expected at low temperature, high temperature, any temperature, or no temperature:

17.11.1

$\Delta\left(H^{\circ}\right) > 0$, $\Delta\left(S^{\circ}\right) > 0$

17.11.2

$\Delta\left(H^{\circ}\right) < 0$, $\Delta\left(S^{\circ}\right) > 0$

17.11.3

$\Delta\left(H^{\circ}\right) > 0$, $\Delta\left(S^{\circ}\right) < 0$

17.11.4

$\Delta\left(H^{\circ}\right) < 0$, $\Delta\left(S^{\circ}\right) < 0$

Exercise 17.4

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

Exercise 17.5

Why does the entropy of a gas increase as the volume of the gas increases? Why does the entropy decrease as the pressure increases?

Exercise 17.6

For each of the following reactions, calculate the values of $\Delta\left(S^{\circ}\right)$, $\Delta\left(H^{\circ}\right)$, and $\Delta\left(G^{\circ}\right)$ at $T = 298K$ and use these to predict whether equilibrium will favor products or reactants at $T = 298K$. Also calculate K_p.

17.11.1

$2CO\left(g\right) + O_2\left(g\right) \rightarrow 2CO_2\left(g\right)$

17.11.2

$O_3\left(g\right) + NO\left(g\right) \rightarrow NO_2\left(g\right) + O_2\left(g\right)$

17.11.3

$2O_3\left(g\right) \rightarrow 3O_2\left(g\right)$

Exercise 17.7

Predict the sign of the entropy for the reaction

$$2H_2\left(g\right) + O_2\left(g\right) \rightarrow 2H_2O\left(g\right)$$

Give an explanation, based on entropy and the Second Law, of why this reaction occurs spontaneously.

Exercise 17.8

For the reaction $H_2\left(g\right) \rightarrow 2H\left(g\right)$, predict the sign of both $\Delta\left(H^{\circ}\right)$ and $\Delta\left(S^{\circ}\right)$. Should this reaction be spontaneous at high temperature or at low temperature? Explain.

Exercise 17.9

For each of the reactions in Exercise 17.6, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.

Exercise 17.10

Using (17.7) and (17.9), show that for a given set of initial partial pressures where Q is larger than K_p, the reaction will spontaneously create more reactants. Also show that if Q is smaller than K_p, the reaction will spontaneously create more products.

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