CLUE

CHEMISTRY, LIFE, THE UNIVERSE & EVERYTHING

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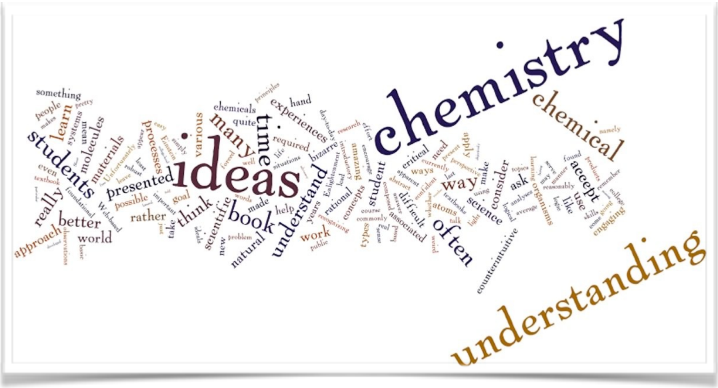
Preface for the reader:



You might well ask, does the world really need another introductory chemistry textbook? The answer is, of course not—not if that book is just a variation on those currently available. Chemistry, and particularly introductory general chemistry, is simply not changing that much and people learn pretty much the same way they always did, at least if we restrict ourselves to the last fe thousand years.[1] On the other hand, there is compelling evidence that the way chemistry is commonly presented, both to the public and in college, is both off-putting and ineffective–a potent combination that leads to the widespread public misunderstanding of chemical principles. How many times do we hear about "natural remedies, without drugs or chemicals," despite the fact that everything is composed of chemicals and the most toxic chemicals known are natural products.[2]

A growing body of research results on student understanding of chemistry indicates, pretty emphatically, that we need better ways to teach and assess students' understanding of the fundamental ideas upon which chemistry is based. These are important ideas that students need to learn, and learn in a robust way that enables them to transfer their understanding to new situations rather than just remember what they were told. It would be even better if we could cultivate an appreciation for how science works and, in our most ambitious moments, light a spark of enthusiasm for the beauty, unity, and bizarre processes that make up the natural world. Our problem is how to approach the Socratic ideal in a practical and economically feasible manner.

In this light, we should 'fess up to where we stand on a number of important issues—we unambiguously accept the liberal ideals of the Enlightenment, namely that intellectual honesty and rigor, rational and logical discourse, and free and dispassionate analyses, together with compassion and empathy, something all too often forgotten by revolutionaries, are critical, both in the context of the scientific enterprise and more generally in making the world a better place for all of its inhabitants. Unfortunately, the ideals of the Enlightenment appear to have fallen somewhat out of favor, at least in some circles. While there is an apparent excess of passion, few appear to be willing to examine objectively or even consider both the positive and negative implications of their positions. Passionate advocacy devoid of rational analysis and the recognition that our understanding of the world is tentative and incomplete, and likely to remain that way for some time into the future, seems to encourage various forms of irrational, and often cruel and violent beliefs, many of which should be dismissed out of hand.

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[1] Take a look at Pauling's General Chemistry and tell us we are wrong.

[2] http://www.the-scientist.com/?articles.view/articleNo/36919/title/Cancer-Causing-Herbal-Remedies/

So, back to the project at hand—how do we build a better chemistry book and course? We freely admit our inspirations. Books like Bill Bryson's "*A Short History of Nearly Everything*" and Einstein and Infeld's "*The Evolution of Physics*" present science in a logical and engaging manner; they are both interesting and stimulating to read. Unfortunately, this is quite different from the style found in most textbooks. So what is missing from the Bryson and Einstein and Infeld books that make them inappropriate for use as a college textbook? Most obviously, they do not concern themselves with determining whether their readers really–that is, accurately–understand and can apply the ideas presented. Therein lies the logic and impetus behind our book and its associated web-based and in-class materials. Our goal is to merge the inherently engaging aspects of chemistry with the active experiences and metacognitive reflections needed to rewire the student's (that is, your) brain to really understand and accurately use chemical knowledge.

While there have been many educational experiments over the last 100 years, we take our inspiration from Socrates (470–399 BCE). Basically, our goal is to present concepts and skills in various ways, ask students to talk about and work with their understanding, and then ask questions about what students actually mean when they use specific words and ideas. Critical to the success of this approach is time: the time required to understand what students think before, during, and after reading the text and working with the applets and activities; the time required for students to recognize and talk about their assumptions; the time required to listen to them, to ask them what, exactly, they mean, and for them to explain, analyze, and where appropriate reconsider, their ideas. Because of the critical link between time and learning, we will not consider some of the topics often presented in standard textbooks and instead will concentrate on more foundational ideas. Does this mean that using this book and its associated materials will leave students unprepared in critical areas of chemistry? No, and we can demonstrate that is not the case. Rather, it leaves students able to work through many of these topics on their own and we will provide web resources to make this possible.

We developed much of the material in this new curriculum using research on how people learn and our own work on how to improve understanding and problem solving in college-level science classes. In previous studies we have found that our methods, which include dramatic reorganization and reduction of materials covered, increase student interactions and activity and lead to equal or better performance on standardized exams, greater conceptual understanding, and improved problem-solving skills. By focusing the time and effort on the foundational ideas we expect that you will achieve a more robust and confident understanding of chemical principles, an understanding that should serve you well in subsequent chemistry and other science courses, not to mention "real life"!

To the Student:

We designed this book to help you attain a confident, competent, and coherent understanding of basic chemistry, in particular of the chemistry associated with organisms and their origins. That said, this is not a chemistry for biologists or non-scientists book but rather an approach to the difficult and often counterintuitive ideas at the heart of chemistry, for an intelligent and engaged student who, often quite reasonably, finds these ideas unbelievable, arbitrary, or incoherent. Our goal is to assist you in developing an understanding of the foundations of chemistry, so that you can apply these ideas to a range of new situations. We are aware that many of you are not excited by the prospect of learning chemistry and we share your concerns—many of the ideas presented are difficult and often counterintuitive and past experiences with chemistry not have been optimal. At the same time, it is possible to approach chemistry from a more reasoned and rational direction, recognizing difficult ideas, why we are forced to accept them, and how we can apply them.

Why is basic chemistry often perceived as boring? One reason maybe the way it is all too commonly presented: a laundry list of facts to remember and exercises to perform, often with little effort made to connect abstract and frankly weird concepts to your lifetime of day-to-day and quite real experiences. For example, it is certainly not obvious that matter is made of a small set of essentially indestructible objects–atoms–connected to one another in various ways; or how such combinations of atoms–molecules–can lead to complex processes like life and dreams. Where did this strange idea come from? How is it that we come to appreciate and accept the reality of things as abstract as atoms and molecules, or that a tree is composed primarily of gas, carbon dioxide, and water molecules, rearranged? Is it even possible for the average person to really accept, understand and learn to work with, such bizarre abstractions? We think we are reasonably average people not withstanding our excessive amounts of formal education and our obsessive efforts to understand what may seem to be insignificant, weird, and occasionally trivial problems. We think that while scientific understanding is not easy, it can be made more engaging by recognizing explicitly which ideas are odd and what types of observations and logic led or forced scientists to accept them.

Throughout our journey we will consider what makes sense from our day-to-day experiences, how that differs from the current models of chemical systems, and what types of observations resolve the apparent contradictions between the two. We encourage you to take your own ideas seriously and consider when they do and do not make scientific sense. This is not an easy task, but it is the only way to understand scientific ideas, rather than simply memorizing words and formulae.

Why think about chemistry from a biological perspective? The answer is simple really. Biological systems, whether cells, organisms, or ecosystems, are the most complicated examples of chemical systems. They rely on chemical reactions and the chemical properties of atoms and molecules to produce truly amazing behaviors. They are the end products of evolutionary processes that have been going on form more that 3.5 billion years; processes based on random variations that are captured and turned into information through natural selection. Molecular analyses strongly support the rather amazing conclusion—namely that all organisms currently living on earth are related and descended from a common ancestor through unbroken lineages.

The underlying unity of life, and its chemical basis, is only one of many amazing, bizarre, and counterintuitive ideas we will encounter. To help you grapple with these ideas we will use various interactive materials that will help you test and strengthen your understanding. Where you feel lost, try to articulate what, exactly, you find confusing and why. You can start a socratic dialog with yourself, and then bring it to your instructor and fellow students. That is the best way to learn, or so claims Socrates.

A note on footnotes: The authors have an inordinate fondness for footnotes. We do not expect you, the student, to read them or the follow the links within them, but they enable us to indulge our interests in various topics. Please be careful to avoid getting lost in them– that may well be a mistake.

Introduction to the course (as opposed to the book)

This text is intended to provide an in-depth introduction to the key ideas in chemistry. We have designed the book to show how these ideas are developed from simple to complex systems and how they relate to each other. We consider three ideas central to an understanding of chemistry: the structure of matter, the properties of matter, and the energy changes involved in the reorganization of matter; all are connected by the interactions or forces that cause matter to interact. We aim to provide compelling reasons why you will find yourself wanting to learn chemistry and to illustrate what you will be able to do with this knowledge once you have learned it.

We hope that you will find the book both readable and engaging, but keep in mind, it is not intended to contain everything that will be learned in this course. It is purposely not cluttered with boxes, asides, and long descriptions about how to solve problems or learn other skills such as learning how to construct a scientific explanation, or developing a model. This is not because these aspects of chemistry are unimportant – quite the contrary – but rather that there is little evidence that reading a book will lead to effective mastery of such skills. Instead, you will work with activities within the class. We have designed these to be interactive and to support and expand on the text. In some cases these ancillary materials introduce ideas that are not, perhaps, as engaging to read about even though they are important to master. These ancillary CLUE materials include:

1. A set of class presentations and activity materials;
2. A set of YouTube videos showing how to do various skills and solve different types of problems; and
3. A set of online activities using the beSocratic system that can be done in class, in recitation, or for homework.

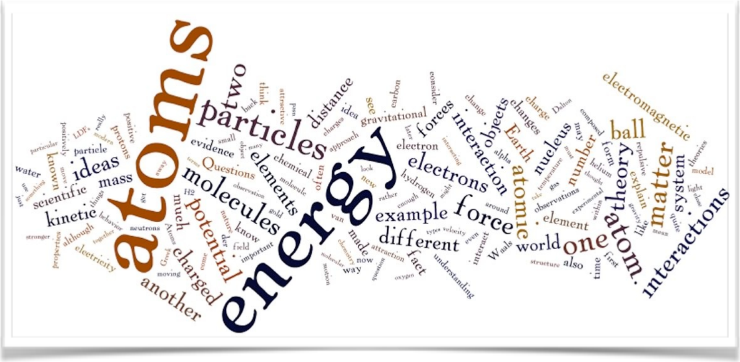
Much like the "questions to answer, questions to ponder, and questions for later" sections of the book, these ancillary activities require you to actively construct answers rather than choose from a list of responses. This is a deliberate focus of the CLUE curriculum because we have compelling evidence that drawing, writing, and constructing answers help students learn more deeply. These materials are also available as worksheets that can be done off-line.

Materials integral to the CLUE curriculum but that are not covered exhaustively in the text are:

1. Common chemistry calculations, illustrated by YouTube videos, including:
   - Stoichiometry;
   - Energy, frequency, and wavelength conversions;
   - Thermochemistry, including specific heat, bond energy, and enthalpy
   - Equilibrium calculations, pH and K_a
2. Common skills, including:
   - Electron configurations, particularly to determine the number of valence electrons;
   - Drawing Lewis structures;
   - VESPR;

- Assigning oxidation numbers; and
- Using curved arrows to predict the outcome of simple reactions.

Chapter 1: Atoms



If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling on being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied. NOBEL LAUREATE RICHARD FEYNMAN, *1963*

Most of us are quite familiar with the core principle of atomic theory—the idea that matter is composed of atoms—because we have been told that this is so since childhood. But how many of us really, and we mean *really* believe it, use it in our day-to-day life, understand its implications, or know the reasons why it is assumed to be true? It seems so completely and totally impossible and improbable because we do not experience atoms directly and it is easy to go through life quite successfully, at least for the vast majority of us, without having to take atoms seriously. The average person's brain is simply not wired to believe in the reality of things like atoms in a concrete and day-to-day way. Yet most scientists, and certainly most chemists, would agree that Feynman’s deceptively simple statement contains the essence of chemistry.

Atomic theory is also critical for understanding a significant number of the underlying concepts of biology and physics, not to mention geology, astronomy, ecology, and engineering. How can one sentence contain so much information? Can we really explain such a vast and diverse set of scientific observations with so little to go on? In the next two chapters we will expand on Feynman’s sentence to see just what you can do with a little imagination and thinking. At the same time, it is worth remembering that the fact that atoms are so unreal from the perspective of our day-to-day experience means that the atomic theory poses a serious barrier to understanding modern chemistry. This is a barrier that can only be dealt with if you recognize it explicitly and try to address and adjust to it. You will be rewiring your brain in order to take atoms, and their implications, seriously. We are aware that this is not an easy task. It takes effort, and much of this effort will involve self-reflection, problem-solving, and question-answering. In an important sense, you do not have to believe in atoms, but you do have to understand them.

1.1 What Do You Think You Know About Atoms?

You almost certainly have heard about atoms and it is very likely you have been taught about them. If asked you might profess to believe in their reality. You might accept that matter, in all its forms, is made up of atoms — particles that are the smallest entities that retain the identity of an element (we will discuss elements in much greater detail in the next few chapters.) It is very likely that you have been taught that atoms are made up of even smaller particles: positively charged protons, uncharged neutrons, and negatively charged electrons. You may even have heard, and perhaps even believe, that protons and neutrons can be further subdivided into quarks and gluons, while electrons are indivisible. Equally difficult to appreciate is that all atoms are organized in a very similar way, with a very tiny, but relatively heavy, positively charged nucleus surrounded by the much lighter, negatively charged electrons.

Part of the difficulty in really understanding atoms is the fact that the forces holding the atomic nucleus together, the so-called strong and weak forces, operate at such infinitesimal distances that we do not experience them directly. This is in contrast to electromagnetism and gravity, which we experience directly because they act over longer, macroscopic or visible distances. A second problem is associated with the fact that to experience the world we need to use energy; at the atomic scale the energy used to observe the system also perturbs it. This is the basis of the Heisenberg uncertainty principle, which you may have encountered or at least heard of before, and to which we will return. Finally, objects at the atomic and subatomic scales behave differently from the macroscopic objects with which we typically interact. A particle of light, a photon, an electron, a proton, or a neutron each behaves as both a particle and a wave. In terms of physics, these are neither particles nor waves; they are quantum mechanical particles. Luckily, the weirder behaviors of atomic and subatomic entities can often, but not always, be ignored in chemical and biological systems. We will touch on these topics as necessary.

Current theory holds that each atom contains a very, very small, but very dense nucleus, which contains protons and neutrons and is surrounded by electrons. These electrons are very light, relatively, but the space occupied by moving electrons accounts for the vast majority of the volume of an atom. Because the number of positively charged protons and negatively charged electrons are equal and the size of the charges are the same but opposite, atoms are electrically neutral when taken as a whole; that is, each positively-charged proton is counterbalanced by a negatively-charged electron.

Often the definition of an atom contains some language about how atoms are the smallest particle identifiable as that element. What do we mean by that? For example, can an atom have chemical properties? And how can ensembles of the same particles, that is protons, electrons, and neutrons, have different properties? This is the mystery of the atom and understanding it is the foundation of chemistry. In this first chapter, we hope to lead you to a basic understanding of atomic structure and inter-atomic interactions. Subsequent chapters will extend and deepen this understanding.

Questions to Ponder

- If you had to explain to a non-scientist why it is that scientists accept the idea that all material things are composed of atoms what evidence would you use?

1.2 Atomic Realities and Scientific Theories

We assume that you have lots of ideas about atoms but did you ever stop to think how we came to accept this information as reasonable or what the reality of atoms implies about how the world we perceive behaves? Atoms are incredibly and unimaginably small. A gold atom with its full complement of electrons is less than a nanometer (1×10^{-9} meters) in diameter and its nucleus, which contains 79 protons and generally around 116 neutrons, has a radius of $\sim 1.5 \times 10^{-14}$ meters. While these sizes are actually unimaginable, there are a number of web-based activities that can help you come to terms with the scales of atoms.[3] There is no way you could see an atom with your eye or with a light microscope, although there are now techniques that allow us to view computer representations of individual atoms using various types of electron and force-probe microscopes. The smallest particle of matter that you can see with your naked eye contains more atoms than there are people in the world. Every cell in your body contains a huge number of atoms. Obviously, whatever we know about atoms is based on indirect evidence; we do not directly experience atoms.

The full story of how we know what we know about the existence and structure of atoms is fascinating, complex, and perhaps fortunately for you, too long to go into in detail. What we do want to do is to consider a number of key points that illustrate how our ideas of atoms arose and have changed over time. We will present the evidence that has made accepting the atomic theory unavoidable if you want to explain and manipulate chemical reactions and the behavior of matter.

Atomic theory is an example of a scientific theory that began as speculation and, through the constraints provided by careful observation, experimentation, and logical consistency, evolved over time into a detailed set of ideas that make accurate predictions and are able to explain an increasing number of diverse, and often previously unknown, phenomena. As scientists made new observations, atomic theory was adapted to accommodate and organize these observations.

A key feature of scientific ideas, as opposed to other types of ideas, is not whether they are right or wrong but whether they are logically coherent and make unambiguous, observable, and generally quantitative predictions. They tell us what to look for and predict what we will find if we look at or measure it. When we look, we may find the world acts as predicted or that something different occurs. If the world is different from what our scientific ideas suggest then we assume we are missing something important: either our ideas need altering or perhaps we are not looking at the world in the right way. As we will see, the types of observations and experimental evidence about matter have become increasingly accurate, complex, and often abstract, that is, not part of our immediate experience. Some of these observations can be quite difficult to understand,

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[3] Scale of the universe: http://htwins.net/scale2/

because matter behaves quite differently on the atomic and sub-atomic scale than it does in the normal, macroscopic world. It is the macroscopic world that evolutionary processes have adapted us to understand, or at least cope with, and with which we are familiar. Yet, if we are to be scientific, we have to go where the data lead us. If we obtain results that are not consistent with our intuitions and current theories, we have to revise those theories rather than ignore the data.

However, scientists tend to be conservative when it comes to revising well-established theories because new data can sometimes be misleading. This is one reason there is so much emphasis placed on reproducibility. A single report, no matter how careful it appears, can be wrong or misinterpreted and the ability of other scientists to reproduce the observation or experiment is key to its acceptance. This is why there are no miracles in science. Even so, the meaning of an observation is not always obvious or unambiguous; more often than not an observation that at first appears to be revolutionary turns out to have a simple and even boring explanation. Truly revolutionary observations are few and far between. This is one reason that the Carl Sagan (1934-1996) quote, "*Extraordinary claims require extraordinary evidence*" is so often quoted by scientists. In most cases where revolutionary data is reported, subsequent studies reveal that the results were due to poor experimental design, sloppiness, or some irrelevant factor. The fact that we do not all have cold fusion energy plants driving perpetual motion refrigerators in our homes is evidence that adopting a skeptical approach that waits for experimental confirmation is wise.

A common misconception about scientific theories is that they are simply ideas that someone came up with on the spur of the moment. In everyday use, the word theory may well mean an idea or even a guess, a hypothesis, or a working assumption, but in science the word theory is reserved for explanations that encompass and explain a broad range of observations. More than just an explanation, a theory must be well tested and make clear predictions relating to new observations or experiments. For example, the theory of evolution predicted that the fossil record would show evidence for animals that share many of the features of modern humans. This was a prediction made before any such fossils were found; many fossils of human-like organisms have since been and continue to be discovered. Based on these discoveries, and on comparative analyses of the structure of organisms, it is possible to propose plausible family trees, known as phylogenies, connecting different types of organisms. Modern molecular genetics methods, particularly genome (DNA) sequencing, have confirmed these predictions and produced strong experimental support for the current view that all organisms now living on Earth are part of the same family–that is, they share a common ancestor that lived billions of years ago. The theory of evolution also predicts that the older the rocks, the more different the fossilized organisms found will be from modern organisms. In rocks dated to ~410 million years ago, we find fossils of various types of fish but not the fish that exist today. We do not find evidence of humans from that period; there are, in fact, no mammals, no reptiles, no insects, and no birds.

A scientific theory is also said to be falsifiable, which doesn't mean that it is false but rather that it may be proven false by experimentation or observation. For example, it would be difficult to reconcile the current theory of evolution with the discovery of fossil rabbits from rocks older than 300 million years. Similarly, the atomic theory would require some serious revision if someone discovered an element that did not fit into the periodic table; the laws of thermodynamics would have to be reconsidered if someone developed a successful perpetual motion machine. A theory that can be too easily adapted to any new evidence has no real scientific value.

A second foundational premise of science is that all theories are restricted to natural phenomena; that is, phenomena that can be observed and measured, either directly or indirectly. Explanations that invoke the supernatural or the totally subjective are by definition not scientific, because there is no imaginable experiment that could be done that might provide evidence one way or another for their validity. In an important sense, it does not matter whether these supernatural explanations are true or not; they remain unscientific. Imagine an instrument that could detect the presence of angels. If such an instrument could be built, angels could be studied scientifically; their numbers and movements could be tracked and their structure and behaviors analyzed; it might even be possible to predict or control their behavior. Thus, they would cease to be supernatural and would become just another part of the natural world. Given these admitted arbitrary limitations on science as a discipline and an enterprise, it is rather surprising how well science works in explaining (and enabling us to manipulate) the world around us. At the same time, science has essentially nothing to say about the meaning of the world around us, although it is often difficult not to speculate on meaning based on current scientific ideas. Given that all theories are tentative, and may be revised or abandoned, perhaps it is wise not to use scientific ideas to decide what is good or bad, in any moral sense.

As we will see, the history of atomic theory is rife with examples of one theory being found to be inadequate, at which point it must be revised, extended, and occasionally totally replaced by a newer theory that provides testable explanations for both old and new experimental evidence. This does not mean that the original theory was necessarily completely false but rather that it was unable to fully capture the observable universe or to accurately predict newer observations. Older theories are generally subsumed as newer ones emerge; in fact, the newer theory must explain everything explained by the older one and more.

Questions to Answer: Scientific Questions and Theories:

- How would you decide whether a particular question was answerable scientifically?
- How would you decide whether an answer to a question was scientific?
- What is the difference between a scientific and a non-scientific question? Provide an example of each.

Questions to Ponder

- What things have atoms in them? Air, gold, cells, heat, light?
- How do you know atoms exist?

1.3 Some History of Atomic Theory

Modern atomic theories have their roots in the thinking of ancient peoples, in particular ancient Greek philosophers who lived over 2500 years ago. At that time the cultural, economic, and intellectual climate in Ancient Greece permitted a huge surge of philosophical and scientific development, the so-called Greek miracle. While most people of that time believed that the world was ruled by a cohort of semi-rational gods a series of philosophers, beginning with Thales of

Miletus (died 546 BCE),[4] were intent on developing rational and non-supernatural explanations for observable phenomena such as what we are made of and where we came from. As we know now, they could not possibly have understood the underlying nature of matter because they lacked the tools to observe and experiment at the atomic scale. However, this does not mean that their ideas were simple idle speculation. The ideas they produced, although not scientific as we understand the term today, contained remarkable insights - some of which appear to be true.

This era gave birth to a new way to approach and explore natural phenomena in order to gain understanding of their complexity and diversity in terms of natural explanations. It is worth considering that such a rational approach did not necessarily have to be productive; it could be that the world is really a totally irrational, erratic, and non-mechanistic place, constantly manipulated by supernatural forces; but given that science cannot address these kinds of ideas, let us just leave them to fantasy authors. The assumption that the world is ruled solely by natural forces has been remarkably productive; that is, consistent with the way the world appears to behave when we look at it dispassionately.

The ancient Greeks developed complex ideas about the nature of the universe and the matter from which it was composed, some of which were accepted for a long time. However, in response to more careful observation and experimental analysis, these ideas were eventually superseded by more evidence-based theories. In large part this involved a process by which people took old ideas seriously, and tried to explain and manipulate the world based on them. When their observations and manipulations failed to produce the expected or desired outcomes, such as turning base metals into gold, curing diseases, or evading death altogether, they were more or less forced to revise their ideas, often abandoning older ideas for newer ideas that seemed to work.

The development of atomic theories is intertwined with ideas about the fundamental nature of matter, not to mention the origin of the universe and its evolution. Most Greek philosophers thought that matter was composed of some set of basic elements, for example, the familiar earth, air, fire, and water. Some philosophers proposed the presence of a fifth element, known as quintessence or aether.[5] These clearly inadequate ideas persist today as part of astrology and the signs of the Zodiac—a poor tribute to some very serious thinkers.

The original elements, that is, earth, air, fire, and water, were thought to be composed of tiny indestructible particles, called atoms by Leucippus and Democritus (who lived around 460 BCE).[6] The atoms of different elements were assumed to be of different sizes and shapes, and their shapes directly gave rise to the properties of the particular element. For example, the atoms of earth were thought to be cubic; their close packing made earth solid and difficult to move. The idea that the structure of atoms determines the observable properties of the material is one that we will return to, in a somewhat different form, time and again. Although the particulars were not correct, the basic idea turns out to be sound.

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[4] http://www.iep.utm.edu/t/thales.htm

[5] Of course if you know your movies, you know that the “Fifth Element” is love.

[6] http://plato.stanford.edu/entries/democritus/

In addition to their shapes, atoms were also thought to be in constant motion, based on watching the movement of dust motes in sunlight, with nothing, or a void, between them.[7] Many centuries later Einstein's analysis of this type of motion, known as Brownian motion, provided strong experimental support for the physical reality of molecules, larger structures composed of atoms, and the relationship between molecular movement, temperature, and energy, which we will consider later on in this chapter.

All in all the combined notions of the Greek philosophers provided a self-consistent and satisfactory basis for an explanation of the behavior of matter, as far as they could tell. The trap here is one that is very easy to fall into, namely that a satisfying explanation for a phenomenon is not necessarily true. Even if it seems to be self-consistent, useful, or comforting, an explanation is not scientific unless it makes testable, quantitative predictions. For example, it was thought that different materials were made up of different proportions of the four ancient elements. Bones were made of water, earth, and fire in the proportions 1:1:2, whereas flesh was composed of these elements in a ratio of 2:1:1.[8] While these ideas are now considered strange, they contain a foreshadowing of the "law of multiple proportions", which would come some 2300 years later and which we will deal with later in this chapter. Some philosophers even thought that the soul was composed of atoms or that atoms themselves had a form of consciousness, two ideas that seem quite foreign to (most of) us today.

Such ideas about atoms and elements provided logical and rational, that is, non-supernatural explanations for many of the properties of matter. But the Greeks were not the only ancient people to come up with explanations for the nature of matter and its behavior. In fact, it is thought that the root of the words alchemy and chemistry is the ancient Greek word Khem, the Greek name for Egypt, where alchemy and chemistry are thought to have originated.[9] Similar theories were being developed in India at about the same time, although it is the Greek ideas about atoms that were preserved and used by the people who eventually developed our modern atomic theories. With the passage of time ancient ideas about atoms and matter were kept alive by historians and chroniclers, in particular scholars in the Arab world. During the European Dark Ages and into medieval times, there were a few scattered revivals of ideas about atoms, but it was not until the Renaissance that the cultural and intellectual climate once again allowed the relatively free flowering of ideas. This included speculation on the nature of matter, atoms, and life. Experimental studies based on these ideas led to their revision and the eventual appearance of science, as we now know it. It is also worth remembering that this relative explosion of new ideas was occasionally and sometimes vigorously opposed by religious institutions, leading to torture, confinement, and executions.[10]

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[7] First description of Brownian motion - Epicurus

[8] *A History of Greek Philosophy by William Keith Chambers Guthrie. p. 212.*

[9] http://www.chm.bris.ac.uk/webprojects2002/crabb/history.html and http://en.wikipedia.org/wiki/Chemistry_(etymology)

[10] An important event was the rediscovery by Poggio of Lucretius's "On the Nature of Things," a poem centered on the atomic nature of the universe (see The Swerve by Stephen Greenblatt). One reason Giordano Bruno was burnt at the stake was the fact that he took these ideas seriously.

Questions to Answer

- What properties ascribed by the Greeks to atoms do we still consider to be valid?

Questions to Ponder

- If earth had atoms that were cubic, what shape would you ascribe to the elements air, water, and fire?

Questions for Later

- If atoms are in constant motion, what do you think keeps them moving?

1.4 Identifying and Isolating Elements

The Greek notion of atoms and elements survived for many centuries and it was eventually fleshed out with the addition of a few more elements, mostly through the efforts of the alchemists. Some elements such as gold were discovered much earlier - mainly because they exist as elements rather than compounds. By the late eighteenth century, the idea of an element as a substance that cannot be broken down into more fundamental substances had begun to be accepted. In 1789 Antoine Lavoisier (1743–1794) produced a list of 33 elements. His list did not include earth, air, fire, and water, but it did contain light and heat, along with a number of modern elements including cobalt, mercury, zinc, and copper. It had already been established that oxygen and hydrogen were elements, while water was not. The stage was set for a rapid growth in our knowledge about the underlying structure of matter. We now know of 91 naturally occurring elements, and quite a number of unnatural, that is, human-made ones which are not found in nature because they unstable. These human-made elements are heavier in atomic terms than the naturally occurring elements and are typically generated by smashing atoms of natural elements into one another; they break down, or decay, rapidly into atoms of other elements. As examples of how science can remove some of the mystery from the universe: our understanding of atoms and elements means that no new natural, light elements are theoretically possible. We know of all the light elements that can possibly exist anywhere in the universe, a pretty amazing fact. Similarly, our current understanding of the theory of general relativity and the laws of thermodynamics make faster-than-light travel and perpetual motion machines impossible, although it does not stop people from speculating about them.

The first modern chemical isolation of an element is attributed to the alchemist Hennig Brand (c. 1630–c. 1710).[11] He isolated phosphorus from urine while in pursuit of the philosopher's stone.[12] While this may seem like an odd thing to do, people have done much stranger things in pursuit of gold or cures for diseases like syphilis. Imagine his surprise when, after boiling off all the water from the urine, the residue burst into flames and gave off a gas that, when condensed, produced a solid that glowed green in the dark. It was for this reason that he named it phosphorus, from the Greek for light-bearer. Similarly, mercury was originally isolated by roasting the mineral cinnabar. Despite

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[11] http://elements.vanderkrogt.net/elem/p.html

[12] The Philosopher's stone was thought to be able to turn base (common) metals into gold, and perhaps even be the key to everlasting life. It was the ultimate goal of the alchemists. Interestingly the first Harry Potter book was titled Harry Potter and the Philosopher's Stone in England but was re-titled in America, because the publishers thought that American children would not be interested in a book with this title, perhaps due a failure to appreciate the importance of philosophy.

being quite toxic, mercury was used as a treatment for syphilis prior to the discovery of effective antibiotics.

Questions to Answer

- Given what you know, how would you explain the difference between an atom and an element?
- What differentiates one element from another?
- What is the difference between an atom and a molecule?
- What is the difference between an element and a compound?

Questions to Ponder

- What types of evidence might be used to prove you had isolated a new element?
- When can unproven/unsubstantiated assumptions be scientific?
- Under what conditions are such assumptions useful?
- Why do you think gold was recognized as an element earlier than many others?

1.5 Evidence for Atoms

It is important to note that from the time that the first ideas of atoms arose, and for thousands of years thereafter, there was not one shred of evidence for the particulate nature of matter or the physical existence of atoms. The idea of atoms was purely a product of imagination, and while there was vigorous debate about the nature of matter, this debate could not be settled scientifically until there was objective empirical evidence one way or another.

So the question arises, how did scientists in the nineteenth century eventually produce clear evidence for the existence of atoms? We have already said atoms are much too small to be seen by any direct method. So what would lead scientists to the unavoidable conclusion that matter is composed of discrete atoms? It is often the case that a huge intuitive leap must be made to explain the results of scientific observations. For example, the story about Isaac Newton (1643–1727) and the falling apple captures this truism, namely the remarkable assumption that the movement of Earth around the Sun, the trajectory of a cannon ball, and the falling of an apple to Earth are all due to a common underlying factor, the force of gravity, which acts at a distance and obeys an inverse square relationship, $1/r^2$ where r is the distance between two objects. This seems like a pretty weird and rather over-blown speculation; how does this "action at a distance" between two objects work? Yet, followed scientifically, it appeared to be very powerful and remarkably accurate. The point is that Newton was able to make sense of the data, something that is in no way trivial. It requires a capacity for deep, original, and complex thought. That said, it was not until Albert Einstein (1874-1955) proposed his general theory of relativity in 1915 that there was a coherent, mechanistic explanation for gravitational forces.

The first scientific theory of atomic structure was proposed by John Dalton (1766–1844), a self-taught Quaker[13] living in Manchester, England.[14] In 1805 Dalton published his atomic theory to explain the observed law of multiple, or definite, proportions, which stated briefly is "when elements combine, they do so in the ratio of small whole numbers", we will return to this idea later on, in much greater detail[15]. Rather surprisingly, Dalton never really explained what led him to propose his atomic theory, although he certainly used it to explain existing rules about how different elements combine. Among these rules was the observation that the total matter present in a system does not change during a chemical reaction, although a reaction might lead to a change from a solid to a gas or vice versa. Dalton's atomic theory (1805) had a number of important components:

- Elements are composed of small indivisible, indestructible particles called atoms.
- All atoms of an element are identical and have the same mass and properties.
- Atoms of a given element are different from atoms of other elements.
- Compounds are formed by combinations of atoms of two or more elements.
- Chemical reactions are due to the rearrangements of atoms, and atoms (matter) are neither created nor destroyed during a reaction.

Based on these tenets he was able to explain many of the observations that had been made, by himself and others, about how matter behaves and reacts. More modern atomic theories have made some modifications, for example to include the existence of atomic isotopes, that is, atoms with different numbers of neutrons, but the same number of protons and electrons, and the conversion of energy into matter and vice versa, but Dalton's core ideas remain valid.

Questions to Answer

- In what ways is Dalton's atomic theory different from the ideas of the Greek philosophers?
- Which tenets of Dalton's theory still hold up today?
- Design an experiment to investigate whether there is a change in mass when water changes phase. What data would you collect? How would you analyze it?

Questions to Ponder

- How did Dalton conclude that there were no half-atoms?
- Which parts of Dalton's theory were unfounded speculation and which parts were based on direct observation?

1.6 The Divisible Atom

> *The opposite of a correct statement is a false statement. But the opposite of a profound truth may well be another profound truth.* NEILS BOHR (1865–1962)

Dalton's theory of atoms as indivisible, indestructible, objects of different sizes, weights, and perhaps shapes, depending on the element, held up for almost 100 years, although there was considerable dissent about whether atoms really existed, particularly among philosophers. By 1900

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[13] Religious dissenters, that is, non-Anglicans, were not allowed access to English universities at that time.

[14] An extraordinary number of discoveries related to the structure of the atom were made by scientists in or from Manchester. There must be something in the air there. It is, of course, completely fortuitous that one of the authors was also born and bred in Manchester!

[15] http://groups.molbiosci.northwestern.edu/holmgren/Glossary/Definitions/Def-L/law_multiple_proportions.html

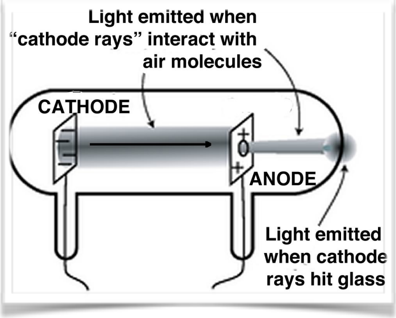
the atomic theory was almost universally accepted by chemists. More evidence began to accumulate, more elements were discovered, and it even became possible to calculate the number of atoms in a particular sample. The first step, along this direction, was made by Amedeo Avogadro (1776–1856). In 1811 he proposed that, under conditions of equal temperature and pressure, equal volumes of gases contained equal numbers of particles (molecules) and that the densities of the gases, that is their weight divided by their volume, were proportional to the weight of the individual molecules. This was expanded on by the Austrian high school teacher Josef Loschmidt (1821–1895) who, in 1865, combined Avogadro's conclusion with the assumption that atoms and molecules move very much as elastic objects, think billiard balls. This enabled him to calculate the force a molecule would exert when traveling at a particular speed, something difficult to measure, and relate that to the pressure, something easily measured. In fact, this assumption enabled physicists to deduce that the temperature of a gas is related to the average kinetic energy of the molecules within it, a concept we will return to shortly.

Probing the Substructure of Atoms

The initial Greek assumption was that atoms were indivisible, essentially unchangeable from their initial creation. However, gradually evidence began to accumulate that atoms were neither indivisible nor indestructible. Evidence for the existence of particles smaller than atoms had been building up for some time, although it was not recognized as such. For example, the well-recognized phenomenon of static electricity had been known since the ancient Greeks. The name electricity comes from the Latin electricus, meaning amber-like. Rubbing amber with fur generates static electricity—the same type of spark that jumps from your finger to a doorknob or another person under dry conditions. In the late 1700s Luigi Galvani (1737–1798) discovered that animals can produce and respond to electricity, perhaps the most dramatic example being the electric eels and rays that stun their prey through electrical shocks. The discovery of bioelectricity was exploited in many novels and movies, beginning with Mary Shelly's (1797–1851) novel Frankenstein and continuing through Mel Brook's (b. 1926) comedy film, Young Frankenstein. Galvani discovered that a dead frog’s leg would twitch in response to exposure to static electricity; it appeared to come back to life, just like Frankenstein’s monster. He assumed, correctly it turns out, that electrical activity was involved in the normal movement of animals. He thought that a specific form of electricity, bioelectricity, was carried in the fluid within the muscles and was a unique product of biological systems, a type of life-specific force. We now recognize that a number of biological phenomena, such as muscle contraction and brain activity, are initiated by changes in electric fields (across membranes) and that the underlying physicochemical principles are similar to those taking place in non-biological systems.

The excitement about electricity and its possible uses prompted Alessandro Volta (1745–1827) to develop the first modern battery, now known as a voltaic pile. He alternated sheets of two different metals, such as zinc and copper, with discs soaked in salt water (brine). It produced the first steady electrical current that, when applied to frog muscles, caused them to contract. Such observations indicated that biological systems can both generate and respond to electrical currents, suggesting that bioelectricity was no different than any other form of electricity. What neither Volta nor Galvani knew was the nature of electricity. What was it, exactly, and how did it flow from place to place? What was in the spark that jumped from finger to metal doorknob, or from Benjamin Franklin's (1705–1790) kite string to his finger? What was this “electrical fluid” made of?

Progress in the understanding of the nature and behavior of electricity continued throughout the 19th century and the power of electricity was harnessed to produce dramatic changes in the way people lived and worked, powering factories, lighting houses and streets, and so on. Yet there was no deep of understanding as to the physical nature of electricity. It was known that electric charge came in two forms, positive and negative, and that these charges were conserved; that is, they could not be created or destroyed, ideas first proposed by Franklin. The electrical (charged) nature of matter was well established, but not where those charges came from or what they were.



A key step to understanding electricity involved unraveling the idea of the indivisible atom and involved a series of experiments by J. J. Thompson (1856–1940), another Mancunian[16] Although the idea of electricity was now well appreciated, Thompson and other scientists wanted to study it in a more controlled manner. They used what were, and are now, known as cathode ray tubes (CRTs). Once common in televisions, these have now been replaced by various flat screen devices. CRTs are glass tubes with wires embedded in them; these wires are connected to metal discs. The inside of the tube is coated with a chemical that glows (fluoresces) in response to electricity. They generally have ports in the walls that can be connected to a vacuum pump, so that most of the air within the tube can be removed, typically the ports are then sealed. When connected to a source of electricity, such as a voltaic pile, the fluorescent material at one end of the tube glows. In a series of experiments (1897) Thompson was able to show that:

- Rays emerged from one disc (the cathode) and moved to the other (the anode).
- “Cathode” rays were deflected by electrical fields in a direction that indicated that they were negatively charged.
- The rays could also be deflected by magnetic fields.[17]
- The rays carried the electrical charge; that is, if the ray was bent, for example by a magnetic field, the charge went with it.
- The metal that the cathode was made of did not affect the behavior of the ray; so whatever the composition of the ray, it appeared to be independent of the element that it came from.

In all of these experiments, it needs to be stressed that "positive" and "negative" are meant to indicate opposite and are assigned by convention. That means that we could decide tomorrow that positive was negative, and negative positive, and nothing would change, as long as we were

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[16] That is, a person from Manchester, England.
[17] This works because the electrons are spinning.

consistent. From these experiments, Thompson concluded that “cathode” rays were carried by discrete charged particles, he called them corpuscles, and he assigned these particles a negative charge. But the truly stunning conclusion he reached was that *these particles must come from within the atoms of the metal cathode*. Because the type of metal did not affect the nature or behavior of the cathode rays, he assumed that these particles were not newly created but must pre-exist within the atoms of the cathode. Moreover, he hypothesized that identical particles must be present in all atoms, not just in the atoms of one particular metal. Do you see how he jumps from experimental results using a few metals to all elements and all atoms? Of course, we now know these particles as electrons but it is difficult to imagine what a huge impact this new theory had on scientists at the time.

Since electrons can be produced by all chemical elements, we must conclude that they enter the constitution of all atoms. We have thus taken our first step in understanding the structure of the atom. —J. J. Thompson, The Atomic Theory, 1914[18]

The discovery of the electron made the old idea of an atom as a little indestructible billiard ball-like objects obsolete, and necessitated a new model. It is an example of a paradigm shift[19]—a fundamental change in scientific thinking driven by new evidence. Thompson’s first version of this new model became known as the plum pudding model.[20] His basic idea was that the atom is a ball of positively charged, but apparently amorphous, matter with electrons studded here and there, like the raisins in a pudding. Because it contained equal numbers of positive and negative charges, the overall structure was electrically neutral. Subsequent work by Thompson and Robert A. Millikan (1868–1953) established that all electrons are identical, each with the same, very small mass and negative charge. The mass of an electron is less than 1/1000th of the mass of a hydrogen atom.

Thompson's proposed plum pudding model of the atom spurred much experimental and theoretical work and led to a remarkable number of subsequent discoveries. For example, it was soon recognized that the β particles emitted by some radioactive minerals and elements, were, in fact, electrons. Other studies found that the number of electrons present in the atoms of a particular element was roughly proportional to half the element's atomic weight, although why this should be the case was unclear.

However, as more and more data began to accumulate, the plum pudding model had to be abandoned because it just could not explain what was being observed. The key experiment that led to a new model of the atom was carried out in 1908 by Ernest Rutherford (1871–1937). As you may have already guessed, he was working at the University of Manchester. In this experiment, he examined how alpha (α) particles, which he knew to be positively charged particles made of the element helium without its electrons, behaved when they were fired at a very thin sheet of metal,

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[18] http://www.aip.org/history/electron/jjsound.htm

[19] A term made popular (although often misunderstood) by T. S. Kuhn, The Structure of Scientific Revolutions, 1st. ed., Chicago: Univ. of Chicago Pr., 1962

[20] This can be a little confusing to those not familiar with plum pudding – a “delicious” English delicacy composed of dried fruit (raisins) in a spongy base, usually prepared by boiling for several days and often served with rum sauce.

such as gold or platinum. In the experiment a narrow parallel beam of α particles was directed at a thin sheet of gold foil and the angles at which the deflected particles scattered were detected. The observed result was completely unexpected. Instead of passing straight through the thin sheet of foil, he found that a few particles were deflected, some of them at large angles. Rutherford wrote, “It is as if I had fired a cannon ball at a piece of tissue paper, and it bounced right back.” Here again, we see a particular aspect of the scientific enterprise, namely that even though only a few alpha particles bounced back, we still need to explain how this could possibly occur. We could not just say, "Only a few particles were bounced so it doesn't matter"; we have to provide a plausible scenario to explain the observation. Often it is paying attention to, and taking seriously, the unexpected result that leads to the most profound discoveries.

Based on these experimental results Rutherford reasoned that the positively charged α particles were being repelled by positive parts of the atom. Because only a very small percentage of alpha particles were deflected, only a very small region of each atom could be positively charged. That is, the positive charge in an atom could not be spread out more or less uniformly, as the plum pudding model assumed; instead it must be concentrated in a very small region. This implied that most of the atom is empty (remember the void of the ancient Greeks?) or occupied by something that poses little or no resistance to the passage of the α particles. What it left unexplained was why positively charged particles (which we now know as protons) concentrated in such a small volume, did not repel one another – the answer to which had to wait to discovery of the strong nuclear force (see below). Again we see a scientist making a huge intuitive leap from the experimental observation to a hypothesis that was consistent with that evidence and that makes specific predictions that can be confirmed or falsified by further experiment and observation. Rutherford's model, which became known as the planetary model, postulated a very, very small nucleus where all of the positive charge and nearly all of the mass of the atom was located; this nucleus was encircled by electrons. In 1920 Rutherford went on to identify the unit of positive charge and called it the proton. In 1932 James Chadwick (1891–1974) (who co-incidentally studied at the University of Manchester) identified a second component of the nucleus, the neutron. Neutrons are heavy, like protons. In fact they are slightly heavier than protons, but have no charge. The identity of the element depends on the number of protons, however the number of neutrons may be different in different atoms of the same element. For example an atom of carbon always has six protons, but it can have different numbers of neutrons. Most carbon atoms have six neutrons (C-12), but some have seven (C-13) and some have eight (C-14).

Questions for Later

- If atoms are mostly empty space, why can’t we walk through walls?
- What is radiation?
  How does an atom change when it emits an alpha particle? Or a beta particle/electron?

Questions to Ponder

- If the original discoverers of electricity had decided that electrons have a positive charge, would that have made a difference in our understanding of electricity?
- Why do you think electrons were the first sub-atomic particles to be discovered?
- How exactly did Rutherford detect alpha particles?
- Can you think of an alternative model of the atom based on Rutherford's observations?

- How would the experiment change if he had used electrons or neutrons?

1.7 Interactions Between Atoms and Molecules

At this point we have arrived at a relatively simple model of the atom. Do not to worry, we will move to more complex and realistic models in the next chapter. In this simple model the atom has a very small but heavy nucleus that contains both protons and neutrons. As we talk about biology now and again, take care not to confuse the nucleus of an atom with the nucleus of a cell; they are completely different - besides the fact that they are of very different sizes. For example, there is no barrier round the nucleus of an atom—an atomic nucleus is a clump of protons and neutrons. Surrounding the atomic nucleus are electrons, in the same number as there are protons. The atom has no net electrical charge since the number of electrons is equal to the number of protons.

Where the electrons actually are in an atom, however, is a trickier question to answer, because of quantum mechanical considerations, specifically the Heisenberg uncertainty principle, which we will return to in the next chapter. For now we are going to assume the electrons are outside the nucleus and moving. We can think of them as if they were a cloud of electron density rather than particles whizzing around (don’t worry we will provide evidence for this model soon). This simple model captures important features and enables us to begin to consider how atoms interact with one another to form molecules and how those molecules can be rearranged—real chemistry!

There are four fundamental forces that we know about at the moment: gravity, the electromagnetic force, the strong nuclear force, and the weak nuclear force. For now we can largely ignore the strong nuclear force that is involved in holding the nucleus together. It is an attractive force between neutrons and protons and is the strongest of all known forces in the universe, ~137 times stronger than the electromagnetic force. The strong nuclear force, acts at very short ranges, ~10^{-15} m, or about the diameter of the nucleus. The other force involved in nuclear behavior, the weak force, plays a role in nuclear stability, specifically the stability of neutrons, but it has an even shorter range of action (10^{-18} m). Because the nucleus is much smaller than the atom itself we can (and will) ignore the weak and strong nuclear forces when we consider chemical interactions. The force we are probably most familiar with is gravity, which is the weakest force, more than 10^{-37} times weaker than the electromagnetic force, and we can ignore it from the perspective of chemistry, although it does have relevance for the biology of dinosaurs, elephants, whales, and astronauts. The electromagnetic force is responsible for almost all the phenomena that we encounter in our everyday lives. While we remain grounded on the Earth because of the gravitational interaction between our body and the Earth, the fact that we don't fall through to the center of the earth is entirely due to electromagnetic interactions. One obvious feature of the world that we experience is that it is full of solid things—things that get in each other's way. If atoms and molecules did not interact with one another, one might expect to be able to walk through walls, given that atoms are mostly empty space, but clearly this is not the case. Similarly, your own body would not hold together if your atoms, and the molecules they form, failed to interact. As we will see, all atoms and molecules attract one another—a fact that follows directly from what we know about the structure of atoms and molecules.

Questions to Ponder

- What would a modern diagram of an atom look like and what could it be used to explain?
- Why don't the protons within a nucleus repel one another?
- Why don't the electrons and protons attract each other and end up in the nucleus?
- How the electrons within an atom interact?

Questions for Later

- Can an atom have chemical and/or physical properties; if so, what are they?
- What are chemical and physical properties? Can you give some examples?
- What distinguishes one element from another?

Interactions Between Atoms: A Range of Effects

The attractions and repulsions between charged particles and magnets are both manifestations of the electromagnetic force. Our model of the interactions between atoms will involve only electric forces; that is, interactions between electrically charged particles, electrons and protons. In order to understand this we need to recall from physics that when charged particles come close to each other they interact. You probably recall that "like charges repel and unlike charges attract", and that this interaction, which is known as a Coulombic interaction, depends on the sizes and signs of the charges, and is inversely proportional to the square of the distance between them (this interaction can be modeled by the equation:

$$F \propto (q_1 \times q_2) / r^2 \text{ (Coulomb's Law)},$$

where q_1 and q_2 are the charges on the particles and r is the distance between them. That is: there is a force of attraction (or repulsion if the two charges are of the same sign) that operates between any two charged particles. This mathematical description of the electromagnetic interaction is similar to the interaction due to gravity. That is, for a gravitational interaction there must be at least two particles (e.g. you and the Earth) and the force of the attraction depends on both masses, and is inversely proportional to the square of the distance between them:

$$F \propto (m_1 \times m_2) / r^2.$$

The difference between the two forces are: a) gravitational interactions are much weaker than electromagnetic interactions and b) gravity is solely an attractive interaction while electromagnetic interactions can be either attractive or repulsive.

Now, let us consider how atoms interact with one another. Taken as a whole, atoms are electrically neutral, but they are composed of discrete electrically charged particles. Moreover, their electrons behave as moving objects.[21] When averaged over time the probability of finding an

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[21] Yes we did tell you to think of electrons as a cloud - because this is a helpful model - but electrons are both particles and "clouds" as we will discuss later, in fact in some instances they appear to be quite close to perfect spheres in shape, In fact "The experiment, which spanned more than a decade, suggests that the electron differs from being

electron is spread uniformly around an atom, the atom is neutral. At any one instant, however, there is a non-zero probability that the electrons are more on one side of the atom than the other. This results in momentary fluctuations in the charge density around the atom and leads to a momentary charge build up; for an instant one side of the atom is slightly positive (δ^+) and the other side is slightly negative (δ^-). This produces what is known as an instantaneous and transient electrical dipole - that is a charge separation. As one distorted atom nears another atom it affects the second atom's electron density distribution and leads to what is known as an "induced dipole". So, for example, if the slightly positive end of the atom is located next to another atom, it will attract the electron(s) in the other atom. This results in an overall attraction between the atoms that varies as $1/r^6$ – where r is the distance between the atoms. Note that this is different than the attraction between fully charged species, the Coulombic attraction, which varies as $1/r^2$. What does that mean in practical terms? Well, most importantly it means that the effects of the interaction will be felt only when the two atoms are quite close to one another.

As two atoms approach, they will be increasingly attracted to one another. But this attraction has its limit - when the atoms get close enough, the interactions between the negatively charged electrons (and positively charged nuclei) of each atom increase very rapidly, which leads to an overall repulsion, which will stop the two atoms approaching so closely.

A similar effect was in also seen in Rutherford's experiment. Recall that he accelerated positively charged alpha particles toward a sheet of gold atoms. As an alpha particle approaches a gold atom's nucleus, the positively (+2) charged alpha particle and the gold atom's positively (+79) nucleus begin to repel each other. If no other factors were involved, the repulsive force would approach infinity as the distance between the nuclei (r) approached 0. (You should be able to explain why.) But infinite forces are not something that happens in the macroscopic, atomic, or subatomic worlds, if only because the total energy in the universe is not infinite. As the distance between the alpha particle and gold nucleus approaches zero, the repulsive interaction grows strong enough to slow the incoming alpha particle and then push it away from the target particle. If the target particle is heavy compared to the incoming particle, as it was in Rutherford's experiments, the target, composed of gold atoms that weigh about 50 times as much as the alpha particle, will not move much while the incoming alpha particle will be reflected away. But, if the target and incoming particle are of similar mass, then both will be affected by the interaction and both will move. Interestingly, if the incoming particle had enough initial energy to get close enough (within $\sim 10^{-15}$ m) to the target nucleus, then the strong nuclear force of attraction would come into play and start to stabilize the system. The result would be the fusion of the two nuclei and the creation of a different element, a process that occurs only in very high-energy systems such as the center of stars or during a stellar explosion, a supernova. We return to this idea in Chapter 3.

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perfectly round by less than 0.000000000000000000000000001 cm. This means that if the electron was magnified to the size of the solar system, it would still appear spherical to within the width of a human hair. (Hudson et al "Improved measurement of the shape of the electron" DOI: 10.1038/nature10104).

Questions to Answer

- How does the discovery that atoms have parts alter Dalton's atomic theory?
- What would the distribution of alpha particles, relative to the incident beam, look like if the positive nucleus took up the whole atom (sort of like the plum pudding)? What if it took up 50% of the atom?
- What does the distribution of alpha particles actually look like (recall that 1 in every 8000 particles were deflected)?

Forces and Energy: an overview.

We would like to take some time to help you think about the interactions (forces) between atoms and molecules, and how these interactions lead to energy changes. These energy changes are responsible for the formation of molecules, their reorganization through chemical reactions, and the macroscopic properties of chemical substances (i.e. everything). While you may have learned about forces and energy in your physics classes, most likely these concepts were not explicitly related to how things behave at the atomic-molecular level. We are going to begin with a discussion of the interactions and energy changes that result from the force of gravity, because these ideas are almost certainly something you are familiar with, certainly more familiar with than electromagnetic interactions – but the purpose of this section is to help you make the connections between what you already know (at the macroscopic level), and how these ideas are transferred to the molecular level, including similarities and differences. For example, Newton's Laws of Motion describe how objects behave when they come into contact, say when a baseball comes in contact with a bat. But often objects interact with one another at a distance. After the ball is hit, its movements are determined primarily by its gravitational interactions with all other objects in the Universe, although because of the nature of the gravitational interaction, by far the most important interaction is between the ball and the Earth (see below).

A force is an interaction between objects that causes a pull (attraction) or a push (repulsion) between those objects. When such an interaction occurs, there is a change in energy of the objects. As noted above, there are four fundamental forces: gravitational, electromagnetic, the strong and the weak nuclear forces. We will have more to say about the electromagnetic force that is relevant for understanding chemical interactions, that is how atoms and molecules behave. Many of the phenomena you are familiar with are based on electromagnetic forces. For example, electromagnetic forces stop the ball from going through the bat – or you from falling down to the center of the Earth.

Now let us consider what happens when you throw a ball straight up into the air. You apply a force to the ball (through the action of your muscles), and once it leaves your hand the only force acting on the ball is gravity (we are, of course, ignoring friction due to interactions with the molecules in the air). The ball, initially at rest, starts moving upward. Over time, you observe the velocity of the ball changes, as the ball slows, stops and falls back to earth. So what forces cause these changes? The answer is the force of gravity, which is a function of the masses of the ball and the Earth, which do not change over time, and the distance (r) between the Earth and the ball, which does. This gravitational force F, can be modeled by an equation that shows it is proportional to the product of the masses of the ball (M_1) and the Earth (M_2) divided by the square of the distance between the objects (r).[22]

In gravitational interactions, the force decreases as the distance between the objects increases (the decrease is proportional to $1/r^2$), which means the further away you get from the Earth the smaller is the attractive force between you and the Earth. If you get far enough away, and you are moving away from the Earth, the interaction will not be enough to keep you attracted to the Earth and you will continue to move away forever.

Of course, **why** objects with mass attract each other is a subject for physics – beyond the scope of this course.[23] What we can say is that the force is mediated by a gravitational field. Any object with mass will interact with other objects with mass through this field. The field can also be said to transfer energy through space between two (or more) objects. That is, the interaction leads to an energy change in the system of interacting objects. In chemistry we are concerned with both the forces that cause interactions and the energy changes that result.

How do forces influence energy? If we take our macroscopic example of your throwing a ball upwards, we know that you transfer some energy to the ball. Of course this begs the question "what do we mean by energy?" and unfortunately we do not have an easy answer, in fact Richard Feynman once famously said "in physics we have no idea of what energy is". Physicists might say energy is the capacity to do work, and then define work as force times distance, which does not really get us anywhere, especially in chemistry where the notion of work is often not helpful. What we can say is that any changes are accompanied by energy changes, and that we can calculate or measure these energy changes.[24]

You may be familiar with what are often referred to as "forms of energy", such as mechanical, or elastic, or chemical, but at the most basic level all forms of energy we will be concerned with can be described either as kinetic energy, potential energy, or electromagnetic energy (e.g. light). Kinetic energy is often called the energy of motion ($KE = {}^1/_2\, mv^2$, where m is the mass and v the velocity of the object), and potential energy the energy of position, or stored energy (it is calculated in various ways as we will see). Changes between kinetic and potential forms of energy involve forces. The ball that you throw straight up and then comes down has changing amounts of kinetic energy (it changes as the velocity of the ball changes) and potential energy (which changes as the distance between the Earth and the ball changes.) As the ball rises, you can observe that the velocity of the ball decreases, and therefore the KE decreases. At the same time the PE increases since the distance between the Earth and ball is increasing. On the way down the opposite is true, the ball starts moving faster – the KE increases and the PE decreases. Recall the

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[22] See http://www.youtube.com/watch?v=p_o4aY7xkXg for an excellent explanation of this phenomenon.

[23] That said, we recommend the description given in Einstein and Infeld's Evolution of Physics: https://archive.org/details/evolutionofphysi033254mbp

[24] The trouble with chemical energy: why understanding bond energies requires an interdisciplinary systems approach. CBE Life Sci. Education,**12**:306-12.

principle of the conservation of energy; after the ball leaves your hand, no energy is added or taken away as the ball is traveling, if one form of energy increases, the other must decrease.

Another important point about energy is that it is a property of a system, rather than of an object. Although it may be tempting to consider that a ball in motion has a certain amount of kinetic energy it is important to remember the frame of reference from which you are considering the ball. Certainly the ball's velocity is related to the KE, but that velocity depends upon where you are viewing the ball from. Usually (almost always) we consider the velocity from the point of view of an observer who is stationary, but if we changed the system we were considering, and viewed the ball while we were also moving, then the velocity of the ball would be different. This may seem quite an abstract point, but it is an important one.

Similarly it is quite tempting to say that the ball has potential energy, but in fact this is also not entirely accurate. It is more accurate – and more useful – to say that the **system of the ball and the Earth** has potential energy – again we are taking a systems perspective here. Unlike kinetic energy, the potential energy in a system also depends on the force that is acting on it, and that force is a function of the position of the objects that are interacting within the gravitational field. For example, a "frictionless" object traveling through a space free of fields (gravitational or otherwise) at a constant velocity has a constant kinetic energy, but no potential energy.

Potential energy (often called stored energy) or the energy of position, raises the question – where is the energy "stored"? A useful way to think about this is that for the example of the ball and the Earth, this energy is stored in the gravitational field. In this way we can accommodate the idea that the PE depends on the distance between the two interacting objects. It will also allow us to generate a more overarching concept of potential energy that will be useful in chemistry, as we extend these ideas to interactions of atoms and molecules. You might ask why then is it OK to say an object has kinetic energy (as long as you specify the frame of reference), and the difference here is that any object in motion can have energy associated with it (for example, you, an atom or a car), but potential energy must be associated with objects that are interacting via a field, be it gravitational or electromagnetic. That said, fields are everywhere – there is no place in the universe where there are no fields (although they can be balanced, leaving the net force zero). What is important here is that i) you understand that objects interact, ii) that these interactions cause a change in energy of the system, and iii) that the interacting forces depend on the distance between the interacting objects (as well as other factors, such as mass, which are constant).

The electromagnetic force: While gravitational interactions are, for all intents and purposes, irrelevant in chemistry (except to hold the beaker down on the lab bench!) they do provide a familiar example of the relationship between the kinetic and potential energies of a system that we can use to explore the electromagnetic interactions that are responsible for the behavior of atoms and molecules. There are some important similarities between gravitational and electromagnetic interactions; both act at a distance, both are mediated by fields, and both display the same relationship between force and distance. There are also important differences. In the context of chemistry, electromagnetic interactions are much stronger and while gravity is always attractive, electromagnetic interactions can be either attractive or repulsive[25].

All electrically charged objects interact via electromagnetic forces. As we have already seen (and will to return to again) atoms and molecules are made up of charged particles (electrons and protons) and these produce unequal charge distributions that lead to the same kinds of interactions. The strength of these interactions between charged particles can be modeled using an equation, Coulomb's Law. You will note that its form is similar to Newton's Law of Gravitation. Instead of the masses of the two interacting objects, however, the electromagnetic force depends on the charges on the two particles (q_1 and q_2). The electromagnetic force typically acts over much shorter distances than gravitation, but is much stronger. It is the force that affects interactions of atoms and molecules.

As with the gravitational force as the charged particles get closer together, the interaction (whether attractive or repulsive) gets stronger. Just like gravity, the interaction between charged particles is mediated by a field, which transfers energy between interacting objects. We can identify (and calculate) the types of energy changes that are occurring as the particles interact. For example two oppositely charged particles are attracted to each other. As they approach one another, the force of attraction becomes stronger, the particles will move faster – and their kinetic energies increase. Given the fact that energy is conserved, the potential energy of the system of particles must decrease to a similar extent.[26] If, on the other hand the two charges are of the same sign, then the force between them is repulsive. So if two particles of the same charge are moving toward each other, this repulsive force will decrease their velocity (and kinetic energy), and increase their potential energy. As the distance between the particles decreases, the repulsion will eventually lead to the two particles moving away from one another.

Of course you may have noticed that there is a little problem with the equations that describe both gravitation and electromagnetic forces. If the forces change as r decreases, what happens as the distance between the interacting objects approaches zero? If we were to rely on the equations we have used so far, as r approaches 0, the force (whether repulsive or attractive) would approach infinity. Clearly something is wrong here since infinite forces are not possible (do you know why?). The ball is stopped by the surface of the Earth - it does not plummet to the center of the Earth, and charged particles do not merge into each other (or fly away at infinite speed). What is it that we are missing? Well, the problem lies in the idea that these equations are really dealing with idealized situations such as point charges or masses, rather than taking into account the fact that matter is made up of atoms, molecules and ions. When two atoms, or two molecules (or two particles made up of atoms or molecules) approach each other, they will eventually get close enough that the repulsions between like charges will become stronger than the attractive forces between unlike charges. As we will see, when two macroscopic objects appear to touch, they do not really – what

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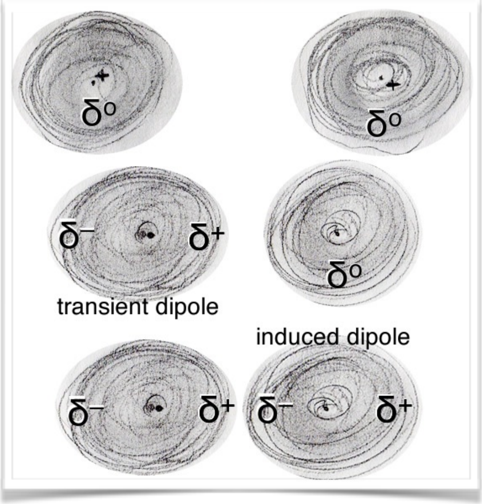
[25] Magnetic, like electrical force can also be attractive or repulsive. Most of us have played with magnets and felt the force of attraction between a north and south pole of a set of magnets, which gets stronger as the magnets get closer together, and the repulsion between two north poles which also gets stronger as the magnets get closer together.

[26] A point we have not considered is why the atoms or molecules stop moving toward each other, which will return to shortly.

stops them is the electron-electron repulsions of the atoms on the surface of the objects http://www.youtube.com/watch?v=BksyMWSygnc. We will revisit all these ideas as we discuss how atoms and molecules interact at the atomic-molecular level, and how electrons behave (quantum mechanically).

Interacting Atoms: Forces, Energy Conservation and Conversion



Let us step back, collect our thoughts, and reflect on the physics of the situation. First, remember that the total matter and energy of an isolated system are conserved; that is the first law of thermodynamics. As we mentioned above, while energy and matter can, under special circumstances, be interconverted, typically they remain distinct. That means in most systems the total amount of matter is conserved and the total amount of energy is conserved, and that these are separate.

So let us consider the situation of atoms or molecules in a gas. These atoms and molecules are moving randomly in a container, colliding with one another and the container's walls. We can think of the atoms/molecules as a population. Population thinking is useful for a number of phenomena, ranging from radioactive decay to biological evolution. For the population of atoms/molecules as a whole, there is an average speed and this average speed is a function of the temperature of the system.[27] If we were to look closely at the population of molecules, however, we would find that some molecules are moving very fast and some are moving very slowly; there is a distribution of speeds and velocities (speed + direction).

As two atoms/molecules approach each other they will feel the force of attraction caused by the electron density distortions, these are known as London dispersion forces, which we will abbreviate as LDFs. The effects of these LDFs depend on the strength of the interaction (that is the magnitude of the charges and the distance between them) and on the kinetic energies of the atoms and molecules. LDF are one of a number of intermolecular forces (IMFs), which we will consider later. LDFs are the basis of van der Waals interactions in biological systems.

To simplify things we are going to imagine a very simple system: assume for the moment that there are just two isolated atoms, atom1 and atom2. The atoms are at rest with respect to one another, but close enough that the LDF-based attractive interactions between them are significant. For this to occur they have to be quite close, since such attractive interactions decreases rapidly, as $1/r^6$ where r is the distance between the two atoms. At this point, the system, which we will define as the two atoms, has a certain amount of energy. The exact amount does not matter, but as long

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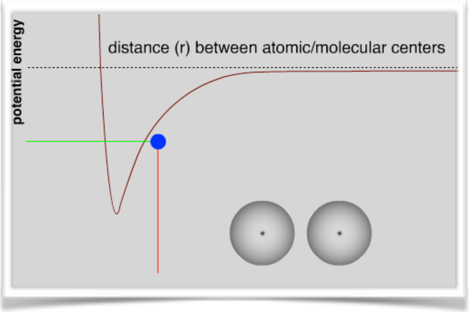
[27] Remember speed is a directionless value, while velocity involves both speed and direction.

as these two atoms remain isolated, and do not interact with anything else, the energy will remain constant.



So what does all this have to do with atoms approaching one another? We can use the same kinds of reasoning to understand the changes in energy that occur as the atoms approach each other. Initially, the system will have a certain amount of energy (kinetic + potential). If the atoms are close enough to feel the effects of the attractive LDFs, they begin to move toward each other, think of a ball falling towards the Earth, and some of the potential energy associated with the atoms' initial state is converted into kinetic energy ($E_K = ½mv^2$).

As they approach each other the LDFs grow stronger, the atoms are more strongly attracted to each other; the system's potential energy decreases and is converted into kinetic energy, the atoms move faster.[28] The total energy remains the same as long as there are no other atoms around. This continues until the atoms get close enough that repulsive interactions between the electrons become stronger and as they approach even more closely the repulsive interactions between the positively charged nuclei also come into play, causing the potential energy in the system to rise. As the atoms begin to slow down their kinetic energy is converted back into potential energy. They will eventually stop and then be repelled from one another. At this point potential energy will be converted back into kinetic energy. As they move away, however, repulsion will be replaced by attraction and they will slow; their kinetic energy will be converted back into potential energy.[29] With no other factors acting within the system, the two atoms will oscillate forever. In the graph showing potential energy versus the distance between the atoms, we see that the potential energy of the system reaches a minimum at some distance. Closer than that and the repulsive electromagnetic forces come into play, further away and the attractive electromagnetic forces (LDF's) are dominant. The distance between the two atoms is a function of the relative strengths of the attractive and repulsive interactions. However, even at the minimum, there is some potential energy in the system, stored in the electromagnetic field between the two atoms. At temperatures above absolute zero (0 K), the pair of atoms will also have kinetic energy – as they oscillate back and forth.

Here we have a core principle that we will return to time and again: a stabilizing interaction always lowers the potential energy of the system, and conversely a destabilizing interaction always raises the potential energy of the system. In an isolated system with only two atoms, this oscillation would continue forever because there is no way to change the energy of the system. This situation

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[28] Imagine, as an analogy that the two atoms are balls rolling down opposite sides of a hill towards a valley, their potential energy falls as they move down - but their kinetic energy rises and they speed up.

[29] To continue our analogy as the balls get to the bottom of the hill, they collide and bounce back - rolling back up the hill, until once again the force of gravity takes over and they start to roll back down. In an ideal (unreal) situation with no friction, this situation would simply continue, until some other factor is introduced.

doesn't occur in real life because two-atom systems do not occur. For example, even in a gas, where the atoms are far apart, there are typically large numbers of atoms that have a range of speeds and kinetic energies present in the system. These atoms frequently collide and transfer energy between one another. Therefore, when two atoms collide and start to oscillate, some energy may be transferred to other particles by collisions. If this happens, a stable interaction can form between the two particles; they will "stick" together. If more particles approach, they can also become attracted, and if their extra energy is transferred by collisions, the particles can form a bigger and bigger clump.

As we discussed earlier, LDFs arise due to the fluctuations of electron density around nuclei and are a feature common to all atoms; all atoms/molecules attract one another in this manner. The distance between atoms/molecules where this attraction is greatest is known as the van der Waals radius of the atom/molecule. If atoms/molecules move closer to one another than their van der Waals radii they repel one another. The van der Waals radius of an atom is characteristic for each type of atom/element. As mentioned earlier, it is only under conditions of extreme temperature and pressure that the nuclei of two atoms can fuse together to form a new type of atom; such a nuclear/atomic fusion event results in the interconversion of matter into energy.[30]

Questions to Answer

- What is potential energy? Can you provide an example?
- What is kinetic energy? Can you provide an example?
- At the atomic level, what do you think potential energy is?
- At the atomic level, what do you think kinetic energy is?
- Why does raising the temperature affect the speed of a gas molecule?

Questions to Ponder

- What is energy (have your ideas changed from before)?

Questions for Later:

- When we talk about potential energy of a system, what does system mean?
- Helium liquefies at around 4K. What makes the helium atoms stick together? (Why don't they turn into a gas?)
- Consider two atoms separated by 1 spatial unit versus 4 spatial units. How much weaker is the interaction between the more distant atoms? How does that compared to the behavior of simple charges (rather than atoms)?

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[30] It is these factors that made the report of cold fusion so strange and so exciting to physicists. The temperatures and pressures required for fusion are so high that they are extremely difficult to achieve under controlled conditions. The failure to reproduce the original cold fusion report reinforces our understanding of how atoms interact. That scientists around the world attempted to reproduce the original observation (and failed), illustrates the open-mindedness of the scientific community. The fact that badly controlled and irreproducible observations were published, illustrates how scientific effort and resources (that is, research funds) can be wasted by inadequate pre-publication review. But science, like all human activities, is imperfect. The price for open-mindedness may be be wasted time and effort, yet it remains critical to scientific process and progress. At the same time, once the replication efforts failed, it became a waste of time (or a delusional obsession) to pursue cold fusion.

1.8 Interactions Between Helium Atoms and Hydrogen Molecules

Now let's take a look at a couple of real systems. We begin by considering interactions between the simplest atoms, hydrogen (H) and helium (He), and the simplest molecule, molecular hydrogen (H_2). A typical hydrogen atom consist of one proton and one electron, although some contain one or two neutrons and form "isotopes" known as deuterium and tritium, respectively. A hydrogen molecule is a completely different chemical entity: it contains two hydrogen atoms, but its properties and behavior are quite different. Helium atoms have 2 protons and 2 neutrons in their nuclei, and 2 electrons in their electron clouds. We will consider more complicated atoms and molecules after we discuss atomic structure in greater detail in the next chapter. One advantage of focusing on molecular hydrogen and helium is that it also allows us to introduce, compare, and briefly consider both van der Waals interactions (due to IMFs) and covalent bonds; we will do much more considering later on.

When two atoms of helium approach each other LDFs come into play and a attractive interaction develops. In the case of He the drop in potential energy due to the interaction is quite small, that is, the stabilization due to the interaction, and it does not take much energy to knock the two atoms apart. This energy is delivered by collisions with other He atoms. In fact at atmospheric pressures, Helium is never a solid and liquid He boils at ~4 K (–268.93ºC), only a few degrees above absolute zero or 0 K (–273.15 ºC).[31] This means that at all temperatures above ~4 K there is enough kinetic energy in the atoms of the system to disrupt the interactions between He atoms. The weakness of these interactions means that at higher temperatures, above 4 K, helium atoms do not "stick together". Helium is a gas at temperatures above 4 K.

Now let us contrast the behavior of helium with that of hydrogen (H). As two hydrogen atoms approach one another they form a much more stable interaction, about 1000 times stronger than the He–He London dispersion forces. In an H–H interaction the atoms are held together by the attraction of each nucleus for both electrons. The attractive force is much stronger and as the atoms get closer this leads to a larger drop in potential energy and a minimum for the two interacting hydrogen atoms that is much deeper than that for He–He. Because of its radically different stability the H–H system gets a new name; it is known as molecular hydrogen or H_2 and the interaction between the H atoms is known as a covalent bond. In order to separate a hydrogen molecule back into two hydrogen atoms, that is, to break the covalent bond, we have to supply energy.[32] This

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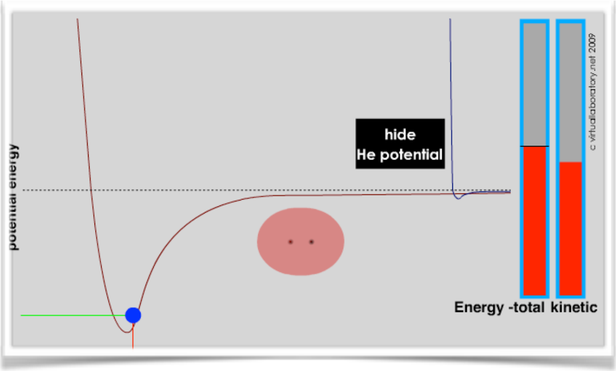
[31] According to Robert Parson, "At 1 atmosphere pressure, Helium does not melt at ANY temperature - it stays liquid down to absolute zero. (If you want to be picky, it is a liquid down to the lowest temperatures that anyone has ever achieved, which are orders of magnitude less than 1 K (http://en.wikipedia.org/wiki/Dilution_refrigerator), and our best theories predict that it will remain a liquid no matter how low the temperature.) To get solid helium you have to increase the pressure to 25 atmospheres or above. This is one of the most dramatic consequences of zero-point energy: the intermolecular forces in He are so weak that it melts under its own zero point energy. (This leads to the peculiar consequence that Helium at zero Kelvin is a liquid with zero entropy.)

[32] In fact this is known as the bond energy – the energy required to break the bond – which in the case of H_2 is 432 kJ/mol.



energy can take several forms: for example, energy delivered by molecular collisions with surrounding molecules or by the absorption of light both lead to the breaking of the bond.

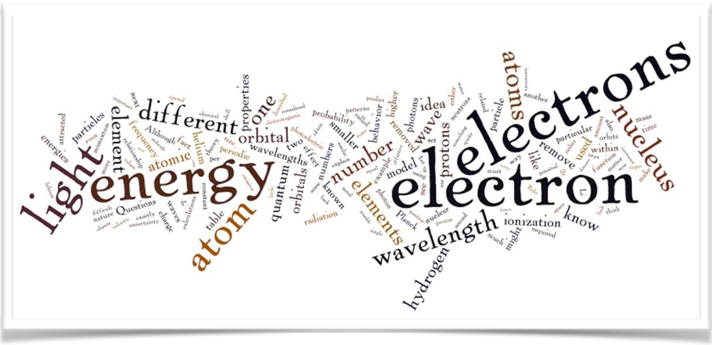
Each H can form only a single covalent bond, leading to the formation of H–H molecules, which are often also written as H_2 molecules. These H–H molecules are themselves attracted to one another through LDFs. We can compare energy associated with the H–H covalent bond and the H_2 - H_2 IMF. To break a H–H covalent bond one needs to heat the system to approximately 5000 K. On the other hand to break the intermolecular forces between separate H_2 molecules, the system temperature only needs to rise to ~20 K; above this temperature H_2 is a gas. At this temperature the IMFs between individual H_2 molecules are not strong enough to resist the kinetic energy of colliding molecules. Now you may ask yourself, why does H_2 boil at a higher temperature than He? Good question! It turns out that the strengths of LDFs depend on several factors including shape of the molecule, surface area, and number of electrons. For example the greater the surface areas shared between interacting atoms or molecules the greater the LDFs experienced and the stronger the resulting interaction. Another factor is the ability of the electron cloud to become charged, a property known as polarizability. You can think of polarizability as the floppiness of the electron cloud. As a rough guide, the further away from the nucleus the electrons are, the more polarizable (floppy) the electron cloud becomes. We will return to this and related topics later on. As we will see, larger molecules with more complex geometries, such as biological macromolecules (proteins and nucleic acids), can interact through more surface area and polarizable regions, leading to correspondingly stronger interactions.

At this point, you are probably (or should be) asking yourself some serious questions, such as, why don't helium atoms form covalent bonds with one another? Why does a hydrogen atom form only one covalent bond? What happens when other kinds of atoms interact? To understand the answers to these questions, we need to consider how the structure of atoms differs between the different elements, which is the subject of the next chapter.

Questions to Answer
- Can you draw a picture (with about 20 helium atoms, represented as circles) of what solid helium would look like if you could see it?
- How would that differ from representations of liquid helium or gaseous helium?
- Now make a similar drawing of H_2. Does this help explain the higher melting point of H_2?

Question to Ponder
- How do the properties of solids, liquids, and gases differ?

Chapter 2: Electrons and Orbitals



Even as he articulated his planetary model of the atom, Rutherford was aware that there were serious problems with it. For example because like charges repel and unlike charges attract, it was not at all clear why the multiple protons in the nuclei of elements heavier than hydrogen did not repel each other and cause the nuclei to fragment. What enables them to stay so close to each other? On the other hand, if electrons are orbiting the nucleus like planets around the Sun, why don't they repel each other, leading to quite complex and presumably unstable orbits? Why aren't they ejected spontaneously and why doesn't the electrostatic attraction between the positively-charged nucleus and the negatively-charged electrons result in the negatively-charged electrons falling into the positively charged nucleus? Assuming that the electrons are moving around the nucleus, they are constantly accelerating (changing direction). If you know your physics, you will recognize that (as established by J.C. Maxwell – see below) a charged object emits radiation when accelerating.[33] As the electron orbits the nucleus this loss of energy will lead it to spiral into the nucleus – such an atom would not be stable. But, as we know, most atoms are generally quite stable.

So many questions and so few answers! Clearly Rutherford's model was missing something important and assumed something that cannot be true with regard to forces within the nucleus, the orbital properties of electrons, and the attractions between electrons and protons. To complete this picture leads us into the weird world of quantum mechanics.

2.1 Light and Getting Quantum Mechanical

While Rutherford and his colleagues worked on the nature of atoms, other scientists were making significant progress in understanding the nature of electromagnetic radiation, that is, light. Historically, there had been a long controversy about the nature of light, with one side arguing that light is a type of wave, like sound or water waves, traveling through a medium like air or the surface of water and the other side taking the position that light is composed of particles. Isaac Newton called them corpuscles. There was compelling evidence to support both points of view, which seemed to be mutually exclusive, and the attempt to reconcile these observations into a single model proved difficult.

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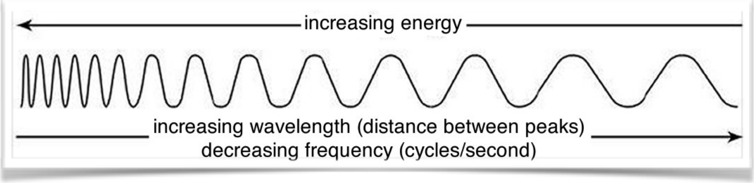
[33] This may (or may not) be helpful: http://www.cv.nrao.edu/course/astr534/PDFnewfiles/LarmorRad.pdf

By the end of the 1800s, most scientists had come to accept a wave model for light because it better explained behaviors such as interference[34] and diffraction,[35] the phenomena that gives rise to patterns when waves pass through or around objects that are of similar size to the wave itself. James Clerk Maxwell (1831–1879) developed the electromagnetic theory of light, in which visible light and other forms of radiation, such as microwaves, radio waves, X-rays, and gamma rays, were viewed in terms of perpendicular electric and magnetic fields. A light wave can be described by defining its frequency (v) and its wavelength (λ). For all waves, the frequency times its wavelength equals the velocity of the wave. In the case of electromagnetic waves, λv = c, where c is the velocity of light.



Although the wave theory explained many of the properties of light, it did not explain them all. Two types of experiments in particular gave results that did not appear to be compatible with the wave theory. The first arose during investigations by the German physicist Max Planck (1858–1947) of what is known as black body radiation. In these studies, an object heated to a particular temperature emits radiation. Consider your own body, which typically has a temperature of approximately 98.6 °F or 36 ºC. Your body emits infrared radiation that can be detected by some cameras.[36] Some animals, like snakes, have infrared detectors that enable them to locate their prey—typically small, warm-blooded, infrared-light-emitting mammals.[37] Because mammals tend to be warmer than their surroundings, infrared vision can be used to find them in the dark or when they are camouflaged.

Planck had been commissioned by an electric power company to produce a light bulb that emitted the maximum amount of light using the minimum amount of energy. In the course of this project he studied how the color of the light emitted (a function of its wavelength) changed as a function of an object's (such as a light bulb filament) temperature. We can write this relationship as λ (wavelength) = f(t) where t = temperature and f indicates "function of." To fit his data Planck had to invoke a rather strange and non-intuitive idea, namely that matter absorbs and emits energy only in discrete chunks, which he called quanta. These quanta occurred in multiples of E (energy) = hv, where h is a constant, now known as Planck's constant, and v is the frequency of light. Planck's constant is considered one of the fundamental numbers that describes our universe.[38] The physics that uses the idea of quanta is known as quantum mechanics.

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[34] http://phet.colorado.edu/en/simulation/wave-interference

[35] Link to "Dr. Quantum" double slit experiment: http://www.youtube.com/watch?v=DfPeprQ7oGc

[36] In fact, there is lots of light within your eyeball, even in the dark, due to black body radiation. You do not see it because it is not energetic enough to activate your photosensing cells. See: http://blogs.discovermagazine.com/cosmicvariance/2012/05/25/quantum-mechanics-when-you-close-your-eyes/

[37] http://www.physorg.com/news76249412.html

[38] h= 6.626068×10^{-34} m^2kg/s (or joule-seconds, where a joule is the kinetic energy of a 2 kg mass moving at a velocity of 1 m/s)

One problem with Planck's model, however, is that it disagreed with predictions of classical physics; in fact as the frequency of the light increased, his measurements diverged more and more from the predictions of the then current, wave-based theory.[39] This divergence between classical theory and observation became known, perhaps over-dramatically, as the ultraviolet catastrophe. It was a catastrophe for the conventional theory because there was no obvious way to modify classical theories to explain Planck's observations; this was important because Planck's observations were reproducible and accurate. Once again, we see an example of the rules of science: a reproducible discrepancy, even if it seems minor, must be addressed or the theory must be considered either incomplete or just plain wrong.

The idea that atoms emit and absorb energy only in discrete packets is one of the most profound and revolutionary discoveries in all of science, and set the stage for a radical rethinking of the behavior of energy and matter on the atomic and subatomic scales. Planck himself proposed the idea with great reluctance and spent a great deal of time trying to reconcile it with classical theories of light. In the next section we will see how this property can be used to identify specific types of atoms, both in the laboratory and in outer space.

Questions to Answer

- What is a constant? What is a function?
- What happens to the energy of a photon of light as the frequency increases? What about as the wavelength increases? (remember: $\lambda v = c$)
- Why is it difficult to detect cold-blooded animals using infrared detectors?

Questions to Ponder

- How can the phenomena of diffraction and interference be used as evidence that light behaves like it a wave?
- How can light be both a wave and a particle?
- Is light energy?

2.2 Taking Quanta Seriously

In 1905, Albert Einstein used the idea of quanta to explain the photoelectric effect, which was described by Philipp Lenard (1862-1947). The photoelectric effect occurs when light shines on a metal plate and electrons are ejected, creating a current.[40] Scientists had established that there is a relationship between the wavelength of the light used, the type of metal the plate is made of, and whether or not electrons are ejected. It turns out that there is a threshold wavelength (energy) of light that is characteristic for the metal used, beyond which no electrons are ejected. The only way to explain this is to invoke the idea that light comes in the form of particles, known as photons, that also have a wavelength and frequency (we know: this doesn't make sense, but bear with us for now). The intensity of the light is related to the number of photons that pass by us per second, whereas the energy per photon is dependent upon its frequency or wavelength, because

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[39] This is known as the Rayleigh-Jeans law.

[40] http://phet.colorado.edu/simulations/sims.php?sim=Photoelectric_Effect

wavelength and frequency of light are related by the formula $\lambda v = c$ where c is the speed of light in a vacuum, is a constant and equal to ~3.0×10^8 m/s. The higher the frequency v (cycles per second, or Hertz), the shorter the wavelength λ (length per cycle) and the greater the energy per photon. Because wavelength and frequency are inversely related–that is, as one goes up the other goes down– energy is directly related to frequency by the relationship $E = hv$ or inversely related to the wavelength $E= hc/\lambda$, where h is Planck's constant. So radiation with a very short wavelength, such as x rays ($\lambda= \sim 10^{-10}$ m) and ultraviolet light (between 10^{-7} to 10^{-8} m), have much more energy per particle than long wavelength radiation like radio and microwaves ($\lambda= \sim 10^3$ m). This is why we (or at least most of us) do not mind being surrounded by radio waves essentially all the time yet we closely guard our exposure to gamma rays, X-rays, and UV light; their much higher energies cause all kinds of problems with our chemistry, as we will see later.

Because of the relationship between energy and wavelength ($\lambda\nu = c$), when you shine long-wavelength, low energy, such as infrared, but high intensity (many photons per second) light on a metal plate, no electrons are ejected. But when you shine short-wavelength, high energy (such as ultraviolet or x rays) but low intensity (few photons per second) light on the plate, electrons **are** ejected. Once the wavelength is short enough (or the energy is high enough) to eject electrons, increasing the intensity of the light now increases the number of electrons emitted. An analogy is with a vending machine that can only accept quarters; you could put nickels or dimes into the machine all day and nothing will come out. The surprising result is that the same **total** amount of energy can produce very different effects. Einstein explained this observation (the photoelectric effect) by assuming that only photons with "enough energy" could eject an electron from an atom. If photons with lower energy hit the atom no electrons are ejected - no matter how many photons there are.[41] You might ask: Enough energy for what? The answer is enough energy to overcome the attraction between an electron and the nucleus. In the photoelectric effect, each photon ejects an electron from an atom on the surface of the metal. These electrons exist somewhere within the atoms that make up the metal (we have not yet specified where) but it takes energy to remove them and the energy is used to overcome the force of attraction between the negative electron and the positive nucleus.

Now you should be really confused, and that is a normal reaction! On one hand we were fairly convinced that light acted as a wave but now we see some of its behaviors can be best explained in terms of particles. This dual nature of light is conceptually difficult for most normal people because it is completely counterintuitive. In our macroscopic world things are either particles, such as bullets, balls, coconuts, or waves (in water); they are not—no, not ever—both. As we will see, electromagnetic radiation is not the only example of something that has the properties of both a wave and a particle; this mix of properties is known as wave–particle duality. Electrons, protons, and neutrons also display wavelike properties. In fact, all matter has a wavelength, defined by Louis de Broglie (1892–1987), by the equation $\lambda = h/mv$ where mv is the

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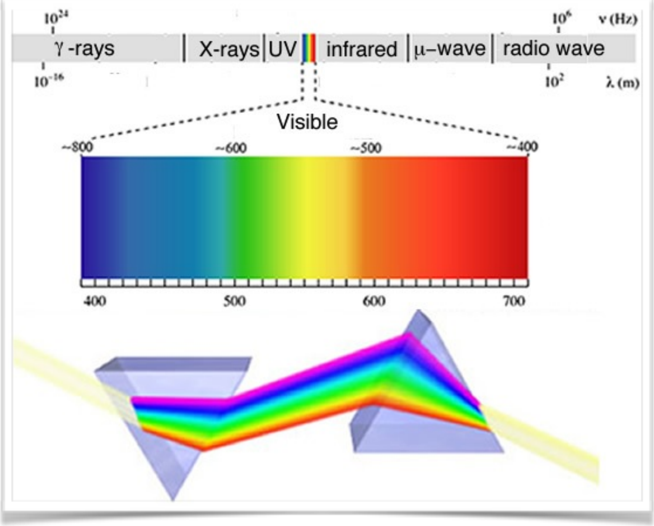
[41] One type of semi-exception is illustrated by what are known as two- and multi-photon microscopes, in which two lower energy photons hit a molecule at almost the same moment, allowing their energies to be combined; see http://en.wikipedia.org/wiki/Two-photon_excitation_microscopy.

object's momentum (mass x velocity) and h is Planck's constant. For heavy objects, moving at slow speeds, the wavelength is very, very small, but it becomes a significant factor for light objects moving fast, such as electrons. Although light and electrons can act as both waves and as particles, it is perhaps better to refer to them as quantum mechanical particles, a term that captures all features of their behavior and reminds us that they are weird! Their behavior will be determined by the context in which we study (and think of) them.

2.3 Exploring Atomic Organization Using Spectroscopy[42]

As we will often see, there are times when an old observation suddenly fits into and helps clarify a new way of thinking about a problem or process. In order to understand the behavior of electrons within atoms scientists brought together a number of such observations. The first observation has its roots in understanding the cause of rainbows. The scientific explanation of the rainbow is based on the fact that light of different wavelengths is bent through different angles (refracted) when it passes through an air–water interface. When sunlight passes through approximately spherical water droplets, it is refracted at the air–water interface, partially reflected (note the difference) from the backside of the water droplet, and then refracted again as it leaves the droplet. The underlying fact that makes rainbows possible is that sunlight is composed of photons with an essentially continuous distribution of visible wavelengths. Isaac Newton illustrated this nicely by using a pair of prisms to show that white light could be separated into light of many different colors by passing it through a prism and then recombined back into white light by passing it through a second prism. On the other hand, light of a single color remained that color, even after it passed through a second prism.



When a dense body, like the Sun or the filament of an incandescent light bulb, is heated, it emits light of many wavelengths (colors)—essentially all wavelengths in the visible range. However,

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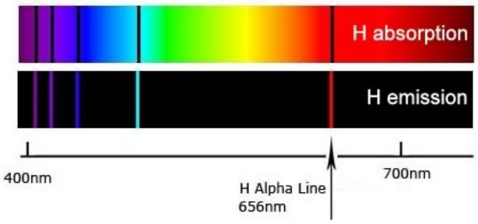
[42] For a more complex explanation, see: http://www.coffeeshopphysics.com/articles/2011-10/30_the_discovery_of_rainbows/



when a sample of an element or mixture of elements is heated, for example in a flame provided by a Bunsen burner, it emits light of only very particular wavelengths. The different wavelengths present in the emitted light can be separated from one another using a prism to produce what is known as an emission spectra. When projected on a screen these appear as distinct, bright-colored lines, known emission lines. In a complementary manner, if white light, which consists of a continuous distribution of wavelengths of light, is passed through a cold gaseous element the same wavelengths that were previously emitted by the heated element will be absorbed, while all other wavelengths will pass through unaltered. By passing the light through a prism we can see which wavelengths of light have been absorbed by the gas. We call these dark areas "absorption" lines within the otherwise continuous spectrum. The emission and absorption wavelengths for each element the same and unique for each element. Emission and absorption phenomenon provide a method (spectroscopy) by which the absorbance or emission of specific wavelengths of light by can be is used to study the composition and properties of matter. Scientists used spectroscopic methods to identify helium, from the Greek "sun", in the Sun before it was isolated on Earth.

In the 1800s, it became increasingly clear that each element, even the simplest, hydrogen, has a distinctive and often quite complex emission/absorption spectra. In 1855 Johann Balmer (1825-1898) calculated the position of the lines in the visible region. In 1888 Johannes Rydberg (1854-1919) extended those calculations to the entire spectrum. These calculations, however, were based on an empirical formula and it was unclear why this formula worked or what features of the atom it was based on—this made the calculations rather unsatisfying. Although useful, they provided no insight into the workings of atoms.

Making sense of spectra:

How do we make sense of these observations? Perhaps the most important clue is again the photoelectric effect; that is, the observation that illuminating materials with light can in some circumstances lead to the ejection of electrons. This suggests that it is the interactions between light and the electrons in atoms that are important. Using this idea and the evidence from the hydrogen spectra Niels Bohr (1885-1962) proposed a new model for the atom His first hypothesis was that the electrons within an atom can only travel along certain orbits at a fixed distance from the nucleus, each orbit corresponding to a specific energy. The second idea was that electrons can jump from one orbit to another, but this jump requires either the capture (absorption) or release (emission) of energy, in the form of a photon. An electron can move between orbits only if a photon of exactly the right amount of energy is absorbed (lower to higher) or emitted (higher to lower). Lower (more stable) orbits are often visualized as being closer to the nucleus whereas higher, less stable and more energetic orbits are further away. Only when enough energy is added in a single packet is the electron removed completely from the atom, leaving a positively-charged ion (an ion is an atom or molecule that has a different number of protons and electrons) and a free electron.

Because the difference in energy between orbits is different in different types of atoms, moving electrons between different orbits requires photons carrying different amounts of energy (different wavelengths).

Bohr's model worked well for hydrogen atoms; in fact, he could account for and accurately calculate the wavelengths for all of hydrogen's observed emission/absorption lines. These calculations involved an integer quantum number that corresponded to the different energy levels of the orbits.[43] Unfortunately, this model was not able to predict the emission/absorption spectrum for any other element, including helium and certainly not for any molecule. Apparently Bohr was on the right track—because every element does have a unique spectrum and therefore electrons must be transitioning from one energy level to another—but his model was missing something important. It was not at all clear what restricted electrons to specific energy levels. What happens in atoms with more than one electron? Where are those electrons situated and what governs their behavior and interactions? It is worth remembering that even though the Bohr model of electrons orbiting the nucleus is often used as a visual representation of an atom, **it is not correct. Electrons do not circle the nucleus in defined orbits.** Bohr's model only serves as an approximate visual model for appearance of an atom–it is not how electrons actually behave!

Questions to Answer

- If the intensity of a beam of light is related to the number of photons passing per second, how would you explain intensity using the model of light as a wave? What would change and what would stay the same?
- Why do we not worry about being constantly bombarded by radio waves (we are), but yet we guard our exposure to x rays?
- Draw a picture of what you imagine is happening during the photoelectric effect.
- Is the energy required to eject an electron the same for every metal?

Questions to Ponder

- Can you think of other scientific ideas that you find nonsensical? Be honest.
- How does the idea of an electron as a wave fit with your mental image of an atom?
- Where is the electron if it is a wave?

Questions for Later

- What trends might you expect in the energies required to eject an electron?
- Why do you think this phenomenon (the photoelectric effect) is most often seen with metals? What property of metals is being exploited here?
- What other kinds of materials might produce a similar effect?

2.4 Beyond Bohr

Eventually, as they considered the problems with the Bohr model, scientists came back to the idea of the wave–particle duality as exemplified by the photon. If light (electromagnetic radiation), which was classically considered to be a wave, could have the properties of a particle, then perhaps matter, classically considered as composed of particles, could have the properties of waves, at least under conditions such as those that exist within an atom. Louis De Broglie (1892–

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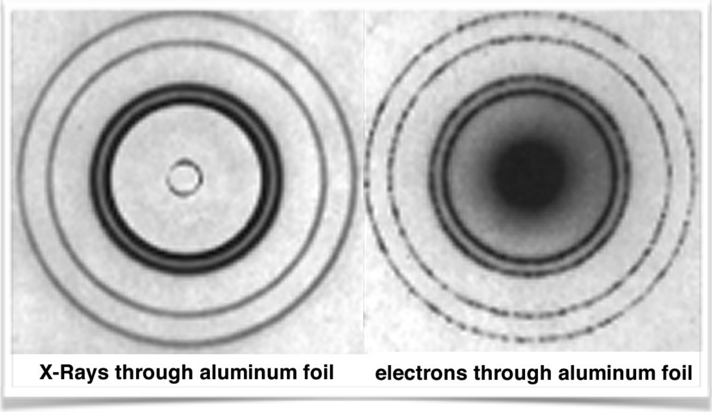
[43] Bohr model applet particle and wave views: http://www.walter-fendt.de/ph11e/bohrh.htm

1987) considered this totally counterintuitive idea in his Ph.D. thesis. De Broglie used Planck's relationship between energy and frequency ($E = h\nu$), the relationship between frequency and wavelength ($c = \lambda\nu$), and Einstein's relationship between energy and mass ($E = mc^2$) to derive a relationship between the mass and wavelength for any particle (including photons).[44] You can do this yourself by substituting into these equations, to come up with $\lambda = h/mv$, where mv is the momentum of a particle with mass m and velocity v. In the case of photons, $v = c$, the velocity of light.

Although the math involved in deriving the relationship between momentum (mv) of a particle and its wavelength λ is simple, the ideas behind it are most certainly not. It is even more difficult to conceptualize the idea that matter, such as ourselves, can behave like waves, and yet this is consistent with a broad range of observations. We never notice the wavelike properties of matter because on the macroscopic scale, the wavelength associated with a particular object is so small that it is negligible. For example, the wavelength of a baseball moving at 100 m/s is much smaller than the baseball itself. It is worth thinking about what you would need to know to calculate it. At the atomic scale, however, the wavelengths associated with particles are similar to their size, meaning that the wave nature of particles such as electrons cannot be ignored; their behavior cannot be described accurately by models and equations that treat them as simple particles. The fact that a beam of electrons can undergo diffraction, a wave-like behavior provides evidence of this idea.



Certainty and Uncertainty

Where is a wave located? The answer is not completely obvious. You might think it would be easier to determine where a particle is, but things get complicated as they get smaller and smaller. Imagine that we wanted to view an electron within an atom using some type of microscope, in this case, an imaginary one with unlimited resolution. To see something, photons have to bounce or reflect off it and then enter our eye, be absorbed by a molecule in a retinal cell, and start a signal to our brain where that signal is processed and interpreted. When we look at macroscopic objects, their interactions with light have little effect on them. For example, objects in a dark room do not begin to move just because you turn the lights on! Obviously the same cannot be said for atomic-scale objects; we already know that a photon of light can knock an electron completely out of an

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[44] Although the resting mass of a photon is zero, a moving photon does has an effective mass because it has energy.

atom (the photoelectric effect). Now we come to another factor: the shorter the wavelength of light we use, the more accurately we can locate an object.[45] Remember, however, that wavelength and energy are related: the shorter the wavelength the greater its energy. To look at something as small as an atom or an electron we have to use electromagnetic radiation of a wavelength similar to the size of the electron. We already know that an atom is about 10^{-10} m in diameter, so electrons are presumably much smaller. Let us say that we use gamma rays, a form of electromagnetic radiation, whose wavelength is $\sim 10^{-12}$ m. But radiation of such short wavelength carries lots of energy, so these are high-energy photons. When such a high-energy photon interacts with an electron, it dramatically perturbs the electron's position and motion. That is, if we try to measure where an electron is, we perturb it by the very act of measurement. The act of measurement introduces uncertainty and this uncertainty increases the closer we get to the atomic molecular scale.

This idea was first put forward explicitly by Werner Heisenberg (1901-1976) and is known as the Heisenberg Uncertainty Principle. According to the uncertainty principle, we can estimate the uncertainty in a measurement using the formula $\Delta mv \times \Delta x > h/2\pi$, where Δ mv is the uncertainty in the momentum of the particle (mass times velocity or where it is going and how fast), Δx is the uncertainty in its position in space (where it is at a particular moment), and h is Planck's constant now divided by 2π. If we know exactly where the particle is ($\Delta x = 0$) then we have absolutely no information about its velocity, which means we do not know how fast or in what direction it is going. Alternatively, if we know its momentum exactly ($\Delta mv = 0$), that is, we know exactly how fast and in which direction it is going, we have no idea whatsoever where it is! The end result is that we cannot know exactly where an electron is without losing information on its momentum, and vice versa. This has lots of strange implications. For example, if we know the electron is within the nucleus ($\Delta x \sim 1.5 \times 10^{-14}$ m), then we have very little idea of its momentum (how fast and where it is going). These inherent uncertainties in the properties of atomic-level systems are one of their key features. For example, we can estimate some properties very accurately but we cannot know everything about an atomic/molecular-level system at one point in time. This is a very different perspective from the one it replaced, which was famously summed up by Pierre-Simon Laplace (1749–1827), who stated that if the positions and velocities of every object in the universe were known, the future would be set:

> *We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eyes. -- Pierre-Simon Laplace (1745-1827)*

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[45] Good reference: http://ww2010.atmos.uiuc.edu/(Gl)/guides/rs/rad/basics/wvl.rxml

It turns out that a major flaw in Bohr's model of the atom was that he attempted to define both the position of an electron (a defined orbit) and its energy, or at least the energy difference between orbits, at the same time. Although such a goal seems quite reasonable and would be possible at the macroscopic level, it simply is not possible at the atomic level. The wave nature of the electron makes it impossible to predict exactly where that electron is if we also know its energy level. In fact, we do know the energies of electrons very accurately because of the evidence from spectroscopy. We will consider this point again later in this chapter.

Questions to Answer

- How does the wavelength of a particle change as the mass increases?
- Planck's constant is $h = 6.626 \times 10^{-34}$ J·s. What are the implications for particles of macroscopic size? (1 J = the kinetic energy of a two-kilogram mass moving at the speed of 1 m/s.)
- What would be the wavelength of the world-record holder for the 100-m sprint? What assumptions do you have to make to answer this question?
- What is the wavelength of a protein of 60,000 daltons? (That is, if the protein has a molar mass of 60,000 g/M, what is the mass of one molecule of the protein?)

Questions to Ponder

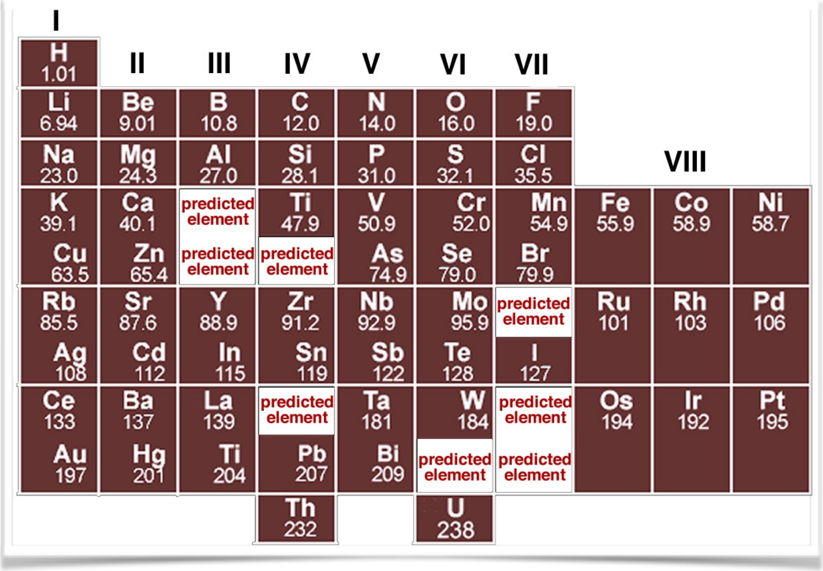
- What is the uncertainty in your momentum, if the error in your position is 0.01 m (remembering that Planck's constant $h = 6.626068 \times 10^{-34}$ J·s)?
- How is it that we experience objects as having very definite velocities and positions?
- Does it take energy to determine your position?
- How is the emission and absorption behavior of atoms related to electron energies?

2.5 Organizing Elements: Introduction to the Periodic Table

Up to this point we have made a number of unjustified assumptions. We have talked about elements but we have not explicitly specified how they are different, so let us do that now. If we start with hydrogen we characterized it by the presence of one proton in the nucleus and one electron surrounding it. Atoms are always neutral, which means that the number of positively-charged particles is equal to the number of negatively-charged particles, and charges come in discrete, equal, and opposite units. The presence of one proton and one electron defines a hydrogen atom but the world is a little more complex than that. A hydrogen atom may also contain one or two neutrons in its nucleus. A neutron can be considered, with the forgiveness of physicists, a proton, an electron, and an uncharged neutrino, and so it is electrically neutral. Neutrons are involved in the strong nuclear force and become increasingly important as the element increases in atomic number. In hydrogen, the neutrons (if they are present) have rather little to do, but in heavier elements the strong nuclear force is critical in holding the nucleus together, because at short distances this force is ~100 times stronger than the electrostatic repulsion between positively charged protons, which is why nuclei do not simply disintegrate. At the same time, the strong force acts over a very limited range, so when particles are separated by more than about 2×10^{-15} m (2 femtometers or fm), we can ignore it.

As we add one proton after another to an atom, which we can do in our minds, and which occurs within stars and supernova, in a rather more complex manner, we generate the various elements. The number of protons determines the elemental identity of an atom, whereas the number of neutrons can vary. Atoms of the same element with different numbers of neutrons are known as isotopes of that element. Each element is characterized by a distinct, whole number (1, 2, 3, …) of protons and the same whole number of electrons. An interesting question emerges here: is the number of possible elements infinite? And if not, why not? Theoretically, it might seem possible to keep adding protons (and neutrons and electrons) to produce a huge number of different types of atoms. However, as Rutherford established, the nucleus is quite small compared to the atom as a whole, typically between one and ten femtometers in diameter. As we add more and more protons (and neutrons) the size of the nucleus exceeds the effective range of the strong nuclear force (< 2 fm), and the nucleus becomes unstable. As you might expect, unstable nuclei break apart (nuclear fission), producing different elements with smaller numbers of protons, a process that also releases tremendous amounts of energy. Some isotopes are more stable than others, which is why the rate of their decay, together with a knowledge of the elements that they decay into can be used to calculate the age of rocks and other types of artifacts.[46]

Each element is defined by the number of protons in the nucleus, and as such is different from every other element. In fact, careful analysis of different elements reveals that there are periodicities (repeating patterns) in the properties of elements. Although John Dalton produced a table of elements with their atomic weights in 1805, it was only when Dimitri Mendeleev (1834–1907) tried to organize the elements in terms of their chemical and physical properties that some semblance of order began to emerge. Mendeleev, a Russian chemistry professor, was frustrated by the lack of organization of chemical information, so he decided to write his own textbook (not unlike your current authors). At the time, scientists had identified about 60 elements and established their masses relative to hydrogen. Scientists had already noticed that the elements display repeating patterns of behavior: and that some elements have very similar properties. It was Mendeleev's insight that these patterns could be used as a guide for arranging the elements in a systematic way. In his periodic table, published in 1869, he placed elements in order of increasing atomic weight in



I	II	III	IV	V	VI	VII	VIII		
H 1.01									
Li 6.94	Be 9.01	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0			
Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
K 39.1	Ca 40.1	predicted element	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.9	Co 58.9	Ni 58.7
Cu 63.5	Zn 65.4	predicted element	predicted element	As 74.9	Se 79.0	Br 79.9			
Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	predicted element	Ru 101	Rh 103	Pd 106
Ag 108	Cd 112	In 115	Sn 119	Sb 122	Te 128	I 127			
Ce 133	Ba 137	La 139	predicted element	Ta 181	W 184	predicted element	Os 194	Ir 192	Pt 195
Au 197	Hg 201	Ti 204	Pb 207	Bi 209	predicted element	predicted element			
			Th 232		U 238				

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[46] see https://www.youtube.com/watch?v=6SxzfZ8bRO4 and https://www.youtube.com/watch?v=1920gi3swe4

repeating rows from left to right; elements with similar chemical properties were placed in vertical columns (known as groups).

Although several other scientists were working on schemes to show patterns in elemental behavior, it was Mendeleev's arrangement that emerged as the basis for the modern periodic table, not only because of the way he arranged the elements but also for what he left out and what he changed. For example he was so sure about the underlying logic of his table that where certain elements seemed out of place, based, for example, on their reported atomic weights, such as tellurium and iodine, he reversed them and he turned out to be correct. Where Mendeleev predicted elements should be, he left gaps in his table to accommodate them. Subsequently, scientists discovered these missing elements (for example germanium, gallium, and scandium). In fact, we now know that it is not atomic weight (that is the number of protons and neutrons) but rather atomic number, Z, (the number of protons and electrons) that increases periodically. This explains why tellurium (atomic mass 127.6, Z = 52) must come before iodine (atomic mass 126.9, Z = 53). The important point to note is that although the modern periodic table is arranged in order of increasing number of protons and electrons, the repetition and patterns that emerge are the property of the electrons, their arrangements, and energies. This is our next subject.

Question to Answer

- Science fiction authors like weird elements. Provide a short answer for why no new elements with atomic numbers below 92 are possible.
- Isotopes of the same element are very similar chemically. What does that imply about what determines chemical behavior?

Questions to Ponder

- Why do you think there were no noble gases in Mendeleev's periodic table?
- Why aren't the atomic weights in Mendeleev's periodic table whole numbers?
- Why would you expect different isotopes of the same element to differ in stability?
- You discover a new element. How would you know where would it should go in the periodic table?

2.6 Orbitals, Electron Clouds, Probabilities, and Energies

Our current working model of the atom is based on quantum mechanics that incorporate the ideas of quantized energy levels, the wave properties of electrons, and the uncertainties associated with electron location and momentum. If we know their energies, which we do, then the best we can do is to calculate a probability distribution that describes the likelihood of where a specific electron might be found, if we were to look for it. If we were to find it, we would know next to nothing about its energy, which implies we would not know where it would be in the next moment. We refer to these probability distributions by the anachronistic, misleading, and Bohrian term orbitals. Why misleading? Because to a normal person, the term orbital implies that the electron actually has a defined and observable orbit, something that is simply impossible to know (can you explain why?)

Another common and often useful way to describe where the electron is in an atom is to talk about the electron probability density or electron density for short. In this terminology, electron density represents the probability of an electron being within a particular volume of space; the higher the probability the more likely it is to be in a particular region at a particular moment. Of course you can't really tell if the electron is in that region at any particular moment because if you did you would have no idea of where the electron would be in the next moment.

Erwin Schrödinger (1887–1961) developed, and Max Born (1882–1970) extended, a mathematical description of the behavior of electrons in atoms. Schrödinger used the idea of electrons as waves and described each atom in an element by a mathematical wave function using the famous Schrödinger equation ($H\Psi = E\Psi$). We assume that you have absolutely no idea what either $H\Psi$ or $E\Psi$ are but don't worry—you don't really need to. The solutions to the Schrödinger equation are a set of equations (wave functions) that describe the energies and probabilities of finding electrons in a region of space. They can be described in terms of a set of quantum numbers; recall that Bohr's model also invoked the idea of quantum numbers. One way to think about this is that almost every aspect of an electron within an atom or a molecule is quantized, which means that only defined values are allowed for its energy, probability distribution, orientation, and spin. It is far beyond the scope of this book to present the mathematical and physical basis for these calculations, so we won't pretend to try. However, we can use the results of these calculations to provide a model for the arrangements of electrons in an atom using orbitals, which are mathematical descriptions of the probability of finding electrons in space and determining their energies. Another way of thinking about the electron energy levels is that they are the energies needed to remove that electron from the atom or to move an electron to a "higher" orbital. Conversely, this is the same amount of energy released when an electron moves from a higher energy to a lower energy orbital. Thinking back to spectroscopy, these energies are also related to the wavelengths of light that an atom will absorb or release. Let us take a look at some orbitals, their quantum numbers, energies, shapes, and how we can used them to explain atomic behavior.

Examining Atomic Structure Using Light

J.J. Thompson's studies (remember them?) suggested that all atoms contained electrons. We can use the same basic strategy in a more sophisticated way to begin to explore the organization of electrons in particular atoms. This approach involves measuring the amount of energy it takes to remove electrons from atoms. This is known as the element's ionization energy which in turn relates directly back to the photoelectric effect.

All atoms are by definition electrically neutral, which means they contain equal numbers of positively- and negatively-charged particles (protons and electrons). We cannot remove a proton from an atom without changing the identity of the element because the number of protons is how we define elements, but it is possible to add or remove an electron, leaving the atom's nucleus unchanged. When an electron is removed or added to an atom the result is that the atom has a net charge. Atoms (or molecules) with a net charge are known as ions, and this process (atom/molecule to ion) is called ionization. A positively charged ion (called a cation) results when we remove an electron; a negatively charged ion (called an anion) results when we add an electron. Remember that this added or removed electron becomes part of, or is removed from, the atom's electron system.

Now consider the amount of energy required to remove an electron. Clearly energy is required to move the electron away from the nucleus that attracts it. We are perturbing a stable system that exists at a potential energy minimum – that is the attractive and repulsive forces are equal at this point. We might naively predict that the energy required to move an electron away from an atom will be the same for each element. We can test this assumption experimentally by measuring what is called the ionization potential. In such an experiment, we would determine the amount of energy (in kilojoules per mole of molecules) required to remove an electron from an atom. Let us consider the situation for hydrogen (H). We can write the ionization reaction as:

$$\text{H (gas)} + \text{energy} \rightarrow \text{H}^{+}\text{ (gas)} + \text{e}^{-}.$$ [47]

What we discover is that it takes 1312 kJ to remove a mole of electrons from a mole of hydrogen atoms. As we move to the next element, helium (He) with two electrons, we find that the energy required to remove an electron from helium is 2373 kJ/mol, which is almost twice that required to remove an electron from hydrogen!

Let us return to our model of the atom. Each electron in an atom is attracted to all the protons, which are located in essentially the same place, the nucleus, and at the same time the electrons repel each other. The potential energy of the system is modeled by an equation where the potential energy is proportional to the product of the charges divided by the distance between them. Therefore the energy to remove an electron from an atom should depend on the net positive charge on the nucleus that is attracting the electron and the electron's average distance from the nucleus. Because it is more difficult to remove an electron from a helium atom than from a hydrogen atom, our tentative conclusion is that the electrons in helium must be attracted more strongly to the nucleus. In fact this makes sense: the helium nucleus contains two protons, and each electron is attracted by both protons, making them more difficult to remove. They are not attracted exactly twice as strongly because there are also some repulsive forces between the two electrons.

The size of an atom depends on the size of its electron cloud, which depends on the balance between the attractions between the protons and electrons, making it smaller, and the repulsions between electrons, which makes the electron cloud larger.[48] The system is most stable when the repulsions balance the attractions, giving the lowest potential energy. If the electrons in helium are attracted more strongly to the nucleus, we might predict that the size of the helium atom would be smaller than that of hydrogen. There are several different ways to measure the size of an atom and they do indeed indicate that helium is smaller than hydrogen. Here we have yet another counterintuitive idea: apparently, as atoms get heavier (more protons and neutrons), their volume gets smaller!

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[47] These experiments are carried out using atoms in the gas phase in order to simplify the measurement.

[48] There are a number different ways of defining the size of an atom, and in fact the size depends on the atom's chemical environment (for example, whether it is bonded to another atom or not). In fact, we can only measure the positions of atomic nuclei, and it is impossible to see where the electron cloud actually ends; remember that orbitals are defined as the surface within which there is a 90% probability of finding an electron. Therefore, we often use the van der Waals radius, which is half the distance between the nuclei of two adjacent unbonded atoms.

Given that i) helium has a higher ionization energy than hydrogen and ii) that helium atoms are smaller than hydrogen atoms, we infer that the electrons in helium are attracted more strongly to the nucleus than the single electron in hydrogen. Let us see if this trend continues as we move to the next heaviest element, lithium (Li). Its ionization energy is 520 Kj/mol. Oh, no! This is much lower than either hydrogen (1312 kJ/mol) or helium (2373 kJ/mol). So what do we conclude? First, it is much easier (that is, requires less energy) to remove an electron from Li than from either H or He. This means that the most easily removed electron in Li is somehow different than are the most easily removed electrons of either H or He. Following our previous logic we deduce that the "most easily removable" electron in Li must be further away (most of the time) from the nucleus, which means we would predict that a Li atom has a larger radius than either H or He atoms. So what do we predict for the next element, beryllium (Be)? We might guess that it is smaller than lithium and has a larger ionization energy because the electrons are attracted more strongly by the four positive charges in the nucleus. Again, this is the case. The ionization energy of Be is 899 kJ/mol, larger than Li, but much smaller than that of either H or He. Following this trend the atomic radius of Be is smaller than Li but larger than H or He. We could continue this way, empirically measuring ionization energies for each element (see figure), but how do we make sense of the pattern observed, with its irregular repeating character that implies complications to a simple model of atomic structure?

Questions to Answer

- Why are helium atoms smaller than hydrogen atoms?
- What factors govern the size of an atom? List all that you can. Which factors are the most important?

Questions to Ponder

- What would a graph of the potential energy of a hydrogen atom look like as a function of distance of the electron from the proton?
- What would a graph of the kinetic energy of an electron in a hydrogen atom look like as a function of distance of the electron from the nucleus?
- What would a graph of the total energy of a hydrogen atom look like as a function of distance of the electron from the proton?

2.7 Quantum Numbers[49]

Quantum numbers (whose derivation we will not consider here) provide the answer to our dilemma. Basically we can describe the wave function for each individual electron in an atom by a distinct set of three quantum numbers, known as n, l, and m_l. The principal quantum number, n, is a non-zero positive integer (n = 1, 2, 3, 4, etc.). These are often referred to as electron shells or orbitals, even though they are not very shell- or orbital-like. The higher the value of n, the higher the overall energy level of the electron shell. For each value of n there are only certain allowable values of l, and for each value of l, only certain allowable values of m_l. Table 2.1 (next page) shows the allowable values of l and m_l for each value of n are shown. There are a few generalizations we can make. Three quantum numbers, n, l, and $m_{l,}$ describe each orbital in an atom and each orbital

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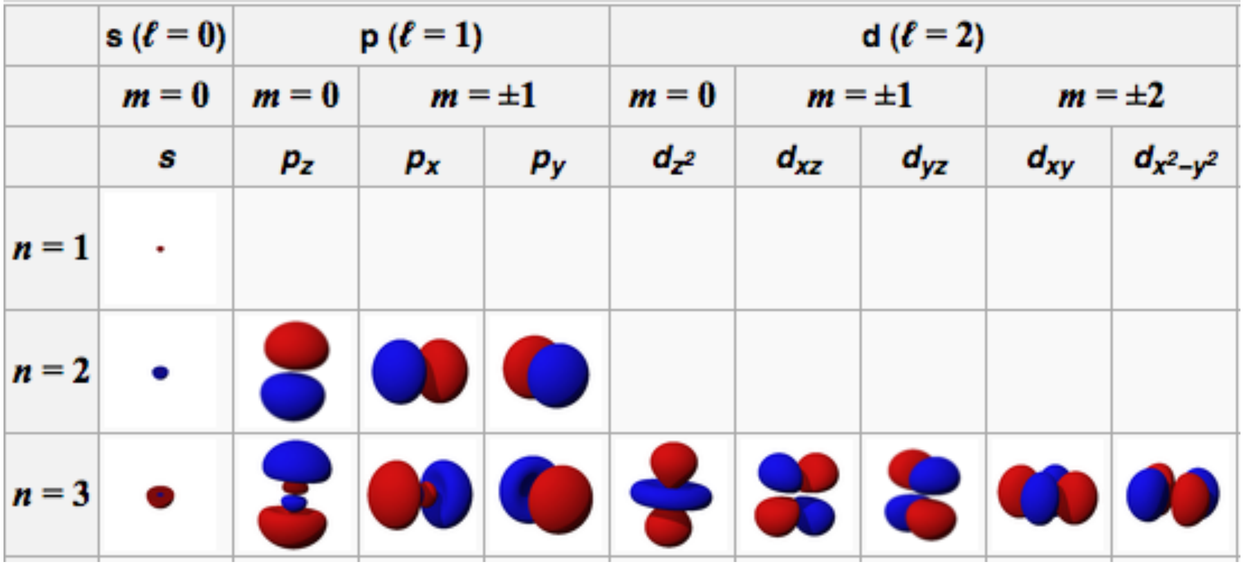
[49] For more information see: http://winter.group.shef.ac.uk/orbitron/AOs/1s/index.html
http://www.uark.edu/misc/julio/orbitals/index.html

can contain a maximum of two electrons. As they are typically drawn, each orbital defines the space in which the probability of finding an electron is 90%. Because each electron is described by a unique set of quantum numbers, the two electrons within a particular orbital must be different in some way.[50] But because they are in the same orbital they must have the same energy and the same probability distribution. So what property is different? This property is called spin. The spin can have values of either + ½ or – ½. Spin is responsible for a number of properties of matter including magnetism.

Hydrogen has one electron in a 1s orbital and we write its electron configuration as $1s^1$. Helium has both of its electrons in the 1s orbital ($1s^2$). In lithium, the electron configuration is $1s^2$ $2s^1$, which tells us that during ionization, an electron is being removed from a 2s orbital. Quantum mechanical calculations tell us that in 2s orbital there is a higher probability of finding electrons farther out from the nucleus than the 1s orbital, so we might well predict that it takes less energy to remove an electron from a 2s orbital (found in Li) than from a 1s orbital (found in H). Moreover, the two 1s electrons act as a sort of shield between the nucleus and the 2s electrons. The 2s electrons feel what is called the effective nuclear charge, which is smaller than the real charge because of shielding by the 1s electrons. In essence, two of the three protons in the lithium nucleus are counterbalanced by the two 1s electrons. The effective nuclear charge in lithium is +1. The theoretical calculations are borne out by the experimental evidence—always a good test of a theory.



	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)				
	$m = 0$	$m = 0$	$m = \pm 1$		$m = 0$	$m = \pm 1$		$m = \pm 2$	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$
$n = 1$									
$n = 2$									
$n = 3$									

Table 2.1 Elemental electron shell organization

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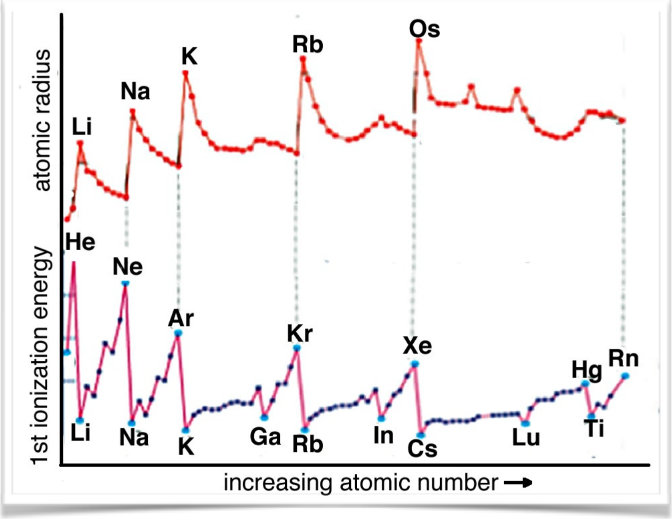
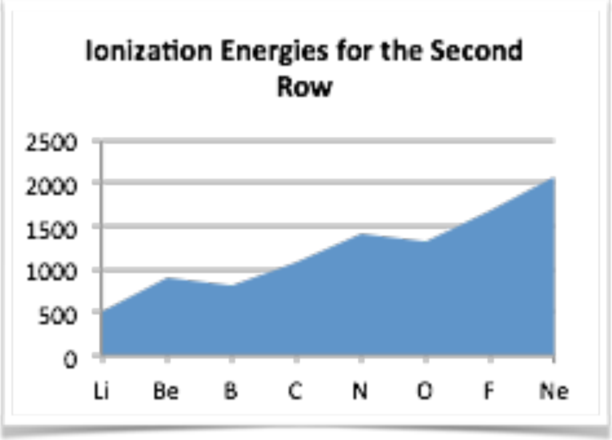
[50] This is called the Pauli exclusion principle, which states that no two electrons may occupy the same quantum state; that is, no two electrons can have the same value for all four quantum numbers.



At this point, you might start getting cocky; you may even be ready to predict that ionization energies across the periodic table from lithium to neon (Ne) will increase, with a concomitant decrease in atomic radius. In the case of atomic radius, this is exactly what we see in the figure – as you go across any row in the periodic table the atomic radius decreases. Again, the reason for both these trends is that same: that is, each electron is attracted by an increasing number of protons as you go from Li to Ne, which is to say that the effective nuclear charge is increasing. Electrons that are in the same electron shell do not interact much and each electron is attracted by all the unshielded charge on the nucleus. By the time we get to fluorine (F), which has an effective nuclear charge of 9 – 2 = +7, and neon (10 – 2 = +8), each of the electrons are very strongly attracted to the nucleus, and very difficult to dislodge. Meaning that the size of the atom gets smaller, and the ionization energy gets larger.

As you have undoubtedly noted from considering the graph, the increase in ionization energy from lithium to neon is not uniform: there is a drop in ionization energy from beryllium to boron and from nitrogen to oxygen. This arises from the fact that as the number of electrons in an atom increases the situation becomes increasingly complicated. Electrons in the various orbitals influence one another and some of these effects are quite complex and chemically significant. We will return to this in a little more detail in Chapter 3 and at various points through the rest of the book.



If we use the ideas of orbital organization of electrons, we can make some sense of patterns observed in ionization energies. Let us go back to the electron configuration. Beryllium (Be) is $1s^2$ $2s^2$ whereas Boron (B) is $1s^2$ $2s^2$ $2p^1$. When electrons are removed from Be and B they are removed from the same quantum shell (n = 2) but, in the case of Be, one is removed from the 2s orbital whereas in B, the electron is removed from a 2p orbital. s orbitals are spherically symmetric, p orbitals have a dumbbell shape and a distinct orientation. Electrons in a 2p orbital have lower ionization energies because they are on average a little further from the nucleus and so a little more easily removed compared to 2s electrons. That said, the overall average atomic radius of boron is smaller than beryllium, because on average all its electrons spend more time closer to the nucleus.

The slight drop in ionization potential between nitrogen and oxygen has a different explanation. The electron configuration of nitrogen is typically written as $1s^2\ 2s^2\ 2p^3$, but this is misleading: it might be better written as $1s^2\ 2s^2\ 2px^1\ 2py^1\ 2pz^1$, with each 2p electron located in a separate p orbital. These p orbitals have the same energy but are oriented at right angles (orthogonally) to one another. This captures another general principle: electrons do not pair up into an orbital until they have to do so.[51] Because the p orbitals are all of equal energy, each of them can hold one electron before pairing is necessary. When electrons occupy the same orbital there is a slight repulsive and destabilizing interaction; when multiple orbitals of the same energy are available, the lowest energy state is the one with a single electron in an orbital. Nitrogen has all three 2p orbitals singly occupied and therefore the next electron, which corresponds to oxygen, has to pair up in one of the p orbitals. Thus it is slightly easier to remove a single electron from oxygen than it is to remove a single electron from nitrogen, as measured by the ionization energy.

To pull together a set of seriously obscure ideas, the trends in ionization energies and atomic radii indicate that electrons are not uniformly distributed around an atom's nucleus but rather have distinct distributions described by the rules of quantum mechanics. Although we derive the details of these rules from rather complex calculations and the wave behavior of electrons, we can cope with them through the use of quantum numbers and electron probability distributions. Typically electrons in unfilled shells are more easily removed or reorganized than those in filled shells because atoms with unfilled shells have higher effective nuclear charges. Once the shell is filled, the set of orbitals acts like a shield and cancels out an equal amount of nuclear charge. The next electron goes into a new quantum shell and the cycle begins again. This has profound implications for how these atoms react with one another to form new materials because, as we will see, chemical reactions involve those electrons that are energetically accessible: the valence electrons.

We could spend the rest of this book (and probably one or two more) discussing how electrons are arranged in atoms but in fact your average chemist is not much concerned with atoms as entities in themselves. As we have said before, naked atoms are not at all common. What is common is combinations of atoms linked together to form molecules. From a chemist's perspective, we need to understand how, when, and where atoms interact. The electrons within inner and filled quantum shells are "relatively inert" which can be translated into English to mean that it takes quite a lot of energy (from the outside world) to move them around. Chemists often refer to these electrons as core electrons, which generally play no part in chemical reactions; we really do not need to think about them much more except to remember that they form a shield between the nucleus and the outer electrons. The results of their shielding does, however, have effects on the strong interactions, commonly known as bonds, between atoms of different types, which we will discuss in Chapters 4 and 5. Reflecting back on Chapter 1, we can think about the distinction between the London Dispersion Forces acting between He atoms and between H_2 molecules versus the bonds between the two H atoms in a H_2 molecule.

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[51] This is often called Hund's rule. Just as passengers on a bus do not sit together until they have to, neither do electrons.

Bonds between atoms involve the valence electrons found in outer, and usually partially filled, orbitals. Because of the repeating nature of electron orbitals, it turns out that there are patterns in the nature of interactions atoms make—a fact that underlies the organization of elements in the periodic table. We will come back to the periodic table once we have considered how atomic electronic structure influences the chemical properties of the different elements.

Questions to Answer

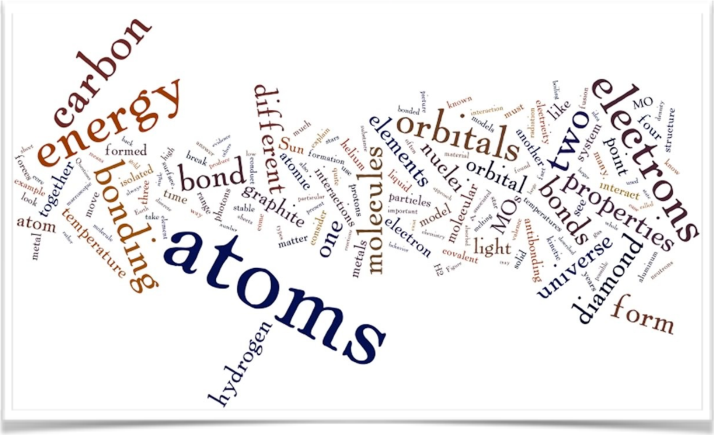
- Try to explain the changes in ionization potential as a function of atomic number by drawing your impression of what each atom looks like as you go across a row of the periodic table, and down a group.

Questions to Ponder

- How does the number of valence electrons change as you go down a group in the periodic table? How does is change as you go across a row?
- How do you think the changes in effective nuclear charge affect the properties of elements as you go across a row in the periodic table?

Chapter 3: Elements, Bonding, and Physical Properties

3.1 Where Do Atoms Come From?



"We are stardust, we are golden, We are billion-year-old carbon."

– WOODSTOCK, JONI MITCHELL

"Sometimes I've believed as many as six impossible things before breakfast."

– ALICE IN WONDERLAND, LEWIS CARROLL

Did you ever stop to ask yourself where the atoms in your body came from? Common answers might be that the atoms in our bodies come from food, water, or air. But these are not the ultimate answers, because we then need to ask, where did the atoms in food, water, and air come from? Where did the atoms in the Earth come from? There are really two general possibilities: either the atoms that make up the Earth and the rest of the universe are eternal or they were generated/created by some process. How do we decide which is true? What is the evidence favoring one model over the other? The answers come not from chemistry, but from astrophysics.

Given that we are thinking scientifically what kinds of evidence can we look for to decide whether atoms (or the universe) are eternal or recently created? Clearly we must be able to observe the evidence here and now and use it to formulate logical ideas that make clear and unambiguous predictions. As we will see we will be called upon once again to believe many apparently unbelievable things. The current organizing theory in astrophysics and cosmology, known as the Big Bang theory, holds that the universe is ~13,820,000,000 ± 120,000,000 years old or 13.82 ± 0.12 billion years - an unimaginable length of time. The Sun and Earth are ~5,000,000,000 years old, and the universe as a whole is ~156 billion light-years in diameter.[52]

The Big Bang theory was put forward in a response to the observation that galaxies in the universe appear to be moving away from one another. Because the galaxies that are further away from us are moving away more rapidly than those that are closer, it appears that space itself is expanding, another seriously weird idea.[53] Based on this observation, we can carry out what scientists call a thought experiment. What happens if we run time backwards, so that the universe is contracting rather than expanding? Taken to its logical conclusion, the universe would shrink until, at some point, all of the universe would be in a single place, at a single point, which would be unimaginably dense. Based on a range of astronomical measurements, this so-called singularity existed ~13.73 x 10^9 years ago, which means the universe is about 13.73 billion years old. The Big

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[52] http://www.space.com/scienceastronomy/mystery_monday_040524.html

[53] http://www.youtube.com/watch?v=th_9ZR2I0_w&feature=c4-overview&list=UUUHW94eEFW7hkUMVaZz4eDg

Bang theory tells us nothing about what happened before 13.73 x 10^9 years ago, and although there is no shortage of ideas, nothing scientific can be said about it, because it is theoretically unobservable, or at least that is what we have been led to believe by astrophysicists!

Thinking About Atomic Origins

The current model of the universe begins with a period of very rapid expansion, from what was essentially a dimensionless point, a process known as inflation. As you might well imagine there is some debate over exactly what was going on during the first 10^{-43} seconds (known as the Planck time) after the universe's origin. Surprisingly, there is a remarkable level of agreement on what has happened since then.[54] This is because there is lots of observable evidence that makes it relatively easy to compare hypotheses, accepting some and ruling out others. Initially remarkably hot (about 10^{23} K), over time the temperature (local energy levels) of the universe dropped to those that are reachable in modern particle accelerators, so we have actual experimental evidence of how matter behaves under these conditions. At 1 picosecond after the Big Bang, there were no atoms, protons, or neutrons, because the temperature was simply too high. There were only elementary particles such as photons, quarks, and leptons (electrons are leptons) - particles that appear to have no substructure. By the time the universe was ~0.000001 seconds old (a microsecond or 1 x 10^{-6} second), the temperature had dropped sufficiently to allow quarks and gluons to form stable structures, and protons and neutrons appeared. A few minutes later the temperature dropped to about 1,000,000,000 K (1 x 10^9 K), which is low enough for some protons and neutrons to stick together and stay together without flying apart again. That is, the kinetic energy of the particles colliding with them was less than the forces (the weak and strong nuclear forces) holding the protons, neutrons, and nuclei together. At this point the density of particles in the universe was about that of our air.

By the time the universe was a few minutes old it contained mostly hydrogen (${}^{1}H^{1}$ = one proton, no neutrons) and deuterium (${}^{2}H^{1}$ = one proton and one neutron) nuclei, with some helium (${}^{3}He^{2}$ and ${}^{4}He^{2}$ = two protons and either one or two neutrons, respectively), and a few lithium (${}^{7}Li^{3}$ = three protons and four neutrons).[55] These nuclei are all formed by nuclear fusion reactions such as

$$ {}^{1}p^{+} + {}^{1}n^{0} \rightarrow {}^{2}H^{+} + \text{gamma radiation and } {}^{2}H^{+} + {}^{2}H^{+} \rightarrow {}^{3}He^{2+} + {}^{1}n^{0}. $$

These fusion reactions take place in a temperature range where the nuclei have enough kinetic energy to overcome the electrostatic repulsion associated with the positively charged protons but less than that needed to disrupt the nuclei once formed. After a few minutes the temperature of the universe fell below ~10,000,000 (10^7) K. At these temperatures, the kinetic energy of protons and

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[54] http://www.astro.ucla.edu/~wright/BBhistory.html

[55] In this nomenclature (described more on the web), the first superscript number is the number of proton and neutrons, while the second superscript number is the number of protons; both numbers are always integers. The letter is the symbol of the element, e.g. He for helium or Li for lithium.

nuclei was no longer sufficient to overcome the electrostatic repulsion between their positive charges. The end result was that there was a short window of time following the Big Bang when a certain small set of nuclei (including $^{1}H^{+}$, $^{2}H^{+}$, $^{3}He^{2+}$, $^{4}He^{2+}$, and $^{7}Li^{3+}$) could be formed. After ~400,000 years the temperature of the universe had dropped sufficiently for electrons to begin to associate in a stable manner with these nuclei and the first atoms (as opposed to bare nuclei) were formed. This early universe was made up of mostly (> 95%) hydrogen atoms with a small percentage each of deuterium, helium, and lithium, which is chemically not very interesting.

The primary evidence upon which these conclusions are based comes in the form of the cosmic microwave background radiation (CMBR), which is the faint glow of radiation that permeates the universe. The CMBR is almost perfectly uniform which means that no matter where you look in the sky the intensity of the CMBR is (essentially) the same. To explain the CMBR, scientists assume that the unimaginably hot and dense early universe consisted almost entirely of a plasma of hydrogen nuclei that produced vast amounts of electromagnetic radiation, meaning that the early universe glowed. The CMBR is what is left of this radiation, it is a relic of that early universe. As the universe expanded it cooled but those photons continued to whiz around. Now that they have to fill a much larger universe individual photons have less energy, although the total energy remains the same! The current background temperature of the universe is ~2.27 K, which corresponds to a radiation wavelength of ~1.9 mm (radiation in the microwave region); hence the name cosmic microwave background radiation.

After a billion years or so things began to heat up again literally (albeit locally). As in any randomly generated object the matter in the universe was not distributed in a perfectly uniform manner and as time passed this unevenness became more pronounced as the atoms began to be gravitationally attracted to each other. The more massive the initial aggregates the more matter was attracted to them. As the clumps of (primarily) hydrogen became denser the atoms banged into each other and these systems, protostars, began to heat up. At the same time the gravitational attraction resulting from the overall mass of the system caused the matter to condense into an even smaller volume and draw in more (mostly) hydrogen. As this matter condensed its temperature increased, as gravitational potential energy was converted into kinetic energy. At a temperature of ~10,000,000 (10^{7}) K the atoms (which had lost their electrons again because of the higher temperature) began to undergo nuclear fusion. At this point we would probably call such an aggregate of matter a star. This process of hydrogen fusion produced a range of new types of nuclei. Hydrogen fusion, or hydrogen burning as it is sometimes called, is exemplified by reactions such as the formation of helium nuclei:

$$4\ ^{1}H^{+} \rightarrow\ ^{4}He^{2+} + 2e^{+} + \text{energy.}$$

When four protons are fused together they produce one helium-4 nucleus, containing two protons and two neutrons, plus two positrons (e^{+} - the antiparticle of the electron), and a great deal of energy. As the number of particles decreases (4 $^{1}H^{+}$ into 1 $^{4}He^{2+,}$), the volume decreases. Gravity produces an increase in the density of the star (fewer particles in a smaller volume). The star's core, where fusion occurs, gets smaller and smaller. The core does not usually collapse totally into a black hole, because the particles have a huge amount of kinetic energy, which keeps them in motion and moving on average away from one another.[56]

As the star's inner temperature reaches ~10^8 K there is enough kinetic energy available to drive other fusion reactions. For example three helium nuclei could fuse to form a carbon nuclei:

$3\ {}^{4}He^{2+} \rightarrow {}^{12}C^{6+}$ + lots of energy (note again, the result is fewer atoms).

If the star is massive enough, a further collapse of its core would increase temperatures so that carbon nuclei could fuse, leading to a wide range of new types of nuclei, including those of elements up to iron (${}^{56}Fe^{26+}$) and nickel (${}^{58}Ni^{28+}$), as well as many of the most common elements found in living systems, such as nitrogen (Ni^7), oxygen (O^8), sodium (Na^{11}), magnesium (Mg^{12}), phosphorus (P^{15}), sulfur (S^{16}), chlorine (Cl^{17}), potassium (K^{19}), calcium (Ca^{20}), manganese (Mn^{25}), cobalt (Co^{27}), copper (Cu^{29}), and zinc (Zn^{30}).

In some instances these nuclear reactions cause a rapid and catastrophic contraction of the star's core followed by a vast explosion called a supernova. Supernovae can be observed today, often by amateur astronomers, in part because seeing one is a matter of luck. They are characterized by a sudden burst of electromagnetic radiation, as the supernova expels most of its matter into interstellar dust clouds. The huge energies involved in such stellar explosions are required to produce the naturally occurring elements heavier than iron and nickel, up to and including Uranium (Ur^{82+}). The material from a supernova is ejected out into the interstellar regions, only to reform into new stars and planets and so begin the process all over. So the song is correct, many of the atoms in our bodies were produced by nuclear fusion reactions in the cores of stars that, at one point or another, must have blown up; we are literally stardust, except for the hydrogen formed before there were stars!

Looking at Stars

At this point you may still be unclear as to how we know all this. How can we know about processes and events that took place billions of years ago? Part of the answer lies in the fact that all the processes involved in the formation of new elements are still occurring today in the centers of stars. Our own Sun is an example of a fairly typical star; it is composed of ~74% (by mass) and ~92% (by volume) hydrogen, ~24% helium, and trace amounts of heavier elements. There are many other stars (billions) just like it. How do we know? Analysis of the emission spectra of the light emitted by the Sun or the light emitted from any other celestial object enables us to deduce which elements are present.[57] Similarly, we can deduce which elements and molecules are present in the

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[56] Nuclear fusion releases huge amounts of energy (some of the mass is transformed into energy). On Earth, controllable nuclear fusion has long been a potential target in the search for new energy sources, but so far the energy required to bring about the initial fusion has not been replaced when the fusion occurs – i.e., nuclear fusion reactors have yet to break even. Uncontrolled nuclear fusion takes place in hydrogen bombs – clearly not a viable option for a useful energy source at the moment. Nuclear fusion does however take place in stars, and is self-sustaining. The reason you can see and feel the energy from the Sun is that is it undergoing nuclear fusion reactions, which supply us with almost all the energy that is used on Earth today.

[57] It has been estimated that it takes between 10,000 to 170,000 years for a photon released during a fusion reaction at the Sun's core to reach its surface. http://sunearthday.nasa.gov/2007/locations/ttt_sunlight.php

clouds between stars by looking at which wavelengths of light are absorbed! Remember that emission/absorption spectra are a result of the interaction between the atoms of a particular element and electromagnetic radiation (light). They serve as a fingerprint of that element (or molecule). The spectrum of a star reveals which elements are present. No matter where an element is found in the universe it appears to have the same spectroscopic properties.

Astrophysicists have concluded that our Sun is a third generation star, which means that the material in it has already been through two cycles of condensation and explosive redistribution. This conclusion is based on the fact that the Sun contains materials (heavy elements) that it could not have formed itself, and so must have been generated previously within larger and/or exploding stars. Various types of data indicate that the Sun and its planetary system were formed by the rapid collapse of a molecular (mostly hydrogen) cloud ~4.59 billion years ago. It is possible that this collapse was triggered by a shock wave from a nearby supernova. The gas condensed in response to gravitational attraction and the conservation of angular momentum; most of this gas (>98%) became the Sun, and the rest formed a flattened disc, known as a planetary nebulae. The planets were formed from this disc, with the small rocky/metallic planets closer to the Sun, gas giants further out, and remnants of the dust cloud distributed in the Oort cloud.[58] As we will see, living systems as we know them depend upon elements produced by second and third generation stars. This process of planet formation appears to be relatively common and more and more planetary systems are being discovered every year.[59]

Stars have a life cycle from birth to death; our Sun is currently about half way through this life cycle. There is not enough matter in the Sun for it to become a supernova, so when most of its hydrogen has undergone fusion, ~5 billion years from now, the Sun's core will collapse and helium fusion will begin. This will lead to the formation of heavier elements. At this point, scientists predict that the Sun's outer layer will expand and the Sun will be transformed into a red giant. Its radius will grow to be larger than the Earth's current orbit. That will be it for life on Earth, although humans are likely to become extinct much sooner than that. Eventually the Sun will lose its outer layers of gas and they may become a part of other stars elsewhere in the galaxy. The remaining core will shrink, grow hotter and hotter, and eventually form a white dwarf star. Over (a very long) time, the Sun will cool down, stop emitting light, and fade away.

Questions to Answer

- How do the properties of isolated atoms or molecules give rise to the world we observe? Why are objects different colors, or have different melting points?
- Do isolated atoms/molecules exist in a state such as solid, liquid, or gas?
- Where do the atoms in your body come from? (Trace their origin back as far as you can.)
- How does the size of the universe influence the density of particles?
- How many protons, neutrons, and electrons does ^{4}He have? How about $^{4}He^{2+}$?
- Generate a graph that estimates the number of atoms in the universe as a function of time, beginning with

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[58] More physics that we will conveniently pass over, but it is worth noting that this is why the planets all move around the Sun in the same direction.

[59] You may want to search the web for "extrasolar planets."

the Big Bang and continuing up to the present day.

- Draw another graph to illustrate the number of elements in the universe as a function of time. Explain your reasoning behind both graphs.

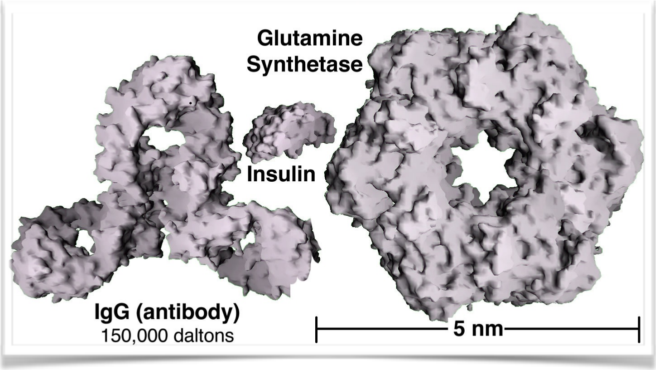
Questions to Ponder

- Can an atom of one element change into an atom of another element?
- Is the number of atoms in the universe constant?
- How does the big bang theory constrain the time that life could have first arisen in the universe?

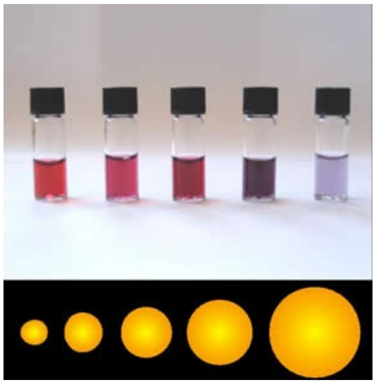
Up to now we have been concerned mainly with isolated atoms, an extremely abstract topic. We now move on to consider the macroscopic behavior of atoms, that is, the behaviors of very, very large numbers of atoms that form the materials that we touch, feel, smell, and observe with our own eyes. Before we do that, it is important to understand and be explicit about what properties atoms, molecules, and their aggregates can and cannot exhibit.

3.2 Micro, Macro, and Emergent Properties

When atoms interact with one another to form molecules or larger structures, the molecules have different properties than their component atoms; they display what are often referred to as emergent properties, where the whole is more than, or different from the sum of its parts. In a similar way groups of atoms or molecules have different properties from isolated atoms/molecules. For example while groups of atoms/molecules exist in solid, liquid, or gaseous states, and often have distinct colors and other properties, isolated atoms/molecules do not; there are no solid or liquid isolated atoms and they do not have a color or a boiling point. So the obvious question is, how many atoms or molecules need to aggregate before they display these emergent properties, before they have a color, before they have a melting point, boiling point, heat capacity, and other properties that isolated atoms do not? The answer is not completely simple, as you are probably slowly coming to expect. As we add more and more atoms or molecules together their properties change but not all at once. You have probably heard about nanoscience and nanotechnologies, which have been the focus of a great deal of research and economic interest in the past decade or so. Nanoparticles are generally classified as being between 1 and 100 nm in diameter (a nanometer is one billionth of a meter or 1 x 10^{-9} m). Such particles often have properties that are different from those of bulk (macroscopic) materials. Nanomaterials can be thought of as a bridge between the atomic-molecular and macroscopic scales.



Assuming that they are pure, macroscopic materials have predictable properties and it doesn't really matter the size of the sample. A macroscopic sample of pure gold behaves the same regardless of its size and if



Archimedes (ca. 287–212 BCE) were alive today, he could tell you whether it was pure or not based on its properties, for example, its density. But gold nanoparticles have different properties depending upon their exact size. For example, when suspended in water, they produce colors ranging from orange to purple, depending on their diameter (see Figure). Often the differences in the properties displayed are due to differences in the ratio of surface area to volume, which implies that intermolecular forces (forces between molecules) are more important for nanomaterials. As we cluster more and more particles together, the properties of the particles change. Biomolecules generally fall into the size range of nanomaterials, and as we will see their surface properties are very important in determining their behavior.

Unfortunately when we are talking about the properties of atoms and molecules versus substances and compounds, it can be difficult, even for experienced chemists, to keep the differences clear. In addition different representations are often used for different organizational levels; it is an important skill to be able to recognize and translate between levels. We will be using a range of representations to picture atoms and molecules; chemists (and we) typically use various shorthand rules, methods, and chemical equations to represent molecular composition, shape, and behaviors. But just knowing the equations, often the only thing learned in introductory chemistry courses, is not sufficient to understand chemistry and the behavior of atoms and molecules. Much of the information implied by even the simplest chemical equations can easily be missed—or misunderstood—if the reader does not also have a mental picture of what the diagram or equation represents, how a molecule is organized and its shape, and how it is reorganized during a particular reaction. We will be trying to help you get these broader pictures, which should you make sense of the diagrams and equations used here. That said, it is always important to try to explicitly identify what you are assuming when you approach a particular chemical system; that way you can go back and check whether your assumptions are correct.

3.3 Scaling Up

Now we have an idea about where atoms come from and we know that individual atoms as well as small groups of atoms (nanoparticles) have properties that are different from large groups of atoms. However, in most cases we are dealing with bulk substances that, unlike atoms or nanoparticles, we can see with our eyes and weigh out on a balance. So how do we scale up from atoms and molecules to the macroscopic substances we deal with every day? We use a conversion factor called the mole.

The mole is an SI unit that is officially defined as “the number of carbon atoms that are in exactly 12 g of C-12.” It turns out that this is about 6.02×10^{23} atoms, to three significant figures. We refer to 6.02×10^{23} as Avagadro’s number, named after the early 19th-century Italian scientist Amedeo Avogadro. Although the mole is an SI unit with an official definition, in practice we use the mole and Avagadro’s number as a counting conversion factor much like a dozen. For example, if you have 2 dozen eggs, you have 2 dozen x 12 eggs/dozen = 24 eggs. The same is true for the mole; if you have two moles of sodium (Na) atoms, you have 2 moles x (6.02×10^{23} Na atoms/mole) = 1.20×10^{24} Na atoms.

Conveniently, the mole also allows us to easily convert between atomic mass units and grams using the periodic table. The average masses shown under each element on the periodic table can be read in either atomic mass units (mass of one atom) or grams per mole (mass of one mole of atoms), which we call molar masses. The table below provides a few examples:

Element	Mass of one Atom	Molar Mass
C	12.011 amu	12.011 g/mol
H	1.0079 amu	1.0079 g/mol
O	15.999 amu	15.999 g/mol
Mg	24.305 amu	24.305 g/mol

We can use this information to determine molar masses for compounds as well. For example, to determine the molar mass of water (H_2O) we would take two times the molar mass of H (2 x 1.0079 g/mol) and add the molar mass of O (15.999 g/mol). This would give us 18.012 g/mol for the molar mass of water. Much like we use density to convert between mass and volume, we can use molar mass to convert between masses and moles. For example, if we have 10.00 g of water we can figure out how many moles of water molecules we have as follows:

10.00 g H_2O x 1 mol H_2O/18.012 g H_2O = 0.555 mol H_2O

Questions to Answer

- Why can't we mass individual atoms or small groups of atoms on a balance? What would be the mass in grams of 100 C atoms?
- What would the molar mass of calcium nitrate be? The formula for calcium nitrate is $Ca(NO_3)_2$.

Questions to Ponder

- If you are reacting sodium (Na) and sulfur (S) together to form a compound according to the following chemical equation, if you reacted 20 grams of Na with 10 grams of S would you expect all of the sodium and sulfur to react? Why or why not?

$$2\ Na + S \rightarrow Na_2S$$

3.4 Elements and Their Interactions

"From the 115 elements you can build a near infinity of molecules, of any type you need, to get all the structural and functional diversity you can ask for. There are at least 100,000 different molecules in the human body. Some 900 volatile aroma components have been found in wine. Chemistry is molecules. We are molecules. Chemistry is a truly anthropic science."

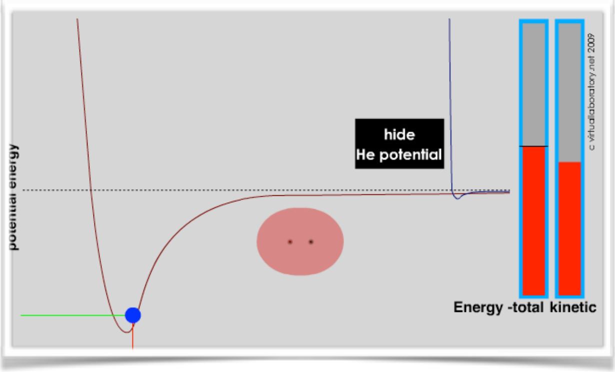
– *ROALD HOFFMAN (1937) QUOTED BY NATALIE ANGIER IN THE CANON*

By this point, you probably have some idea or mental image of the basic (low resolution) structure of atoms. We will therefore return to some questions left unanswered at the end of Chapter 1. Why is it that two hydrogen atoms form a strong stable (covalent) bond, a bond that requires temperatures above 5000 K to break, whereas two helium atoms and two hydrogen molecules have only a weak (London dispersion forces) attraction for each other that is broken at very low temperatures (4–20 K)? Because temperature is a measure of the kinetic energy present in the system we have to ask, what gives rise to this huge difference? Is there something fundamentally different going on in these situations? Other potentially troubling questions may also come to mind, in particular, how can pure samples of different elements be so different? Why is carbon either black (graphite) or transparent (diamond)? Why are some elements more or less inert (such as gold, which does not tarnish) while others, such as iron (which rusts) and phosphorus (which bursts into flames) are highly reactive? To answer these questions will lead to an understanding of the basics of chemistry or how atoms interact with one another under various conditions. We will approach the answers in a step-by-step manner. In some cases where the answers are very complex (as is the case for why gold is yellow and mercury is a liquid), we will sketch out the answer but probably not provide a satisfying explanation. Luckily, most of the chemistry we need to address is not nearly so arcane!

Before we consider these and other questions, let us recap what we think we know about atoms and electrons. Most of an atom's mass is localized in a very small region, the nucleus, surrounded by electrons that occupy most of the volume of the atom. Electrons have a number of strange properties because they are quantum mechanical particles. This means that under some conditions their behavior is best described by considering them as negatively charged particles, and under other conditions it is more helpful to consider them as waves; they are really both (and neither). Because of the uncertainty principle when we know the energy of each electron rather accurately we do not (and cannot) know where, exactly, a particular electron is at a particular moment in time. In fact, because all electrons are identical, if we had two electrons and turned away from them we could not tell which was which when we turned back. Within an atom each electron has a discrete energy and is characterized by its set of quantum numbers; no two electrons in an atom have the same set of quantum numbers. Perhaps you will be disappointed (or perhaps pleased) to know that a rigorous quantum mechanical (and relativistic) treatment of atoms and their interactions is beyond the scope of this book.[60] That said, we can give a reasonable overview of how the behavior of atoms can be explained in terms of atomic and molecular electron orbitals. We will also indicate where our description is an over-simplification.

It is worth remembering that there are very few (if any) instances when we come across isolated atoms. Although we often describe matter as being composed of atoms, that is a bit of an abstraction; most atoms are stuck to other atoms by bonds and interactions. As mentioned previously, this leads to emergent properties that are quite distinct from those of the isolated atoms of which they are composed. It is the interactions between atoms and molecules that makes surfaces solid.

If isolated atoms are rare, the obvious question is, why are they rare? What determines when and how atoms interact? The answer is simple really and based on a principle we have already encountered (and that we will return to time and again): systems will adopt the lowest energy state accessible to them. The reason is that at the lowest accessible energy state, the forces of attraction and repulsion are equilibrated. It would take more energy to move the components of the system (that is atoms in molecules, or electrons in atoms) because the forces acting on them would increase. Interactions and bond formation lead to lower potential energy. Whether the bonded system is stable will then depend upon the strength of the interaction/bond and the forces that impact the molecule. For example, surrounding molecules/atoms with a range of kinetic energies may collide with the molecule. If this kinetic energy of the impacting particle is larger than the interaction/bond energy, the collision can disrupt the interaction or break the bond(s) between them; if not, the interaction/bond will be stable. At the same time, there must be overarching principles governing which interactions occur and which do not; otherwise everything would clump together, which would be messy and not particularly interesting. These principles arise from the way electrons are organized in different types of atoms.



Thinking about the nature of the chemical bond

There is no single explanation that captures all the properties observed when atoms interact to form a bond[61]. Instead we use a range of models of bonding. Now, what do we mean by model? Models are much more limited than theories, which have global application and can be proven wrong through observation and experimental data. Models are more like strategies that

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[60] For those who want more, rest assured that you will find out if you take more advanced classes either in physics or physical chemistry.

[61] This study shows images of bonds forming http://www.sciencemag.org/content/340/6139/1434.abstract

simplify working with and making predictions about complex systems. A model often applies to only very specific situations. For example the Bohr model of the atom applies only to hydrogen and then only under quite specific circumstances. We are going to consider a variety of bonding models, some of which you may already be familiar with, but it is important that you remember that different models are used depending upon which properties you want to predict and explain.

Discrete Versus Continuous Molecules

Having considered the bonding situation with hydrogen and helium, the simplest two elements, we can now move on to consider other elements and the types of molecules that they form. In this discussion, we begin with molecules made up of a single type of atom. More complex molecules made of atoms of multiple elements will be considered in the next and subsequent chapters. As the number of protons in the nucleus of an element's atoms increases, from 1 in hydrogen to 10 in neon, we find dramatic changes in physical properties that correlate with whether the elemental form is discrete or continuous. The discrete forms are either monoatomic—meaning that they exist as separate atoms (such as He and Ne) with no covalent bonds between them (although they do interact via van der Waals interactions)—or diatomic molecules (such as H_2, N_2, O_2, and F_2), meaning that they exist as molecules that have only two atoms. The elements that exist as small molecules have very low melting points (the temperatures at which they change from a solid to a liquid) and low boiling points (the temperatures at which they change from a liquid to a gas). But don't confuse these phase transitions with the breaking of a diatomic molecule into separate atoms. Phase transitions, which we will discuss in greater detail later, involve disruption of interactions **between** molecules (intermolecular forces), such as London dispersion forces, rather than interactions **within** molecules, that is, covalent bonds.

Table 3.1 The First 10 Elements in Their Naturally Occurring Elemental State

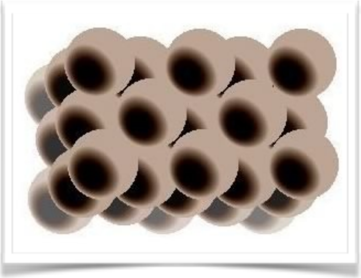
Elemental Form	H_2 molecular	He atomic	Li continuous	Be continuous	B continuous	C continuous	N_2 molecular	O_2 molecular	F_2 molecular	Ne atomic
Melting Point	13.81 K	0.00 K	453.65 K	1560 K	2348 K	3823 K	63.15 K	54.36 K	53.53 K	24.56 K
Boiling Point	20.28 K	4.22 K	1615 K	2744 K	4273 K	4098 K	77.36 K	90.20 K	85.03 K	27.07 K
Bp-Mp (*)	6.47 K	3.27 K	1161 K	1184 K	1925 K	275 K	14.21 K	35.84 K	31.5 K	2.51 K
Name	hydrogen	helium	Lithium	beryllium	boron	carbon	nitrogen	oxygen	fluorine	neon

* boiling point (Bp) minus melting point (Mp).

In contrast to the elements that form discrete molecules, the atoms of the other elements we are considering (that is Li, Be, B, C) interact with one another in a continuous manner. Rather than forming discrete molecules, these elements can form ensembles of atoms in which the number of atoms can range from the small (a few billion) to the astronomical (very, very large). Whether the materials are at the nano- or the macroscopic levels, the atoms in these ensembles are held together by bonds that are very difficult to break, like the bond in H–H. That is, a lot of energy must be put into the system to separate the component atoms. However, unlike hydrogen, the atoms that form these structures must form bonds with more than one other atom.

A consequence of this difference in organization is a dramatic increase in both the melting and boiling points compared to atomic (He, Ne) and molecular (H_2, N_2, O_2, and F_2) species (Table 3.1). The reason is that when a substance changes from solid to liquid (at the melting point) the component particles have to be able to move relative to one another. When the substance changes from a liquid to a gas (at the boiling point) the particles have to separate entirely. Consequently the magnitude of the melting and boiling points gives us a relative estimate of how strongly the particles are held together in the solid and liquid states. As we have already seen temperature is a measure of the average kinetic energy of the molecules in a system. For elements that exist as discrete atoms or molecules the only forces that are holding these **particles** together are London dispersion forces, which are relatively weak compared to covalent bonds. In contrast, the elements that exist as extensive networks of atoms joined by bonds require much more energy to break as the material goes from solid to liquid to gas.

3.5 Metals



Metals are a particularly interesting class of continuous molecule. They have quite a wide range of properties at normal temperatures, from liquid (like mercury) to extremely hard (like tungsten). All metals conduct electricity but not all equally. How can we explain all these properties? Let us use aluminum (Al) as an example because most of us have something made of aluminum such as a pan or aluminum foil. With modern instrumentation it is quite easy to visualize atoms and a variety of techniques have been used to image where the aluminum atoms are in the solid structure. What emerges is a picture of aluminum nuclei and their core electrons, packed like spheres where one layer of spheres rests in the interstices of the underlying and overlying layers; where the positions of the electrons are within this structure not well defined.

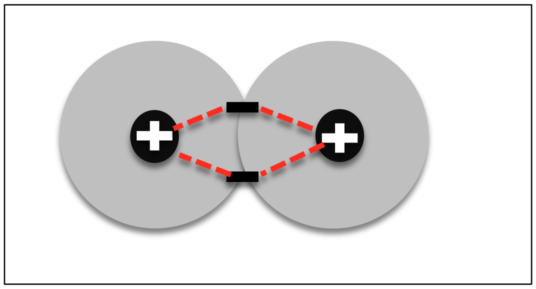
In H–H the electrons involved in bonding are located (most probably) between the two nuclei. In contrast in aluminum and other metals the valence electrons are not closely associated with each nucleus. Instead they are dispersed over the whole macroscopic piece of metal.

In this model the atomic cores are packed together and surrounded by a cloud of electrons that serve as the “glue” that binds them together. There are no discrete bonds in this type of structure. When a piece of metal is put under physical stress (for example it is stretched or deformed) the atoms can move relative to one another but the electrons remain spread throughout the structure. As electrons are free to move throughout the metal, this explains why metals can conduct electricity (which requires the movement of charged particles, in this case the electrons). Metals can also often be slowly deformed into different shapes without losing their structural integrity or electrical conductivity—they are malleable! They can be melted (increased atomic movement), become liquid, and then allowed to cool until they solidify; throughout this process they retain their integrity and their metallic properties and so continue to conduct electricity.[62] This is quite different from how other substances (such as diamond or water) behave. The hardness of a solid metal depends on how well its atoms packed together and how.

Questions to Answer

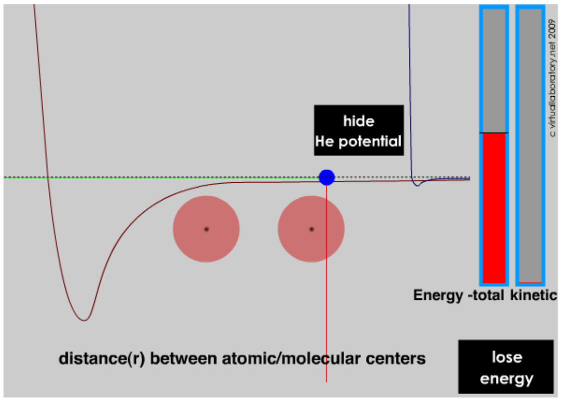
- What properties indicate that a substance is metallic?
- How can metallic properties be explained by the atomic-molecular structure of Al (for example)?
- Why does aluminum (and for that matter all metals) conduct electricity? What must be happening at the atomic-molecular scale for this to occur?
- Why is it OK to use different models to describe bonding in different species?

3.5 The Nature of Covalent Bonds



Recall from Chapter 1, when two H atoms come together there is an attraction between the nucleus of one H atom and the valence electron of the other H atom and vice versa. This results in the pair of valence electrons being localized between the two H nuclei in what we call a covalent bond. Covalent bonding generally occurs between nonmetal atoms as the attractive force of the nucleus of one atom for the electron of another is not strong enough to completely remove that electron from the other atom. As a result, the atoms "share", or possibly more accurately "fight" over the electron pair like in a tug of war.

This attraction results in a decrease in potential energy. The idea that—all other things being equal—a system will move to the lowest accessible energy state (losing the excess energy to their surroundings), where the forces of attraction and repulsion are equal, is applicable to a wide range of situations. The potential energy of the system falls as the distance between the atoms decreases until the system reaches a balance between the stabilizing interaction of bond formation and the destabilizing repulsion of the two nuclei. The energy difference between the separated atoms and the minimum energy is called the bond energy and this amount of energy must be supplied to the system to break the two atoms apart again. The distance between the nuclei when the bond energy is at its minimum is the bond length. When a bond is formed between two atoms energy is always released to the surroundings and the new material is always more stable than the two separate atoms. Because energy is conserved a bond cannot form unless this bond energy is transferred from the interacting atoms to the rest of the system (usually by colliding with other atoms and transferring energy). Making



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[62] We need to mentions (at least) what electricity is, i.e. the flow of electrons.

bonds is always exothermic (meaning that energy is released not absorbed). This implies that energy (from the surrounding system) is always needed to break a bond. To break a bond energy must be transferred from the surroundings. Bond breaking is endothermic meaning it requires energy from the external world, normally delivered through collisions with other molecules. Recall from our earlier discussion that this interaction results in a much deeper potential energy (PE) well than the LDF interaction that occurs between two He atoms.

When we consider more complex chemical reactions we will find that these generally involve both bond breaking and bond formation; the overall reaction will be exothermic when more energy is released from bond formation than is used for bond breaking. Conversely a reaction is endothermic (that is, uses energy) if more energy is required to break bonds than is released in bond formation. The important point is that we have to consider the system as a whole, including all of the bonds formed and broken. We will come back to this topic (in much greater depth) in Chapters 5 and 7.

Questions to ponder

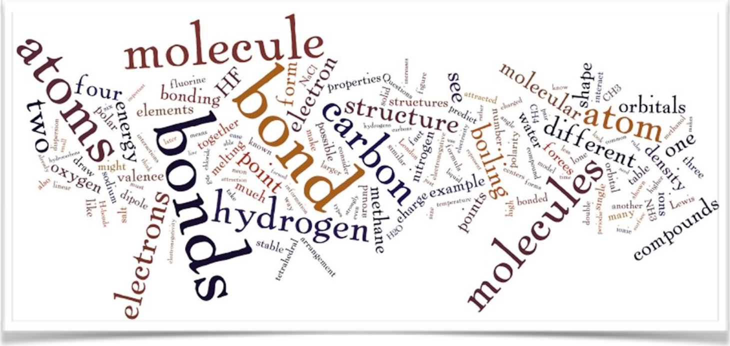
- Are all bonds the same?
- What factors might influence bond strength?
- Why are the properties of atoms and molecules different?

Questions to Answer

- Where are the electrons in H_2 when the temperature is greater than 5000 K?
- What would a molecular-level picture of H_2 (g) look like?
- What would a molecular-level picture of H (g) look like?
- Where does the energy to break a bond come from?
- Where does the energy released upon bond formation go?
- The melting point of molecular hydrogen (H_2) is ~14 K (-259 °C). Draw a molecular level picture of what molecular hydrogen looks like below this temperature (as a solid). Why are the molecules of hydrogen sticking together?
- The boiling point of molecular hydrogen (H_2) is ~20 K (-253 °C). Draw a molecular level picture of what molecular hydrogen looks like above this temperature (as a gas).
- Molecular hydrogen dissociates at high temperatures (> 6000 K). Draw a picture of what you imagine this might look like. Why do you think it takes such a high temperature to bring about this change?

This chapter has brought us to a point where we should have a fairly good idea of the kinds of interactions that can occur among atoms of the same element. We have seen that the properties of different elements can be explained by considering the structure of their atoms and in particular the way their electrons behave as the atoms interact to form molecules or large assemblies of atoms. What we have not considered yet is how atoms of different elements interact to form compounds (substances that have more than one element). In Chapter 4 we will take up this subject and much more.

Chapter 4: Heterogeneous Compounds



Up until this point we have considered only bonds between atoms of the same element. While this makes things simpler, it leaves out the vast majority of the compounds that exist in the world and their chemistries. Moreover, pure elements are rare in nature. Much of the efforts of alchemists, early chemists, and the modern refining industry involve determining how to (economically) separate specific types of atoms (elements) away from others. Modern chemistry is concerned (largely) with putting atoms together to form new and useful molecules. Both involve understanding the concepts underlying how atoms interact.

4.1 3D and 2D Representations

To extend our discussion to the wider world of what we might call heterogenous molecules, that is, molecules made up of atoms of more than one element, we will begin with carbon. Why carbon? Well, here are some reasons. Carbon is the fourth most abundant element in the universe (~3,032 atoms per million), after hydrogen (~705,700 atoms per million), helium (~275,200 atoms per million), and oxygen (~5,920 atoms per million). Carbon is distinguished from most other elements in its ability to form a vast array of diverse compounds by bonding with itself and other elements with bonds that are not too strong and not too weak. Under the conditions that persist on the surface of the Earth carbon compounds are stable enough to hang around but not stable enough to persist forever, so they are not dead ends. Carbon is a key building block of the major molecules of life: proteins, nucleic acids, lipids, and carbohydrates. We are carbon-based life forms! Carbon compounds are also used in a wide range of synthetic materials, such as pharmaceuticals, polymers, and high-tech materials; we also consume a lot of carbon compounds by burning them for fuel.

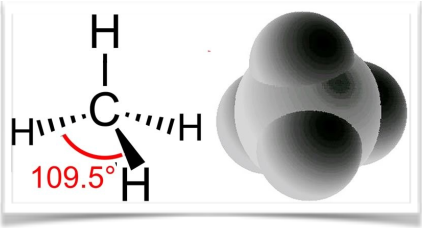
4.2 Carbon: Always Tetravalent and Often Tetrahedral

Atoms combine in many different ways. We have already seen an example of how a covalent bond can form between two hydrogen atoms producing molecular (H_2) as opposed to the atomic form of hydrogen. Similarly atoms of carbon can be linked together in various ways to form diamond, graphite, and graphene (see below). Now we move on to molecules involving atoms of carbon and other elements. In keeping with our ongoing attempt to keep things simple (or better put, as simple as possible), let us start by examining the types of molecules that can be formed by combining carbon with hydrogen. There are many such molecules, and collectively they are known as hydrocarbons. The simplest such compound is methane CH_4, a major component of natural gas.

As in all its compounds and its elemental forms, carbon is tetravalent, which means that it always forms four bonds. We will now consider in greater detail why this is so, what forms the bonds can take, and what are the consequences of this fact. In this discussion, we will be building on the ideas introduced when we talked about diamond, graphite, and graphene.

To answer these questions we need to return to the ideas (introduced in Chapter 2) about the quantization of electron energy levels. Carbon has a total of six electrons, two of which are in a filled (1s) quantum shell, and four valence electrons; it is these valence electrons that can take part in bonding. Remember that the formation of a bond always lowers the energy of a system. It therefore makes sense that a carbon atom would form as many bonds as possible, resulting in the most stable possible molecular species.

What happens if we combine hydrogen with carbon? Do we get a compound with properties intermediate between the two? Absolutely not. We begin with what we know: in methane the carbon atoms make four bonds, one to each of four hydrogen atoms. We also know, from experiment, that the shape of the methane molecule is tetrahedral; there is a carbon at the center and the four C–H bonds pointing towards the corners of a four-sided figure. As C has four valence electrons, pairing one of those valence electrons with the valence electron from one H atom can form a covalent bond. With four valence electrons and four H atoms, the result is four C-H bonds in methane. The electrons in the 1s orbital of Carbon (the core electrons) are not used because the amount of energy needed to use those electrons is greater than the energy that would be released upon bond formation (they are held tightly to the nucleus by the electromagnetic force). It turns out to be a general rule that electrons in the core of the atom—in filled shells—tend not to take part in bonding. This means we need only consider the valence electrons when thinking about bonding.

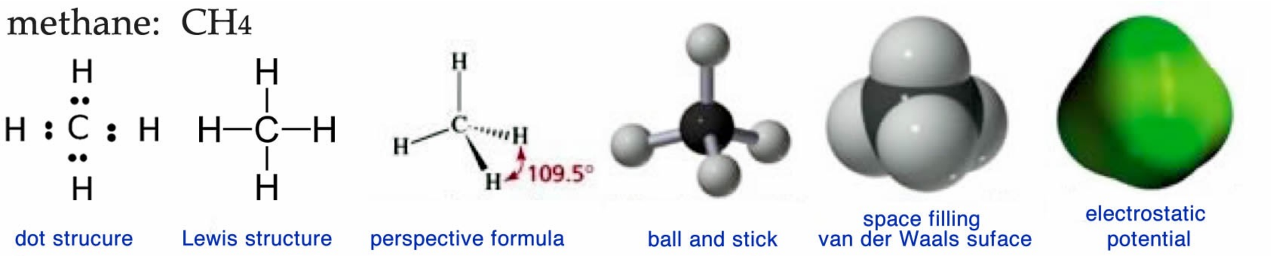


Because carbon has four valence electrons and each of the four hydrogens has one electron the result is a total of eight electrons distributed in four bonding orbitals around the C atom. It turns out when there are four bonds around a central atom angle between orbitals (and the C–H bonds) is 109.5°. Another way to say this is that the H–C–H bond angle is 109.5°. We can predict that this will be the case based on theoretical calculations; these have been confirmed by experimental observations.

But why should this be true? How many different arrangements are there for four hydrogens bonded to a single carbon? Why aren't the hydrogens all arranged in a single plane (around a central C with 90° bond angles) rather than in the tetrahedral arrangement? The planar arrangement, which is known as a square planar geometry, is actually possible and is sometimes observed under some special conditions, usually in molecules involving transition metals as we will see later). The square planar arrangement is not as stable as the tetrahedral arrangement for carbon because each C–H bond can be considered as a region of high electron (negative charge) density. Given that like repels like, each bond repels the others and moves as far away from the other bonds as possible. The optimum bond angle turns out to be 109.5° away from each of their neighbors. At that point, if they moved away from one orbital they would move closer to another.

You may want to convince yourself of this geometric fact by using a marshmallow, toothpicks, and gumdrops! This principle goes by the unwieldy name of valence shell electron pair repulsion (VSEPR) and can be used to predict (once you get the hang of it) the three-dimensional (3D) structure of simple molecules—assuming that you know how the atoms within a molecule are connected. For example, using VSEPR logic, you should be able to present a compelling argument for why the C–H bonds in methane do not adopt a square planar orientation, as well as the general shape of many other types of molecules. You can even go further, in methane all four atoms attached to the central carbon are the same but what if they are different? You should be able to make plausible predictions about how bond angles would change if one of the attached groups is larger than the others – how would that influence bond angles?

One problem for many people is that 3D visualization of molecular structures is not easy. It is particularly tricky when one is called upon to translate the more or less abstract two-dimensional (2D) representations (Lewis and dot structures ↓) that you find printed on the page of a book, into a 3D model you can manipulate with your hands or in your mind. In addition, chemists (and molecular biologists) have an annoying tendency of representing complex 3D structures using various 2D representations, which can be confusing if you don't know what you are looking at (or for). You have probably already seen some of these different structures, and we will consider a number of them below. Each provides specific kinds of information about the molecule. Note that actual 3D physical models and web activities can be very helpful in solidifying your ideas about structure.



If we were able to see a methane molecule, what we observe would probably be closest to the electrostatic potential map. This visualization provides a picture of the surface of the molecule, generally color coded to represent fluctuations in electron density. Notice that there are no color fluctuations on this model of methane indicating that there are no (permanent) electron cloud distortions in the molecule—the surface of the molecule is uniformly electrically neutral. What is not so easy to discern from this representation is the fact that the methane is tetrahedral or that the central carbon atom is bonded to four hydrogen atoms, a fact that is much easier to appreciate in the other representations. The electrostatic potential representation is very useful for large biological molecules for several reasons: it is much simpler than the other kinds of models because individual atoms are not represented; it shows the molecule's shape; and it shows where charges and partial charges are located.

The space-filling or van der Waals model gives more structural information in that the individual atoms that make up the molecule are distinguished by color (black for carbon, white for hydrogen, red for oxygen, and blue for nitrogen.) The surface of the model represents the molecule's van der Waals radius, which is the distance where attraction turns to repulsion when two molecules approach one another. As its name implies, such models represent the space occupied by each atom.

The ball-and-stick model of methane shows the central carbon (black ball) attached to four hydrogens (white balls) by sticks that represent the bonds between the atoms. Although this model is probably the easiest to visualize, it is misleading because it could give the impression that bonds are like sticks holding the atoms together. It also does not represent either the actual volume occupied by the molecule or its electrostatic surface features. Another problem with all three of the preceding types of models is that you need a computer and specialized software (or some artistic ability) to draw them, which may not always be convenient or possible.

One strategy to address this problem is through what is known as a perspective formula. In a perspective formula the atoms are represented by their atomic symbols (for example, C or H) and bonds are represented by various kinds of lines. A normal line is meant to indicate a bond that is in the plane of the paper, a wedged line  represents a bond that is coming out of the plane toward you (the reader), and a hatched line  represents a bond that is coming out of the plane, but away from you. This convention makes it easier to draw 3D perspective structures by hand without specialized software (or graphical talent.) We can, in fact, go one step further and draw methane without indicating its 3D structure at all. Structures that show all the bonds, atoms, and any valence electrons that are not in bonds, but do not attempt to accurately represent the 3D shape of a molecule are called Lewis structures. The Lewis structure for methane (see above) and the molecular formula CH_4 represent a chemical shorthand that can provide a huge amount of information; we will see even more extreme examples as we go on. However, to be able to understand these representations, you must already know that the methane molecule is tetrahedral and the rules that apply to the geometry of carbon bonds, because neither is shown explicitly. If you didn't know these things, you might even be tempted to assume that methane is organized with a square planar geometry or that the hydrogens are all located to one side of the carbon atom, neither of which is true!

Why, you might ask, would one want to draw structures with so much information missing? Perhaps, like medieval alchemists, modern chemists want to keep their secrets from the average person. Perhaps they just like secret codes and mystical symbols. Or perhaps it is because these shorthand representations of molecules are just much more compact and easy to draw, particularly when we get to large molecules with lots of atoms.[63] Drawing Lewis structures is an important and useful chemistry skill and we will return to it in more detail shortly. Once you have mastered it you will be able to look at a molecular formula such as CH_4 (or C_5H_{12}) and (together with other information) be able to visualize the 3D structure of the molecule represented and predict many of the substance's physical and chemical properties.

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[63] We do not believe that their intent is to torment students, and perhaps they have just forgotten that not every student knows or remembers all of the rules.

For example, models of the methane molecule predict that it is symmetrical. Again, this might not be entirely obvious just by looking at the structure, but if you make a model, or look at a rotatable interactive 3D model on the web you will see that it does not matter which way you look at the structure—all the C–H bonds are the same, and all the bond angles are the same. A little more information (which we will discuss later on) will let you deduce that there are no permanent electron density distortions in the molecule—just as is shown by the electrostatic potential map. Together these enable you to deduce that methane molecules are attracted to one another solely through London dispersion forces (like helium atoms or hydrogen molecules). Given how weak these interactions between molecules are we might be brave enough to predict that the melting and boiling points of methane are low (melting and boiling occur at relatively low temperatures) and we would be right! Methane melts at 91 K and boils at 112 K.[64]

Question to Answer

- Why (when present) are the four bonds formed by carbon usually arranged so that they point towards the corners of a tetrahedron?

Questions to Ponder

- If bond formation is stabilizing, why doesn't carbon form six bonds, given that it has six electrons?
- Why doesn't helium bond with carbon?
- What would be the consequences if carbon bonds with other atoms were very weak?
- What would be the consequences if carbon bonds with other atoms were very strong?

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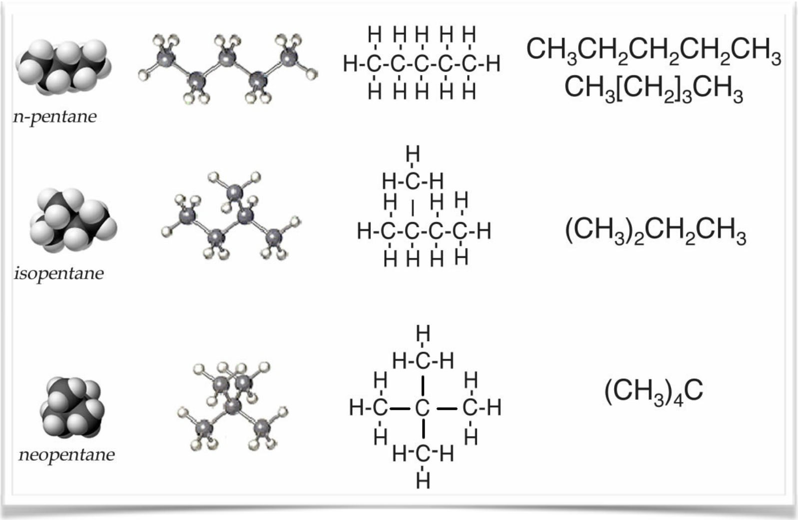
[64] Unless otherwise noted, we always consider melting and boiling points at atmospheric pressure.

4.3 Collapsing Real Structures Down to 2-Dimensional Representations

Now, an obvious problem with complex three-dimensional molecules, even those made up only of hydrogen and carbon, is how to convey their structure when they must be depicted in two dimensions, like when you are writing on paper. Research indicates that students (that is, most people) have a tough time with this task, which is why we will describe various approaches here.

Before we begin, we need to have some rules. Let us use the set of possible molecules that contain 5 carbon atoms and 12 hydrogen atoms; these are generically known as pentanes. You can begin with a piece of paper and a pencil; how many different molecules can you draw with the composition of C_5H_{12}? Clearly C_5H_{12} does not uniquely define the structure of the molecule; it is better to use their distinct names: pentane, isopentane, and neopentane (→). Each of the different molecules you have drawn has the same molecular formula but a different shape and, it turns out, different properties. For example, pentane has a boiling point of 308 K, whereas the boiling points of isopentane and neopentane are 301 K and 283 K, respectively. Their shape, rather than their elemental composition, influences the strength of the attractions between the individual molecules, which in turn influences their boiling points. We call these kinds of related compounds structural isomers, which means they have the same composition (for example C_5H_{12}) but their constituent atoms are connected differently to give different structures and shapes.



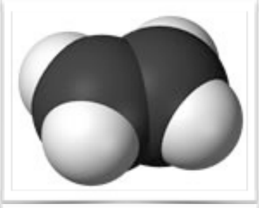
It is common to use a number of different types of representations to picture molecules. One way is through what are known as text formulas (or linear formulae). In this scheme, pentane is written $CH_3–CH_2–CH_2–CH_2–CH_3$, which can also be written as $CH_3–[CH_2]_3–CH_3$. This captures some of the structural subtleties of pentane, but not all. For example, it does not illustrate the fact that the molecule is not strictly linear. Nevertheless, we can already anticipate complications. How would we write isopentane? The most obvious way would be $(CH_3)_2CHCH_2CH_3$. Neopentane is written as $(CH_3)_4C$. Does that make sense? Try deciphering them. We will return to this point later on in this chapter.

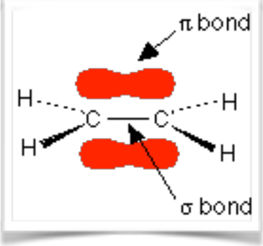
If we followed the logic of this approach we could draw a more complete representation of pentane, isopentane, and neopentane as Lewis structures, but again, we are missing the three-dimensionality. You might even be led to think that the molecules are actually flat when they are much more like balls. Although it is possible to make the representation a little more realistic by trying to indicate three-dimensionality using the wedge and dash symbols, these structures become very complicated very fast. It is not really practical to draw out full 3D structures for larger, complex molecules. One important skill you will need to master is the ways that short-hand structures (such as Lewis structures) can provide information about the 3D structure of a molecule that allows us to predict chemical and physical properties.

Questions to Answer

- What are the advantages and disadvantages of each type of structure?

4.4 Shapes of Molecules with Double (and Triple) Bonds





We can apply the same thinking about the arrangement of bonds around the carbon atoms in $CH_2{=}CH_2$ in much the same manner as we did for $CH_3{-}CH_3$. In ethene each carbon atom is surrounded by three centers of electron density, two Hs and one C. Note that the double bond counts as a single center of electron density (→).The presence of a double bond has distinct effects on molecular shape. The minimum energy arrangement for three centers is a two-dimensional arrangement in which the groups are oriented at about 120° to one another; an arrangement known as trigonal planar geometry.

There is one more common type of bond that carbon can form, which is a triple bond. For example each carbon in C_2H_2 (ethyne) is surrounded by only two centers of electron density, shown in the figure (→). The lowest energy arrangement around each carbon is a line in which the angle between the bonds is 180°.

We see that under most conditions, a carbon atom can participate in a maximum of four bonds; either four single bonds, two single bonds and a double bond, or one single bond and a triple bond.

Questions to Answer

- Given a particular hydrocarbon, what factors would influence your prediction of its melting and boiling points? Can you generate some tentative rules?
- How does the presence of a double bond influence the structure of a hydrocarbon?
- Why do you think there is no tetrabonded from of carbon (that is C four bonds C)?

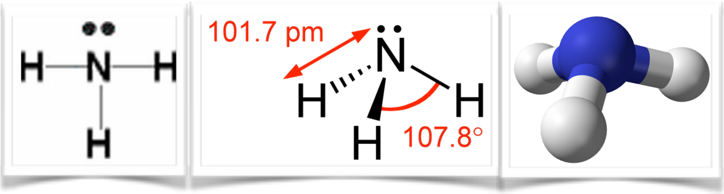
Questions to Ponder

- What limits the size and shape of a hydrocarbon?

4.5 Bonding in Nitrogen, Oxygen, and Fluorine

Even though the bonding of hydrogen and carbon atoms can generate a remarkable array of molecules, the hydrocarbons are really rather boring (chemically). They take part in a rather limited range of reactions and would not, on their own, be expected to produce anything like life. Of course there are many other elements, and their properties add chemical complexity to molecular behavior. From the perspective of living systems two of the most interesting elements are nitrogen and oxygen. Carbon has six electrons (two core and four valence) and can form four bonds with neighboring atoms. Nitrogen has seven electrons: two core and five valence: $1s^2$, $2s^2$, $2px^1$, $2py^1$, $2pz^1$. So if you are following the rules, you might well assume that nitrogen would be able to form five bonds (after all, it has five valence electrons). But when we look carefully, we never see a nitrogen atom making five bonds, and in all stable compounds it makes only three bonds. We can explain this observation in several ways. One factor is that nitrogen atoms are too small to support five centers of electron density around themselves because the bonds begin to overlap, which is destabilizing, just like we saw with bulky groups around a carbon. Another factor is that there are only four orbitals available in nitrogen in the second quantum shell. If nitrogen were to form five bonds it would have to use orbitals from the next quantum shell (3), but these orbitals are so high in energy that the energy required would not be offset by the energy released upon on bond formation. Together these factors mean that nitrogen, and in fact all elements in the second row of the periodic table, are limited to bonding arrangements with no more than four centers of electron density. As we will see later on, elements in the next row, such as phosphorus (P) and sulfur (S), are larger and have more available orbitals for bonding. These elements can form up to six centers of electron density.

The simplest compound of nitrogen is molecular nitrogen, N_2. The two nitrogen atoms are bonded together by a triple bond. Molecular nitrogen, N_2 is a stable (relatively nonreactive) molecular compound.[65] A common nitrogen-containing molecule is ammonia (NH_3), which is analogous to methane (CH_4). In ammonia the nitrogen atom is bonded to three hydrogen atoms. These three bonds involve three of nitrogen's valence electrons; the remaining two valence electrons occupy a non-bonding orbital and are referred to as a lone pair. Given the molecular hybridization orbital model that we are using this implies that four sp^3 orbitals are formed from the nitrogen atom's 2s and 2p orbitals leading to four electron density centers around the nitrogen. The figure shows three representations of ammonia. The first indicates the N–H bonds but fails to show the lone pair orbital. The second uses the wedge and dash convention and dots to illustrate the geometry of both bonds and the lone pair. The actual shape of the molecule is determined by the arrangements of electron clouds and the bonded atoms. In NH_3 all three bonds are equivalent (N–H) and so must be symmetrical, but the lone pair orbital is different because it takes up more space than bonding pairs, can you imagine why? This has a subtle effect on the shape of the molecule. The angles between the C–H bonds in CH_4 are equal and 109.5° while the angles between the N–H bonds in NH_3 are slightly smaller, 107.8°. The shape



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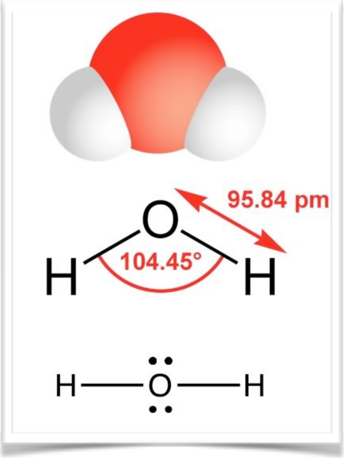
[65] However, a nitrogen compound with some structural similarities to diamond has been identified. It was synthesized from N_2 at high pressure and temperatures. In this polymeric nitrogen, each nitrogen is connected to three neighbors via single bonds, in a similar way that diamond has carbons connected to four neighbors. However this polymeric nitrogen is highly unstable and reactive – unlike diamond. http://www.nature.com/nmat/journal/v3/n8/abs/nmat1146.html

of the molecule itself (as outlined by the atoms) is a triangle-based pyramid rather than a tetrahedron. Finally the Lewis structure (the most abstract representation), indicates the bonds and lone pair electrons but gives an unrealistic depiction of the molecule's geometry. It is up to the reader to supply the implicit information contained in the structure about bond angles and overall shape.

Bonding of Oxygen and Fluorine

Let us now consider oxygen (O) which has eight electrons, two in the core and six valence ($1s^2$, $2s^2$, $2px^2$, $2py^1$, $2pz^1$). As with nitrogen, oxygen does not use all its electrons to form six bonds because it is too small and the orbitals that would need to be used to make six bonds are too high in energy to be energetically accessible; that is, not enough energy would be released upon bond formation to "pay for" that energy.



The simplest oxygen-containing molecule is molecular oxygen, O_2. On our simple covalent bond model the two oxygen atoms are connected by a double bond The next simplest, stable, most common, and by far the most important compound of oxygen at least from the perspective of living organisms, is water (H_2O). In water there are two O–H bonds and two lone pair non-bonding orbitals. As in the case of nitrogen, the oxygen atom is surrounded by four centers of electron density (see a pattern here?), two bonds, and two lone pairs. Again, the lone pair orbitals are larger than the O–H bonding orbitals, which distorts the tetrahedral symmetry of the molecule. Instead of equal angles of 109° between the orbitals, the angle between the O–H bonds is 104.5°. When we use a Lewis structure to represent the structure of H_2O, it is critical to include all valence shell electrons.

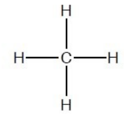
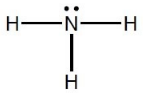
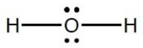
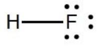
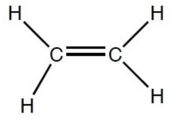
CH4	NH3	H2O	HF	Ne
-258.7°F (-161.5°C)	-28.01°F (-33.34°C)	212°F (100°C)	67.1°F (19.5°C)	-410.9°F (-246.1°C)

Continuing on across the periodic table we see that fluorine is the next element after oxygen. It has nine electrons: two core and seven valence. Rather than forming seven bonds fluorine only forms a single bond for basically the same reasons that oxygen only forms two bonds. Hydrogen fluoride, HF, has one bond, but four centers of electron density around the fluorine. Because HF has only two atoms, they must by definition lie on a line and therefore we do not need to discuss its shape.

Compound	Molar mass (g/mole)	Boiling point	Bond type	Bond length (pm)	Atomic radius (pm)
CH_4	16	–161 °C	C–H (in CH_4)	109	C - 70
NH_3	17	– 33 °C	N–H in (NH_3)	101	N - 65
H_2O	18	100 °C	O–H (in H_2O)	96	O - 60

Compound	Molar mass (g/mole)	Boiling point	Bond type	Bond length (pm)	Atomic radius (pm)
HF	20	19.5 °C	F–H in (HF)	92	F - 50
Ne	20	–246.08°C	not applicable	not applicable	Ne - 38

As we will see, a valid Lewis structure makes it possible to extrapolate a significant amount of information about a molecule's chemical and physical properties. A confusing point is that the Lewis structure can be written in a number of apparently different ways, which are actually equivalent. The key to remember is that the Lewis structure does not attempt to depict a molecule's actual three-dimensional structure. It is a shorthand (a "cartoon" if you like) that assumes you already know the arrangement of orbitals. No matter how it is drawn, the actual structure of a H_2O molecule is the same with a 104.5º bond angle between the O–H bonds.

Centers of electron density	**Example**	**Electron pair geometry**	**Bond angle**	**Molecular shape**
4		tetrahedral	109º	tetrahedral
4		tetrahedral	107.8º	trigonal pyramid
4		tetrahedral	104.5º	bent
4		tetrahedral	N/A	N/A
3		Trigonal planar	120º	trigonal planar
2		linear	180º	linear

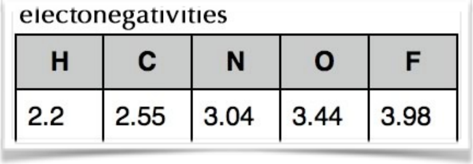
The tendency to form four centers (bonds or non-bonding pairs) has led to the rather misleading "octet rule", which states that some elements tend to form molecules that have eight electrons around any atom (except for hydrogen). Unfortunately, the octet rule is far from being a rule because there are many exceptions, as we will see later. For example many of the elements past the second row of the periodic table are capable of bonding to more than four other atoms and some elements form stable compounds with less than eight electrons. It is important to remember that the octet rule is not the reason why atoms bond with each other, but it is a useful heuristic when constructing Lewis structures for the second row elements (C, N, O, F).

Polarized Bonds and Electronegativity

Earlier we saw that the boiling points of hydrocarbons tend to increase as the number of carbons in the compound increases and that molecules with similar molecular weights have similar but not identical boiling points, with the shapes of the molecules having an effect, although a relatively small one. The attractions between hydrocarbons are due to London dispersion forces that depend on the size, surface area, and shape of the molecule. The larger these forces, the more strongly molecules will stick together and the more energy (higher temperature) will be needed to overcome these attractions.

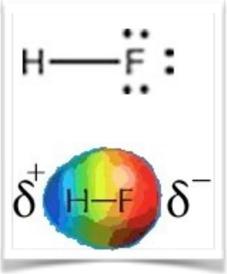
Let us consider the boiling points of some common second row compounds involving bonds with hydrogen, that is, CH_4, NH_3, H_2O and HF, and neon (Ne), which does not form bonds with hydrogen (the compounds of lithium, beryllium, and boron with hydrogen are much less common.) These compounds all have about the same molecular weight but different shapes. Based on our experiences with hydrocarbons, we would be well justified in predicting that they would have somewhat similar boiling points. Unfortunately, this prediction is not supported by experimental evidence (see Table). There is no clear trend, so something is going on that we have not yet considered. To explain this data we have to return to an idea that we discussed in Chapter 3, namely that the size of atoms decreases as you go across a row of the periodic table. Not only does the size (radius) of the atoms decrease (from 70 pm for carbon to 38 pm for neon) but so does the length of the bonds between the atoms and hydrogen (from 109 pm to 92 pm). This is both surprising and counterintuitive (which is why we are reminding you about it!)

Remember that the size of the atom is based on a balance between the attraction between the negatively charged electrons to the positively charged protons in the nucleus, the repulsions between the electrons as they get close to each other, and of course the arcane, but highly accurate rules of quantum mechanics. The reason that the atom's size is decreasing as the number of protons increases is that each electron in the valence shell is attracted by an increasing number of protons in the nucleus. The more protons, the larger this attractive force. At the same time, the electrons in the same valence shell do not tend to repel each other as much as you might suspect because they are in different orbitals. Therefore the effective nuclear charge increases from left to right across the periodic table. This increase in effective nuclear charge doesn't just affect the electrons in isolated atoms; it also affects the electrons in bonds. The ability to attract the electrons in bonds is called electronegativity, and because it derives from the same effect as that that determines effective nuclear charge and atomic radius, electronegativity also tends to increase from left to right across a row in the periodic table. It also decreases from top to bottom in a group of the periodic table. This makes sense because the further electrons are from the nucleus, the less they will be attracted to it. The exceptions to this rule are the noble gases (helium, neon, argon, etc.); because they do not form bonds with other elements (under normal circumstances) their electronegativities are usually not reported.


electonegativities

H	C	N	O	F
2.2	2.55	3.04	3.44	3.98

Electronegativities of selected elements



Fluorine is the most electronegative element and the Lewis structure of HF shows one H–F bond and three lone pairs. Fluorine attracts electrons very strongly—even the ones in the H–F bond so that the fluorine atom ends up with more than its fair share of electrons and the hydrogen atom ends up with less. One way to think about this is that the electron density in the H–F bond is shifted closer to the fluorine atom and away from the hydrogen atom (→). The result of this is that the fluorine atom has more negative charge than positive charge and the hydrogen atom has more positive than negative charge. We indicate this by writing a δ^- charge on the fluorine atom and a δ^+ charge on the hydrogen atom (δ is often used to denote a small increment, that is less than 1). That means that there is an unequal distribution of charge in the molecule. The HF molecule has a permanent dipole, that is, a separation of charge; the H–F bond is said to be polarized and the molecule is considered polar. Permanent dipoles are different from the transient dipoles associated with London dispersion forces. Because of their permanent dipoles molecules of HF interact with one another both attractively and repulsively, more strongly in some orientations than in others. HF molecules are attracted to each other much more strongly than neon atoms, for example, because of the presence of these permanent dipoles. This results in a much higher boiling point for HF than for neon (see above). That is, much more energy has to be supplied to the system to overcome the force of attraction and to separate HF molecules from each other than is needed to separate neon atoms. An important point to note is that HF only has one bond, and the polarity of the bond is the same as the polarity of the whole molecule. As we will see, this is not the case in molecules with more complex structures.

It is relatively easy to predict whether a particular bond is polar by looking at the electronegativity differences between the atoms in that bond. Typically, elements on the left-hand side of the periodic table (metals) have rather low electronegativities and elements over toward the right-hand side (non-metals) have higher electronegativities. There are several ways to calculate electronegativities but in general it is not very useful to memorize specific numbers. It is helpful, however, to understand the trends and to be able to predict bond polarities. Because fluorine is the most electronegative element it can be expected to make the most polarized bonds with hydrogen.[66] So let us take this logic a bit further. If HF has the most polar bonds then HF molecules should stick together with the strongest attractions and HF should have the highest boiling point. But oh no! Water's boiling point is significantly higher (100 °C compared to 19 °C for HF). What is going on? Oxygen is not as electronegative as fluorine and so the O–H bond is not as polar as the H–F bond. Why then is the boiling point of H_2O 81 °C higher than HF? To answer this question we need to consider another factor that affects the polarity of a molecule – and that is molecular shape.

Questions to Answer

- Why do you think that the trends in effective nuclear charge, ionization energy, and electronegativity are correlated?
- What does correlated mean?

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[66] Another way to talk about polarity is to say the bond (or molecule) has a dipole moment (unit Debye)- that is the magnitude of the charges x distance separating them.

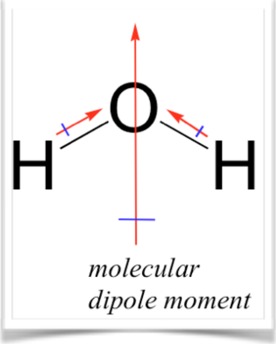
- Can you draw a picture of (say) four H–F molecules sticking together?
- Is there any arrangement that they might take up or would they stick together in a totally random way?

Questions to Ponder

- Why would you not expect polymeric oxygen, that is molecules similar to hydrocarbon chains (or perhaps you would)?

4.6 Molecular Shapes, Polarity, and Molecular Interactions

Now we really have to begin to use our 3D thinking and consider several additional factors: the shape of the molecules and how they interact. Much of this thinking is best done hands on with molecular models but we will outline the logic involved here. The HF molecule has a simple shape; it is linear with (partially) positively and (partially) negatively charged ends. In contrast, the H_2O molecule has a more complex shape; it has two polar O–H bonds. To understand how this affects the polarity of the molecule we have to take into account the number of bonds, their polarization, and the overall shape of the molecule. Bond polarity is a vector quantity, which means it has both a magnitude and a direction. This is where an understanding of the 3D structure of the molecule becomes critical. Each O–H bond is polarized and the overall polarity of the molecule is determined by the vector sum of these bond polarities (that is you have to take into account both the magnitude and the direction of the bond dipoles). This may sound a bit complicated but in practice it is relatively easy to predict qualitatively what the overall polarity of the molecule is as long as you keep in mind its 3D structure. In water the two O–H bonds are at an angle of about 107° to each other (→). If we add the bond dipole moments up you can see that the overall direction of the dipole for the molecule bisects that angle, as shown in the figure. Now you might think that this exercise is a bit of a waste of time—surely it would make sense that if a molecule has polar bonds, then the molecule itself should be polar. However, as we will see shortly this is not always the case.



If we apply a similar analysis to ammonia (NH_3) we see that the N–H bond is polar with a δ^+s on the hydrogen atoms and a δ^- on the nitrogen atom. Remembering that the actual shape of NH_3 is a triangular based pyramid, with an H–N–H bond angle of ~105°, we can see that there is an overall dipole moment in ammonia. Therefore ammonia is a polar molecule.

If we contrast this with methane, however, we see two differences. The first is that carbon is not nearly as electronegative as nitrogen, oxygen, or fluorine, so the C–H bond is not as polar. That said, there is an electronegativity difference and so the electron density in the C–H bond is distorted towards the carbon atom (because it is a little more electronegative than the hydrogen atom.) At the same time, CH_4 is symmetrical (tetrahedral.) If we add up all the bond dipoles they cancel each other out giving a molecular dipole moment of zero. Even if we were to replace the hydrogen atoms in methane with fluorine atoms to give CF_4 (carbon tetrafluoride) the resulting molecule would still be non-polar, despite the fact that the electronegativity difference between carbon and fluorine is greater than that between hydrogen and oxygen! This is another example of something counterintuitive: something made up of polar parts that is not polar.

The Famous Hydrogen "Bond"

Now that we have a better idea of how the shape and types of bonds in a molecule can affect its polarity, let us look a little more closely at how molecules interact with each other. The first thing to note is that globally non-polar molecules interact solely via London dispersion forces just like atoms of neon or helium. The boiling point of neon is –246 °C while the boiling point of CH_4 is –161 °C. This means that methane molecules are more strongly attracted to each other than are neon atoms. We can explain this based on the fact that a methane molecule is larger than a neon atom. Because the electrons in methane molecules are dispersed over a larger area and their distribution (in space) is easier to distort, we say methane molecules are more polarizable. At the same time because methane molecules are non-polar, the boiling point of methane is much lower than that of substances made of polar molecules of similar size.[67]

Let us consider three such molecules: HF (bp 19.5 °C), H_2O (bp 100 °C), and NH_3 (bp -33 °C). All three are polar so they stick together but why are there such large differences in their boiling points? The answer lies in the fact that the molecules interact with one another in multiple ways. They all interact via London dispersion forces and dipole–dipole interactions. In addition, a new type of interaction, known as a hydrogen bond (or H-bond) is also possible. The term H-bond is somewhat misleading because these are much weaker than covalent bonds and do not involve shared electrons; the energy required to break a typical hydrogen bond is between 5 and 30 kJ/mole, whereas it requires over 400 kJ/mole to break a C–C bond.[68] In biological systems and in liquid water, H-bonds are continuously breaking and reforming. Hydrogen bonds are formed between two separate molecules.[69] In contrast to London dispersion forces, but like covalent bonds, H-bonds have a direction; they form when the hydrogen of one molecule, which is covalently bonded to an O, N or F, is attracted by the lone pair on an O, N of F of a neighboring molecule.

H-bonds are a special case of an electrostatic interaction involving a hydrogen atom that is bonded to a very electronegative atom (typically oxygen or fluorine) and an electronegative atom

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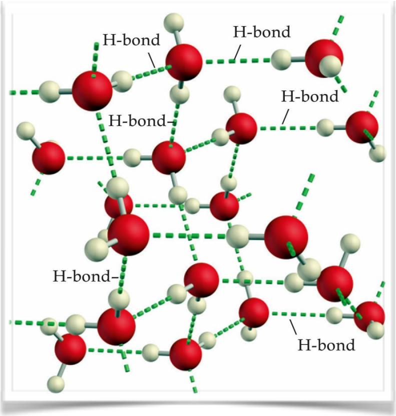
[67] It is worth keeping in mind the distinction between the molecules a substance is composed of, and the substance itself. Molecules do not have a boiling point, substances do.

[68] Remember what a mole is, and that a kilojoule (kJ) is a unit of energy.

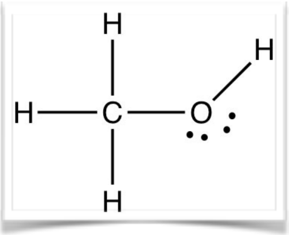
[69] In larger molecules, such as proteins and nucleic acids, H-bonds can also form between distinct regions of a single molecule.

that has lone pairs of electrons. When a hydrogen is bonded in this way most of the electron density moves toward the electronegative atom, leaving a relatively large δ+ on the hydrogen. Water is a particularly important example of a molecule able to engage in hydrogen bonding, because each molecule of water has the possibility of forming four H-bonds (→). Each of the hydrogen atoms within a water molecule can bond to another water molecule, while each oxygen atom has two lone pairs that can interact with the electron-deficient hydrogen atoms of two different neighboring water molecules, shown in the figure. The ability to form large numbers and networks of hydrogen bonds is responsible for many of the unique properties of water including its relatively high melting point, boiling point, heat capacity, viscosity, and low vapor pressure. In contrast, HF and NH_3 can form, on average, only two H-bonds per molecule. Can you figure out why this is so? Because there are fewer H-bonds to break, they have lower boiling points. HF has a higher boiling point than NH_3 because the H-bonds in HF are stronger than those in NH_3. (Can you figure out why?) In addition to their role in the bulk properties of substances like water, we will see that H-bonds play a critical role in the organization of biological systems, from the structure of DNA and proteins, to the organization of lipid membranes and catalytic mechanisms (but more about that later).

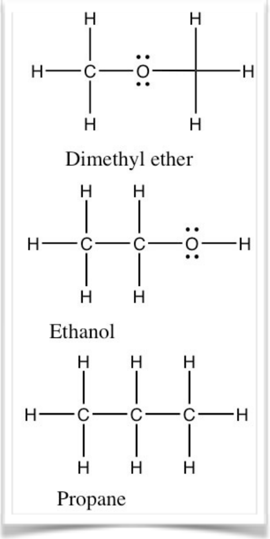


Other Polar Bonds

We have seen that when hydrogen is covalently bonded to oxygen, nitrogen, or fluorine, the result is that the covalent bond is highly polarized and the majority of the electron density is located on the most electronegative atom. This means that the hydrogen atom has very little electron density remaining around it. Because hydrogen is such a small atom, the resulting positive charge density on the hydrogen atom is high. This leads to unusually strong attractions (H-bonds) with atoms that have lone pairs with which the positively charged hydrogen atom can interact. H-bonding is unique to molecules in which a hydrogen atom is covalently bonded to an oxygen, nitrogen, or fluorine atom. However, there are uneven charge distributions possible whenever two atoms with different electronegativities form a bond. Consider, for example, methanol (CH_3OH). It has several different types of bonds with different distributions of charge in them. The familiar O–H bond in methanol is very much like the O–H bond found in water. That is, it is highly polarized and the hydrogen atom is a small, dense region of highly positive charge that can attract and will be attracted to regions of high electron density such as the lone pairs on oxygen. The methanol molecule also has a C–O bond and three C–H bonds. If we consider the differences in electronegativity we can predict the polarization of these bonds. Remember that carbon and hydrogen have quite similar electronegativities, and so the C–H bond is not very polarized. Carbon and oxygen, in contrast, are quite different in their electronegativities and the result is that the C–O bond is strongly polarized, with the δ+ located on the carbon atom and the negative end of the bond dipole on the oxygen atom. As we will see later this has implications for how methanol (and all C–O containing compounds) interact (and react) with other substances.



An inspection of the Lewis structure can reveal (to the trained mind!) a huge amount about the structure and polarity of a molecule and taking that one step further we can make predictions about the properties of the compound. For example if we compare the relative boiling points of methanol (CH_3OH, bp 65 °C) and ethane (CH_3CH_3, bp -88.6 °C) we see (just as you already predicted no doubt) that methanol has a much higher boiling point because it takes more energy to separate molecules of methanol. The question arises: is this because methanol can form an H-bond with itself? Can you draw a picture of how this happens? Or is it because of the C–O dipole? We can look at this idea a little more closely by comparing the boiling points of three compounds that have similar molecular weights (so that they experience similar London dispersion forces), but different types of bonds in them.



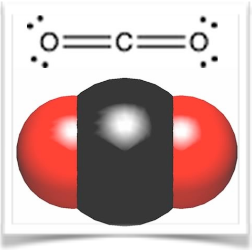
If we classify the kinds of bonds as before we see that dimethyl ether has non-polar C–H bonds and polar C–O bonds. The C–O–C bond angle is about 104°. Because each atom (except for H) is surrounded by four centers of electron density, the molecule is not linear as pictured. (Why not?) The molecule as whole is polar but cannot form hydrogen bonds with itself because none of the hydrogen atoms have a significant δ+ as they would if they were bonded to an oxygen atom. We call the type of forces between dimethyl ether molecules, dipole–dipole forces. On the other hand, an ethanol molecule—which has exactly the same molecular weight and formula—can form hydrogen bonds with itself because it has an O–H bond, and so has a small partially positively charged hydrogen atom. This minor difference has a huge effect on boiling point: ethanol boils at 78 °C whereas dimethyl ether boils at –23 °C. Both of them are considerably higher than propane at -44 °C (remembering that absolute zero is –273.15 °C). From comparing these three similar compounds we can see that a simple dipole–dipole attraction increases the boiling point by 21 °C, and on top of that the H-bonding attraction in ethanol is worth another 99 °C, bringing the boiling point of ethanol to 78 °C.

Intermolecular Forces

Taken together, London dispersion forces, dipole-dipole interactions, and hydrogen bonds comprise a set of attractive forces that make separate molecules stick together. These are collectively named intermolecular forces, IMFs. These forces are caused by either permanent or temporary distortions of the electron cloud in a molecule – which leads to electrostatic attractions between separate molecules. For small molecules, the typical order for strengths of IMFs is: H-bonding (where available) > dipole–dipole interactions > London dispersion forces. At the same time, because London dispersion forces increase with molecular size and the extent of surface-surface interactions, they are often the predominant intermolecular force between large biological macromolecules.

The Importance of Shape

While we are on the subject of carbon and oxygen containing compounds, let us take a look at one of the most common compounds of carbon and oxygen, carbon dioxide. You can draw the structure of CO_2 with the carbon atom in the middle, double bonded to each of the oxygen atoms. That is, CO_2 has two quite polar bonds in it, and so we might reasonably predict that its boiling point might lie somewhere between dimethyl ether and ethanol. But, as you probably already know, this is not the case. CO_2 exists as a gas at room temperature. In fact CO_2 does not have a liquid phase at standard atmospheric pressure; it changes directly from a solid to a gas, a process called sublimation, at -78 °C. How is such behavior to be understood, particularly given that CO_2 has about the same molar mass as ethanol (CH_3CH_2OH), which is a liquid at room temperature? Once again we have to make sure we have considered all the factors that affect molecular polarity including bond polarity and shape. If you reflect back to the ideas about bond polarity and structure you will see that we have another case here of a molecule with polar bonds, but no overall polarity. CO_2 has a linear structure so the bond polarities cancel each other out (they are at 180° from each other) (→). CO_2 has no overall molecular polarity, even though it has polar bonds. Therefore the molecules do not stick together very well and it is a gas at room temperature.



Questions to Answer

- What is the direction of the molecular dipole moment in ammonia? Draw out a picture showing how you came up with the answer. Does it matter which way you draw the molecule? What if you draw it upside down? Will that affect the direction of the dipole (in the real world)?
- Why are the interactions between H_2O molecules stronger than those between HF molecules even though the polarity of the HF bond is larger than the polarity of the OH bond?
- Why don't more than four water molecules interact with a central water molecule?
- What would you predict would be the relative boiling points of methanol (CH_3OH) and ethane (CH_3CH_3), which have similar molecular weights?
- What would you predict would be the relative boiling points of methanol (CH_3OH) and ethanol (CH_3CH_2OH)?
- What kind of compound (or what structural feature) would you expect might be attracted to the $\delta+$ located on the carbon atom in methanol?

Questions to Ponder

- What would be the consequences (for life, the universe, and everything) if water molecules were linear?

4.7 Ionic Bonding

Our discussion up to now has centered on types of bonds that involve valence electrons being shared between (or more correctly being fought over – attracted to the opposite nuclei) different atoms. We have seen that we can consider electron density to be equally distributed between the bonding atoms, or that it may be distorted by being attracted to the more electronegative atom. What we have not looked at yet is the extreme case of this kind of distortion, in which the valence electrons are attracted so much by the electronegative atom that they are transferred completely. This kind of bonding is called ionic bonding (as you are almost certainly already aware).

Let us take a look at some common ionic compounds and see if we can make some sense of their properties from a consideration of their atomic-molecular structure. For the sake of simplicity we will confine ourselves (for the moment) to binary compounds (compounds with only two elements in them.) The most familiar of these compounds is sodium chloride (NaCl), common table salt. NaCl is a continuous compound that extends in three-dimensional array much like diamond (see Chapter 3.) NaCl is a solid at room temperature, with a very high melting point (801 °C), similar to the melting points of silver (961.78 °C) and gold (1064.18 °C), although much lower than the decomposition temperature of diamond (3550 °C). An interesting difference between diamond and sodium chloride occurs on heating. Remember diamond does not melt; it decomposes once enough energy is added to the system to break the C–C bonds. Under normal circumstances, the carbon atoms react with oxygen (O_2) in the air to form carbon dioxide—a process that requires the addition of lots of energy to reverse (as we will see later). On the other hand NaCl melts (solid → liquid) and freezes (liquid → solid) at 801 °C, much like water, just at a higher temperature. Based on this difference, we might be tempted to conclude that covalent bonds are not broken when salt melts but that something stronger than the H-bonds that hold water molecules together are broken. What could that be?

A hint comes from studies first carried out by the English chemist Humphrey Davy.[70] Davy used a voltaic pile to study the effects of passing electricity through a range of substances.[71] Solid table salt did not conduct electricity, but liquid (molten) salt did. Not only did it conduct electricity, but when electricity (electrons) was passed through it, it decomposed to produce globules of a shiny, highly reactive metal (sodium, Na) and a pale green gas (chlorine, Cl_2). Davy correctly (as it turned out) deduced that the elements in table salt (what we now know as sodium and chlorine) are held together by what he termed electrical forces. Just what caused those electrical forces was not discovered until the atomic nature of matter was elucidated over 100 years later.

It takes a great deal of energy to change table salt into its constituent elements. First the salt has to be heated to its melting point, and then electrical energy must be added to release the elements sodium and chlorine. The reverse reaction, combining the elements sodium and chlorine (don't do this at home), produces sodium chloride and releases a great deal of energy (411 kJ/mol). Given the release of energy, we suspect that bonds are being formed during this reaction.

One of the important principles of chemistry is that structure on the atomic-molecular level is reflected in the behavior of materials in the real world. So, let us review some of the real-world properties of sodium chloride:

- It forms colorless crystals that are often cubical in shape and are hard and brittle.
- It has a high melting point and conducts electricity when melted, but not in the solid state.

Based on these properties, and what we know about interactions, bonds, and electricity, we can

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[70] While Davy is well known now for his experiments on the nature of salts, he began his chemical career in his early twenties researching medical uses of gases. He apparently became very fond of nitrous oxide (N_2O, laughing gas), which he reported was an enjoyable recreational drug and a cure for hangovers (ref SALT).

[71] In 1800 the first electric battery, the Voltaic Pile, was developed. It was promptly put to use by a growing number of scientists. For example, molecular hydrogen and oxygen could be produced by passing electricity through water.

begin to make hypotheses about how atoms are organized in NaCl. For example, the fact that NaCl is a stable, crystalline solid at room temperature and that it melts at a high temperature implies that forces holding the atoms together are strong. The regular shape of salt crystals implies that bonds holding the atoms together extend in three dimensions with some regular pattern. If you take a large salt crystal and give it a sharp knock, it breaks cleanly along a flat surface. Diamond also behaves in this way. The ability of molten, but not solid, salt to conduct electricity suggests that melting leads to the appearance of moveable, electrically charged particles. The current interpretation of all these observations and experiments is that in the solid state salt (NaCl) is held together by the coulombic (electrical) attractions between sodium (Na^+) and chloride ($Cl^–$) ions. So when sodium metal (Na) reacts with chlorine (Cl_2) gas, sodium and chloride ions are produced. In the solid state, these ions are strongly attracted to each other and cannot move, but they can move in the molten (liquid) state, and their movement is what conducts electricity (electrons).

One way to think of ionic bonding is that it is the extreme limit of a polar covalent bond. Typically, simple ionic compounds are formed from elements on the left-hand side of the periodic table (metals, such as sodium) and elements on the right-hand side (non-metals, such as chlorine). The non-metals tend to have a high electronegativity as a result of their high effective nuclear charge, whereas the metals have low electronegativity because their valence electrons are not very strongly attracted to their nuclei. When a metal atom meets a non-metal atom the non-metal attracts the valence electrons from the metal, so that for all intents and purposes electrons move from the metal atom (which then has a net positive charge) to the non-metal atom (which now has a net negative charge). This effect, however, applies only to the electrons in the unfilled valence shells. Electrons in a metal atom’s filled core orbitals require a lot more energy to remove. Why? Because they are closer to the positively charged nucleus (recall the jump in ionization energy when an electron is removed from the core). If there is a single outer-shell electron (as is the case with Na and other Group I metals) that electron is often lost, and the resulting atom (now called an ion) has a single positive charge (for example, Na^+). If there are two outer-shell electrons, as in the case of the Group II metals, such as calcium and magnesium, both can be lost to produce doubly charged ions, such as Ca^{++} and Mg^{++} (usually written as Ca^{2+} and Mg^{2+}). At the other side of the periodic table, the non-metals show exactly the opposite pattern, gaining electrons to become negatively charged ions.[72]

Questions to Answer

- The melting point of table salt is over 800 °C. Why is it so high?
- What properties do you associate with a solid?
- What happens on the atomic-molecular level when a solid melts?
- Why don’t metals tend to gain electrons? Why don’t non-metals lose electrons?
- What happens to the size of a sodium atom when it loses an electron to become Na^+?
- What happens to the size of a chlorine atom when it gains an electron and becomes $Cl^–$?

Questions to Ponder

- Why doesn’t solid table salt conduct electricity?
- Why does molten table salt conduct electricity?

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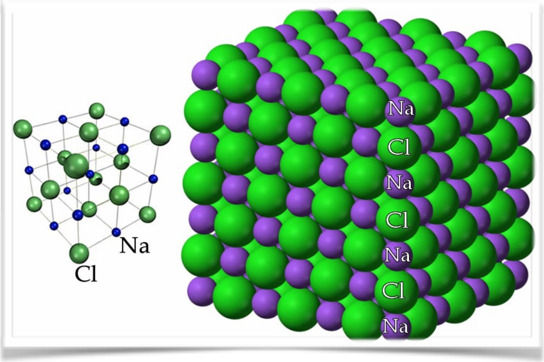
[72] Positively charged ions are known as cations and negatively charged ions are known as anions.

Back to Sodium Chloride



By this point, we have concluded that NaCl is composed of Na^+ ions (cations) and Cl^- ions (anions), but we have not yet discussed how these ions are arranged with respect to one another in space. As you may have come to expect, there is usually more than one way to represent a chemical structure. Different models emphasize different features of a substance but none of them are real in the sense that if we could look at the molecular-level structure, these models are not what we would see. At the same time, visible cubes of salt crystals provide a clue to atomic-molecular structure. If we follow the structure down from the macroscopic to the molecular, this cubic/rectangular structure is retained. A diagram of sodium chloride showing the relative positions of the ions, shown here, illustrates this cubic organization.

Another way to look at NaCl is to think of each Na^+ ion as being surrounded by six Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions. Such an arrangement is possible because of the relative sizes of the sodium and chloride ions; the smaller Na^+ ions can sit in the holes between the larger Cl^- ions (why are the chloride ions bigger than the sodium ions?). One consequence of this arrangement is that there is not an "ionic" bond that is analogous to a covalent bond. Our model of bonding here is best understood as this three-dimensional lattice of interacting ions. The alternating network of positive and negative ions makes for a very stable structure that is difficult to disrupt. The implication? Lots of energy is required to break these interactions and allow the ions to move with respect to one another. Many ionic compounds are organized in similar kinds of crystalline structures. A complexity (to which we will return in Chapter 6) is that many ionic compounds, including NaCl, are highly soluble in water, which means they interact strongly with water molecules. Often salts crystallize together with water molecules and form hydrated (with water) forms, as opposed to anhydrous (without water) forms.

How Ionic Bonding Explains the Properties of Ionic Compounds

Let us return to the properties of ionic compounds and see how this molecular-level (microscopic) model of bonding explains their properties. First, their high melting points arise from the fact that enough energy must be supplied so that multiple (strong) coulombic interactions (recall each cation is surrounded by six anions and vice versa) between the ions must be overcome. In contrast for water, it is only the intermolecular forces between molecules that must be overcome to melt ice; IMFs are significantly weaker than full ionic interactions. Similarly it takes even more energy to vaporize

(liquid → gas) NaCl.

Now let us predict the melting points of different ionic compounds. Remember that the force between the ions is a Coulombic attraction: F α (q^+ x q^-) / r^2, where q^+ and q^- are the charges on the ions, and r is the distance between them. This equation tells us that as the charge on the ions increases, so does the force of attraction, but as the distance between them increases, the force of attraction decreases. That is, the coulombic attraction should be larger for small, highly charged ions, and this should be reflected in the melting points of ionic compounds. Even when we don't factor in the size of the ions, q_1 x q_2 = 4 which means that the attractive forces for CaO should be on the order of 4 times those for NaCl. Indeed, the melting point of calcium oxide (CaO) which has $q_1 = 2^+$ and $q_2 = 2^-$ is 2,572°C.

Questions to Answer

- Draw a molecular level picture of liquid water, and a molecular level picture of liquid sodium chloride. Use this picture to explain why it takes more energy to melt solid salt than it does to melt solid water.
- Arrange these ionic compounds in order of increasing melting point: NaCl, KBr, CaO, Al_2O_3. Look up your answers and see if your predictions were correct.
- Arrange these materials in order of increasing melting point: CH_4, $MgBr_2$, HF, $C_{(diamond)}$. Look up your answers and see if your predictions were correct.
- What do you think happens to the size of the particle when a chlorine atom gains an electron to become a chloride ion? (hint recall that the size of an atom depends on the balance between the attractions between the electrons and the nucleus, and the repulsions between the electrons)
- What do you think happens to the size of the particle when a sodium atom loses an electron to become a sodium ion?

The differences in physical properties between the three substances shown in the table below can be explained based on the strength and character of electrostatic attractions between particles in each substance. $CaCO_3$ is a continuous ionic compound composed of oppositely charged ions attracting one another. Discrete CO_2 molecules associate with one another via LDFs. Ca is a metallic substance in which nuclei are surrounded by a "sea" of delocalized electrons.

Property	**$CaCO_3$**	**CO_2**	**Ca**
Physical state	White crystalline solid	Colorless gas	Silver, shiny solid
Molar mass (g/mol)	100.1	44.01	40.01
Density (g/mL)	2.71	0.00198	1.55
Melting point (°C)	1339 at high pressure	-56.6 (at 5.11 atm)	842
Boiling point (°C)	decomposes	Sublimes at -78.6	1484
Electrical Conductivity as solid	None	None	High
Electrical Conductivity as liquid	High	None	High

Chapter 5: Systems Thinking

Let us recap where we are with atoms, at least from a chemistry perspective:

- Atoms interact electrostatically with each other in a variety of ways, from transient interactions that result in weak (easy to overcome) attractions to strong (bonding) interactions that are much more difficult to break.
- When atoms interact they form more stable systems, where the attractive and repulsive interactions are equal. The potential energy of the system decreases but the total energy of the system remains constant. The total energy of the interacting atoms (the system) can decrease if it is transferred to the surroundings, usually by collisions with other molecules or atoms but the emission of a photon is also possible.
- Whether weak or strong, all types of interactions require energy to overcome. Typically this energy is derived from collisions with surrounding molecules, although absorption of a photon can also overcome interactions.
- The ways that atoms interact depend upon the arrangements of the electrons within them. Different types of atoms have different “internal” arrangements of electrons.
- When atoms bond to form new materials (compounds), the properties of those compounds are emergent—that is, they are quite different from the properties of the isolated component atoms.
- The macroscopic properties of materials depend upon the types of bonds present and their spatial organization, which influences molecular shape, the distribution of charges within the molecule, and intermolecular interactions.
- Some materials are continuous (diamond, metals, ionic compounds), whereas others are composed of discrete molecular units (water, methane, lipids, proteins).
- If you know the temperature at which phase changes occur in a material (solid to liquid, liquid to gas, etc.), you can make predictions about how much energy is required to overcome the interactions between the particles that make up the material.

Now we are ready to draw all these ideas together and make connections between the macroscopic and molecular levels. Understanding these connections allows us to predict how and when chemical changes will occur, which is the heart of chemistry.

5.1 Temperature

Up to now the major types of change we have considered are phase changes (solid to liquid, liquid to gas, etc.) Now we will look at the elements of a phase change in greater detail starting with temperature. If you look up the definition of temperature you will probably find something like “the degree of heat of an object.” However, it is actually quite difficult to give a simple definition of temperature, (typically abbreviated as T). If you were already taught about temperature in physics courses, please bear with us as we work our way through it, sometimes it is helpful to think about things you already know in new ways!

A useful macroscopic way of thinking about temperature is that it tells you in which direction thermal energy (often called heat) will move—energy always moves from a hotter (higher-temperature) object to a cooler (lower-temperature) one. This may seem like an obvious statement about how the physical world works but do you really know why it must be the case? Why doesn’t heat flow from cooler to warmer? Is there some principle that will allow us to explain why? We will be coming back to these questions later on in this chapter.

Students often confuse temperature and thermal energy, and before we go on we need to have a good grasp of the difference between them. The temperature of an object is independent of the size of the object, at least until we get down to the atomic/molecular level where temperature begins to lose its meaning as a concept.[73] The temperature of a drop of boiling water is the same as the temperature of a pan (or an ocean) of boiling water: 100 °C at sea level. At the same time the total amount of thermal energy in a drop of water is much less than that in a large pot of water at the same temperature. A drop of boiling water may sting for a moment if it lands on you, but a pan of boiling water will cause serious damage if it splashes over you. Why? Even though the two are at the same temperature, one has relatively little thermal energy and the other has a lot; the amount of energy is related to the size of the system. In addition, the amount of thermal energy depends on the type, that is, the composition of the material. Different amounts of different substances can have different amounts of thermal energy, even if they are at the same temperature (weird but true).

Kinetic Energy and Temperature

Another way of thinking about temperature is that it is related to the energy of the particles in the sample: the faster the particles are moving, the higher the temperature. It may well take different amounts of energy to get particles moving at the same average kinetic energy. For a simple monoatomic gas, like helium or neon, the only motion that the atoms can do is to move from one place to another in a straight line until they bump into something else, such as another atom or

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[73] Instead of talking about the temperature of an isolated atom or molecule, we talk about its kinetic energy.

molecule.[74] This kind of motion is called translational motion and is directly linked to the kinetic energy of the atom or molecule. That is, the average kinetic energy of a gas is directly related to the temperature. In any given gaseous sample of moving atoms there are many collisions per unit time but these collisions do not alter the total energy of the system (it is conserved).[75] What these collision can, and often do, alter is the relative kinetic energies of the two (or more) colliding atoms: if one slows down, the other will speed up (remember, we are now talking only about monoatomic species; things get more complicated with more complex molecules).

Any single atom or molecule has kinetic energy, but not a temperature. This is an important distinction. Populations of molecules have a temperature related to their average velocity but the concept of temperature is not relevant to individual molecules, they have kinetic energy but not a temperature. This is an important idea, temperature as a characteristic of a system not its individual components. While a system has a unique temperature, the individual molecules that make up the system can have quite different kinetic energies. Because of collisions between molecules, an individual molecule's kinetic energy can be changing rapidly, even though the temperature of the system is constant. When it comes to chemical reactions, it is individual kinetic energies that will be critical (we consider this point in greater detail in Chapter 7).

5.2 Thinking About Populations of Molecules

Within a population of atoms and molecules, the many collisions that occur per second lead to a range of speeds and directions (that is, velocities) of the atoms/molecules. When large numbers of particles are involved in a phenomenon, their individual actions are not important, for example when measuring temperature or pressure. We treat large numbers of molecules as a population. A population is characterized by the distribution of the number or probability of molecules moving with various velocities.[76] This makes it possible to use statistical methods to characterize the behavior of the population. Although any particular molecule behaves differently from one moment to the next, depending upon whether it collides with other molecules or not, the behavior of the population is quite predictable.[77]

From this population perspective, it is the distribution of kinetic energies of atoms or molecules that depends upon the temperature of the system. We will not concern ourselves with deriving the equations that describe these relationships, but rather focus on a general description of the behavior of the motions of atoms and molecules in various states of matter.

Let us think about a population of molecules at a particular temperature in the gas phase. Because of their constant collisions with one another, the population of molecules has a distribution

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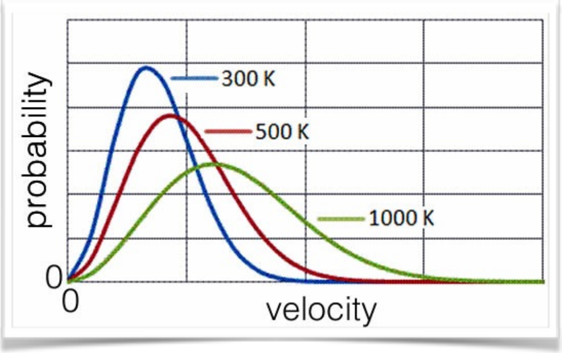
[74] We can ignore gravitational effects because at the molecular level they are many orders of magnitude weaker than the forces between atoms and molecules.

[75] We can also, for all practical purposes, ignore the fact that $E = mc^2$; the conversions between energy and matter are insignificant for chemical processes.

[76] Although this distribution of speeds of atoms was first derived mathematically, it is possible to observe experimentally that atoms in a gas are moving at different speeds.

[77] Interestingly, this is like our approach to the decay of unstable atoms. We cannot predict when a particular atom will decay, but in a large enough population, we can very accurately predict the number of atoms per second that will decay.



of speeds. We can calculate the probability of a particular molecule moving at a particular speed. This relationship is known as the Maxwell–Boltzmann distribution, shown in the graph. Its shape is a function of the temperature of the system; typically it rises fairly steeply from zero (all of the curves begin at zero – why is that do you think?) to a maximum, which then decreases and tails off at higher velocities (which correspond to higher kinetic energies). Because we are plotting probability versus kinetic energy (or rms velocity or speed) we can set the area under the curve to be equal to one (or any other constant). As the temperature changes, the area under the curve stays constant. Why? Because we are completely certain that each particle has some defined amount of kinetic energy (or velocity or speed), even if it is zero and even if we could not possibly know it (remember the uncertainty principle). As the temperature is increased, the relative number of particles that are moving at higher speeds and with more kinetic energy increases. The shape of the curve flattens out and becomes broader. There are still molecules moving very slowly, but there are relatively fewer of them. The most probable speed (the peak of the curve) and the average speed (which is a little higher since the curve is not symmetrical) increase as the temperature increases.

Questions to Answer

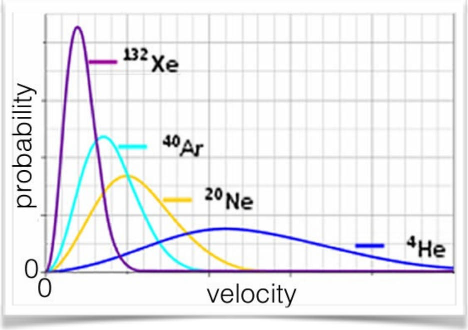
- What happens to the average speed of molecules as temperature increases?
- When molecules collide, why don’t they stick together?
- What do you think happens to the average speed as molecular weight increases (assuming the temperature stays the same)?
- Imagine a system composed of two different types of molecules, one much heavier than the other. At a particular temperature, how do their average kinetic energies compare? Which, on average, is moving faster?

Questions to Ponder

- How large does a system have to be to have a temperature, 10 molecules or 10,000,000?
- If one considers the uncertainty principle, what is the slowest velocity at which a molecule can move?
- If you place a thermometer into a solution, why does it take time for the reading on the thermometer to correspond to the temperature of the solution?

Temperature, Kinetic Energy and Gases

Now here is an unexpected fact: the average kinetic energies of molecules of any gas at the same temperature are equal (since KE = 3/2kT, the identity of the gas does not matter). Let us think about how that could be true and what it implies about gases. Under most circumstances the molecules in a gas do not significantly interact with each other; all they do is collide with one another like billiard balls. So when two gases are at the same temperature, their molecules have the same average kinetic energy. However, an even more unexpected fact is that the mass of the molecules of one gas is different from the mass of the molecules of the other gas. Therefore, given that the average kinetic energies are the same, but the molecular masses are different, the average velocities of molecules in the two gases must be different. For example, let us compare molecular hydrogen (H_2) gas (molecular weight = 2 g/mol) with molecular oxygen (O_2) gas (molecular weight = 32 g/mol), at the same temperature. Since they are at the same temperature the average kinetic energy of H_2 must be equal to the average kinetic energy of O_2, then the H_2 molecules must be moving, on average, faster than the O_2 molecules.[78]



So the average speed at which an atom or molecule moves depends on its mass. Heavier particles move more slowly, on average, which makes perfect sense. Consider a plot of the behavior of the noble (monoatomic) gases, all at the same temperature. On average helium atoms move much faster than xenon atoms, which are over 30 times heavier. As a side note, gas molecules tend to move very fast. At 0 °C the average H_2 molecule is moving at about 2000 m/s, which is more than a mile per second and the average O_2 molecule is moving at approximately 500 m/s. This explains why smells travel relatively fast: if someone spills perfume on one side of a room, you can smell it almost instantaneously. It also explains why you can't smell something unless it is a gas. We will return to this idea later.

Questions to Answer

- Why don't all gas particles move with the same speed at a given temperature?
- Where would krypton appear on the plot above? Why?
- Consider air, a gas composed primarily of N_2, O_2, and CO_2. At a particular temperature, how do the average kinetic energies of these molecules compare to one another?
- What would a plot of kinetic energy versus probability look like for the same gas at different temperatures?
- What would a plot of kinetic energy (rather than speed) versus probability look like for different gases (e.g., the noble gases) at the same temperature?

Questions to Ponder

- If gas molecules are moving so fast (around 500 m/s), why do most smells travel at significantly less than that?

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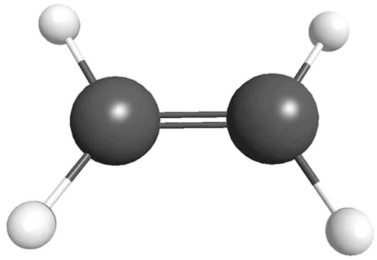
[78] We use average speed and velocity to describe the motion of the particles in a gas, but it is more accurate to use the root mean square (rms) of the velocity, that is, the square root of the average velocity. However, for our purposes average speed (or velocity) is good enough.

- Why does it not matter much if we use speed, velocity, or kinetic energy to present the distribution of motion of particles in a system (assuming the particles are all the same)?

5.3 Vibrating, Bending, and Rotating Molecules

As we have already seen the average kinetic energy of a gas sample can be directly related to temperature by the equation KE = $^1/_2\, mv_{avg}^2$. So, you might reasonably conclude that when the temperature is 0 K, all movement stops. However, if a molecule stops moving we should be able to tell exactly where it is, right? Oh no! That would violate the uncertainty principle, which means there will need be some uncertainty in its energy! At 0 K (a temperature that cannot be reached, even in theory) the system will have what is called zero point energy: the energy that remains when all the other energy is removed from a system (a quantum mechanical concept completely irrelevant to normal life).


https://www.youtube.com/watch?v=FnUGeYkFCCw

For monoatomic gases, temperature is a measure of the average kinetic energy of molecules. But for systems made up of more complex molecules composed of multiple atoms, there are other ways to store energy besides translation (that is, moving through space). In these situations energy added to a system can not only speed up the movement of molecules but also make them vibrate, bend, and rotate (recall we discussed this briefly in Chapter 4)(FIG→). These vibrations, bends, and rotations are distinct for each type of molecule; they depend upon molecular shape and composition. Perhaps not surprisingly, they are quantized. This means that only certain packets of energy can be absorbed or released depending on which vibrations or rotations are involved.[79] Because of that, we can use these molecule-specific energy states to identify molecules and determine their structure at the atomic level. Just as we can identify atoms of elements by their electronic spectra (how their electrons absorb and emit photons as they move from one quantum level to another), we can identify molecules by the way they absorb or emit photons as the molecule moves from one vibrational or rotational state to another. Because it takes less energy to move between vibrational states, photons of infrared or microwave frequencies are typically involved in this analysis. This is the basis for infrared spectroscopy, a topic that we will return to in a separate work.

As materials become more complex in structure, more energy is needed to increase their temperature because there are more ways for a complex molecule to vibrate, bend, and rotate; some of the added energy is used up in vibrations and rotations as well as translations. The amount of energy required to raise the temperature of a particular amount of substance is determined by the molecular-level structure of the material. We can do experiments to determine how adding energy to a substance affects its temperature. Although the word heat is sometimes used to

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[79] Translational energies are also quantized but the quanta are so small that in practice we do not need to worry about that.

describe thermal energy, in the world of physics it is specifically used to describe the transfer of thermal energy from one thing to another. So, we will stick with thermal energy here.

The units of thermal energy are joules (J).[80] Thermal energy is the sum of the kinetic and other potential energies of the particles in a system. There are two commonly used measures of how much energy it takes to change the temperature of a substance and, conversely, how much energy a substance can store at a given temperature: specific heat capacity (J/g °C) and molar heat capacity (J/mol °C). The specific heat of a substance tells you how much energy is required to raise the temperature of a mass (1 g) of material by 1 °C; the molar heat capacity tells you how much energy is required to raise the temperature of a mole of particles by 1 °C. The specific heats and molar heat capacity of a substance depend on both the molecular structure and intermolecular interactions (for solids and liquids, but not gases). Usually, more complex substances have a higher molar heat capacity because larger molecules have more possible ways to vibrate, bend, and rotate. Substances with strong IMFs tend to have higher heat capacities than those with weaker IMFs because energy must be used to overcome the interactions between molecules, rather than make the substance move faster - which increases the temperature.

Heat Capacity and Molecular Structure

It takes 4.12 J to raise 1 gram of water 1 °C (or 1 K.) If you add energy to a pan of water by heating it on a stove top energy is transferred to the molecules of water by collisions with the pan, which in turn has heated up from contact with the heating element[81]. The addition of energy to the system results in the faster movement of molecules, which includes moving from place to place, rotating, bending, and vibrating. Each type of movement adds to the overall thermal energy of the material. Although the molecules in a gas very rarely interact with one another, those in a solid and liquid interact constantly. The increase in temperature as a function of added energy is relatively simple to calculate for a gas; it is much more complicated for liquids and solids, where it depends upon molecular structure and intramolecular (within a molecule) as well as intermolecular (between molecules) interactions.

Consider the molar heat capacities and specific heats of water and the hydrocarbon alcohols (which contain an -OH group) methanol, ethanol, and propanol. As you can see in the table below, water has an unusually high specific heat, even though it is smaller than the other molecules. Their specific heats are pretty much constant, but their molar heat capacities increase with molar mass.

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[80] There are a number of different energy units, including calories, but they are all measures of the same thing, so we will stick to joules here.

[81] Alternatively in microwave ovens, the water molecules gain energy by absorbing microwave radiation which makes them rotate. When they collide with other molecules this energy can also be transformed into vibrations and translations, and the temperature of the water heats up.

Name	Formula	Molar Mass, g	Molar Heat Capacity J/mol °C	Specific Heat J/g °C
Water	H_2O	18	75.4	4.18
Methanol	CH_3OH	32	81.0	2.53
Ethanol	CH_3CH_2OH	48	112	2.44
Propanol	$CH_3CH_2CH_2OH$	60	144	2.39

So an obvious question is, why is the specific heat of water so much higher than that of these alcohols? The reasons for this (apparent) anomaly are:

1. Water molecules are smaller so there are more molecules per gram than there are in the larger, more complex substances.
2. Each water molecule can form up to four hydrogen bonds, but the alcohols can only form a maximum of two hydrogen bonds each (why is this?). As thermal energy is added to the system some of that energy must be used to overcome the attractive forces between molecules (that is, hydrogen bonds) before it can be used to increase the average speed of the molecules. Because there are more hydrogen bonds forming attractions between water molecules, it takes more energy to overcome those interactions and raise the kinetic energy of the water molecules. The end result is a smaller increase in temperature for the same amount of energy added to water compared to methanol, ethanol, and propanol.

The relatively high specific heat of water has important ramifications for us. About 70% of the Earth's surface is covered with water. Because of water's high specific heat, changes in the amounts of solar energy falling on an area between day and night are "evened out" by the large amount of water in the oceans. During the day, the water absorbs much of the energy radiated from the sun, but without a drastic temperature increase. At night, as the temperature falls, the oceans release some of this stored energy, thus keeping the temperature fluctuations relatively small. This effect moderates what would otherwise be dramatic daily changes in surface temperature. In contrast, surface temperatures of waterless areas (like deserts), planets (like Mars), and the Moon fluctuate much more dramatically, because there is no water to absorb and release thermal energy.[82] This moderation of day–night temperature change is likely to be one of the factors that made it possible for life to originate, survive, and evolve on the early Earth. As we go on, we will see other aspects of water's behavior that are critical to life.

Removing Thermal Energy from a Gas

Now that we have been formally introduced to the concepts of heat, thermal energy, and temperature, we can examine what happens when energy is added or removed from matter. We begin with a gas because it is the simplest form of matter. We can observe a gas system by looking

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[82] The situation on planets like Venus and Jupiter is rather more complex.

at a sealed container of water vapor. We can reduce the temperature by cooling the walls of the container; as gas molecules collide with the walls, some of their energy is transferred to the wall and then removed by the cooling system. Over time, the average kinetic energy of the molecules (temperature) decreases. We know that all molecules are attracted to one another by London dispersion forces. In the case of water molecules, there are also interactions mediated by the ability to make hydrogen bonds and dipole–dipole interactions. As temperature increases, these relatively weak interactions are not strong enough to keep molecules stuck together; they are broken during molecular collisions. As the temperature drops, and the average kinetic energy decreases, more and more of these interactions persist for longer and longer times. This enables groups of molecules to form increasingly larger and heavier aggregates. Assuming that our container is on the surface of the Earth, molecules fall out or condense out of the gaseous phase to form a liquid. Because the molecules in the liquid are interacting closely with one another, the volume occupied by these aggregates is much smaller than the volume occupied by the same number of molecules in a gas. The density (mass/volume) of the liquid is higher, and eventually these drops of liquid become large enough to feel the effect of gravity, and are attracted towards the Earth. As the drops of liquid fall to the bottom of the container they merge with one another and the liquid phase below separates from the gaseous phase above. The temperature where the liquid phase first appears is the boiling (or condensation) point of the material (for water it is 100 ºC under atmospheric pressure at sea level). If we continue to remove energy from the system at a fairly slow, steady rate, **the temperature will not change** until almost all the water vapor has condensed into liquid. Why do you think this is so? It may be easier to think about the reverse process: when water boils, the temperature of the water does not change until almost all the water in the liquid phase has vaporized, even though energy is being added to the system. What is that energy being used for?

Even at temperatures well below the boiling point there are still some molecules in the gaseous phase. Why? Because within the liquid, some molecules are moving fast enough (and are located close enough to the liquid–gas boundary) to break the interactions holding them in the liquid. When they leave the liquid phase, the average kinetic energy of the liquid drops (the molecules that leave have higher than average kinetic energy) and some of the kinetic energy of the escaping molecules is used to break free of the interactions holding them together in the liquid phase. The escaping molecules now have lower kinetic energy. This is the basis of the process known as evaporative cooling. The same process explains how the evaporation of sweat cools your body.

Questions to Answer

- Can you measure thermal energy directly? Why or why not?
- What can we measure changes in? How does that allow us to figure out changes in thermal energy of a system?
- Draw a graph of the change in temperature when equal amounts of thermal energy are added at the same rate to equal masses of water, ethanol, and propanol.
- Does each sample reach the same temperature? Why or why not?
- Plot the temperature change versus time as a sample of water vapor moves from a temperature of 110 ºC to 90 ºC.

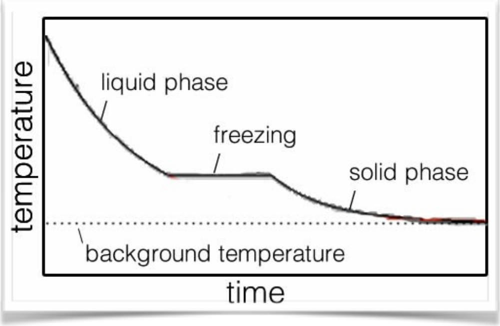
- Draw a molecular-level picture of what the sample looks like at 110 °C and 90 °C. Explain what is happening in each different part of your graph.
- When energy is added to and the water boils, the temperature stays at 100 °C until almost all the water is gone. What is the energy being used for?

Questions to Ponder

- What would life be like if we lived on a planet with no water, but instead the oceans were filled with methanol or ammonia (or filled with hydrocarbons as on Titan, a moon of Saturn)?
- After it's just finished raining, why do pools of water disappear even when the temperature is below the boiling point of water?
- Clouds are made from small droplets of water, why don't they fall to Earth?

Liquids to Solids and Back Again

Within a liquid, molecules move with respect to one another. That is why liquids flow. What does that mean at the molecular level? It means that the molecules are (on average) moving fast enough to break some, but not all, of the interactions linking them to their neighbors. But let us consider what happens as we remove more and more energy from the system through interactions of the molecules with the container's walls. With less energy in the system, there is a decrease in the frequency with which molecules have sufficient energy to break the interactions between them, and as a result interactions become more stable. Once most interactions are stable the substance becomes a solid. The temperature at which the material goes from solid to liquid is termed the melting point. A liquid becomes a solid at the freezing point. For water at atmospheric pressure, this is 0 °C (or 273.15 K). Just like the boiling/condensation point, the temperature does not change appreciably until all the liquid has solidified into ice, or all the ice has melted (→).



Molecular shape and the geometry of the interactions between molecules determine what happens when water (or any other liquid) is cooled and eventually freezes. In the case of frozen water (ice) there are more than 15 types of arrangements of the molecules, ranging from amorphous to various types of crystalline ice. In amorphous ice, the molecules occupy positions that are more or less random with respect to their neighbors; in contrast the molecules in crystalline ice have very specific orientations to one another. The form of ice we are most familiar with is known as Ice I_h, in which the water molecules are organized in a hexagonal, three-dimensional array. Each molecule is linked to four neighboring molecules through hydrogen bonds. This molecular-level structure is reflected at the macroscopic level, which is why snowflakes are hexagonal. Once frozen, the molecules can no longer move with respect to one another because of the bonds between them; the ice is solid and retains it shape, at both the visible and the invisible (molecular) level. However, because we are not at absolute zero (0 K or -273.15 °C), the molecules are still vibrating in place.

Now, what would happen if we heated our container transferring energy from the surroundings into the system (the ice)? As energy is added to the ice the water molecules vibrate more and more vigorously and eventually the hydrogen bonding interactions holding the molecules in place are overcome and the molecules become free to move relative to one another other. The ice melts. At this temperature (0 ºC, 273.15 K) all the energy entering the system is used to overcome intermolecular attractions, rather than increase the speed of molecular motion. If the system is well mixed, the temperature stays at 0 ºC until all of the ice has melted. Then the temperature starts to rise again as the water molecules, now free to move relative to each other, increase in kinetic energy.

Because of the arrangement of water molecules in Ice I_h, the hexagonal "cages" of water molecules within the crystal have empty space within them. As the hydrogen bonds break, some of the water molecules can now move closer together to fill in these open spaces. The structure of the ice collapses in on itself. This open network of molecules, which is not present in liquid water, means that Ice I_h is less dense than liquid water, which is why it floats on liquid water. We don't think much of this commonplace observation, but it is quite rare for a solid to be less dense than the corresponding liquid. More typically, materials (particularly gases, but also liquids and solids) expand when heated as a consequence of the increased kinetic energy, making the particles vibrate more vigorously and take up more space.

5.4 Open Versus Closed Systems

In our discussion, the container of water vapor (gas) is our system: the part of the universe we are observing. It is separated from the rest of the universe (its surroundings) by the walls of the container (its boundary[83].) When we remove energy from the system or add energy to it, that energy goes to or comes from the surroundings. Our system is not an isolated system. If it were, neither energy nor matter would move between the system and the surroundings. In practice it is difficult to construct a perfectly isolated system (although an insulated or styrofoam coffee cup with a lid on is not a bad approximation.) We can also distinguish between open and closed systems: in an open system both matter and energy can enter or leave (we can keep track of both) whereas in a closed system the amount of matter is constant and only energy can enter or leave. Whenever we look at a system our first task is to decide whether the system is isolated, open, or closed. All biological systems are open (both energy and matter are being exchanged with the surroundings.) In the absence of such an exchange, a biological system would eventually die.[84]

Let us consider a beaker of water without a lid as our open system. As the temperature rises, some of the water molecules have enough energy to escape from the body of the water. The liquid water evaporates (changes to a gas). Any gases that might be dissolved in the liquid water, such as oxygen (O_2) or nitrogen (N_2), also move from the liquid to the gaseous phase. At the boiling point, all the energy being supplied to the system is being used to overcome the intermolecular

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[83] The boundary between a system and surroundings depends on how you define the system. It can be real (as in the beaker) or imaginary (as in some ecosystems). In biological systems, the boundary may be the cell wall, or the boundary between the organism and its surroundings (e.g., skin).

[84] The only exception would be cryptobiotic systems, like the tardigrads mentioned earlier.

forces, as it was at the melting point. However, this time the molecules are completely separated from one another, although they still collide periodically. Thus energy is used to overcome attractive forces and the individual molecules fly off into the gas phase where the distances between them become so great that the attractive forces are insignificant.[85] As the liquid boils, its temperature does not rise until all of it has been transformed from liquid to vapor. As the gas molecules fly off, they carry with them some of the system's energy.

Questions to Answer

- Begin with an ice cube in a beaker and end with water vapor. Draw a graph of the energy input versus the temperature of the system. Is your graph a straight line?
- What would happen to the mass of the beaker and water during this process?
- Can you reproduce the hexagonal symmetry of ice by using a model kit? What property of hydrogen bonds makes the structure so open?
- As the temperature rises in liquid water, what do you think happens to the density? Draw a plot of density versus temperature for a mass of water beginning at -10 ºC, up to 50 ºC.
- What happens when the temperature has risen such that the molecules have enough energy to overcome all the attractions between the separate molecules? Focus not on the covalent bonds but the attractions between separate molecules.

Questions to Answer, continued

- During evaporation and boiling do water molecules ever return to the liquid?
- Estimate the temperature at which the bonds within a water molecule break. How does that temperature compare to the boiling point of water? Why aren't they the same temperature?
- How would an open and a closed system differ if you heated them from 30 to 110ºC?

Questions to Ponder

- Are boiling and evaporation fundamentally different processes?
- Under what conditions does evaporation not occur? What is happening at the molecular level?
- What is in the spaces in the middle of the hexagonal holes in Ice I_h?
- What would be the consequences for a closed or isolated biological system?

Questions for Later

- As you heat up a solution of water, predict whether water molecules or dissolved gas molecules will preferentially move from the liquid to the gaseous phase (or will they all move at the same rate?). What factors do you think are responsible for "holding" the gas molecules in the water?
- What do you think happens to the density of the gas (in a closed system) as you increase the temperature?
- What would happen if you captured the gas in a container?
- What would happen if you took that gas in the container and compressed it (made the volume of the container much smaller)?

5.5 Thermodynamics and Systems

The study of how energy in its various forms moves through a system is called thermodynamics. In chemistry specifically it is called thermochemistry. The first law of thermodynamics tells us that energy can be neither created nor destroyed but it can be transferred

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[85] Remember that London dispersion forces fall off as $1/r^6$, where r is the distance between the molecules.

from a system to its surroundings and vice versa.[86] For any system, if we add up the kinetic and potential energies of all of the particles that make up the substance we get the total energy. This is called the system's internal energy, abbreviated as E in chemistry.[87] It turns out that it is not really possible to measure the total internal energy of a system. But we **can** calculate the **change** in energy.

Because we cannot measure energy changes directly we have to use some observable (and measurable) change in the system. Typically we measure the temperature change and then relate it to the energy change. For changes that occur at constant pressure and volume this energy change is the enthalpy change, ΔH. If we know the temperature change (ΔT), the amount (mass) of material and its specific heat, we can calculate the enthalpy change:

$$\Delta H \text{ (J)} = \text{mass (g)} \times \text{specific heat (J/g °C)} \times \Delta T \text{ (°C)}.$$[88]

When considering the enthalpy change for a process, the direction of energy transfer is important. By convention, if thermal energy goes out of the system to the surroundings (that is, the surroundings increase in temperature), the sign of ΔH is negative and we say the process is exothermic (literally, "heat out"). Combustion reactions, such as burning wood or gasoline in air, are probably the most common examples of exothermic processes. In contrast, if a process requires thermal energy from the surroundings to make it happen, the sign of ΔH is positive and we say the process is endothermic (energy is transferred from the surroundings to the system).

Questions to Answer

- You have systems (at 10 °C) composed of water, methanol, ethanol, or propanol. Predict the final temperature of each system if equal amounts of thermal energy (q) are added to equal amounts of a substance (m). What do you need to know to do this calculation?
- Draw a simple sketch of a system and surroundings. Indicate by the use of arrows what we mean by an endothermic process and an exothermic process. What is the sign of ΔH for each process?
- Draw a diagram to show the molecular level mechanism by which thermal energy is transferred in or out of a system. For example how is thermal energy transferred as an ice cube melts in a glass of water?

Questions to Ponder

- What does the difference in behavior of water, methanol, ethanol, and propane tell us about their molecular behavior/organization/structure?

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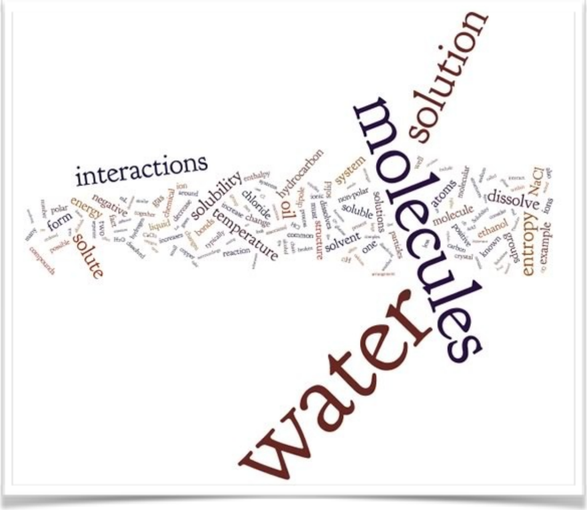
[86] In fact, we should say mass-energy here, but because most chemical and biological systems do not operate under the high-energy situations required for mass to be converted to energy we don't need to worry about that (for now).

[87] Or U if you are a physicist. This is an example of how different areas sometimes seem to conspire to make things difficult by using different symbols and sign conventions for the same thing. We will try to point out these instances when we can.

[88] One important point to note is that this relationship only works when the thermal energy is used to increase the kinetic energy of the molecules—that is, to raise the temperature. At the boiling point or freezing point of a liquid the energy is used to break the attractions between particles and the temperature does not rise.

Chapter 6: Solutions



We have covered quite a number of topics up to this point: the structure of atoms, discrete molecules, covalent network solids, and metals; how atoms and molecules interact, through London dispersion forces, dipole-dipole interactions, hydrogen bonds, and covalent and ionic bonds. We have discussed how changes in energy lead to solid, liquid, and gas state changes. So far, so good, but is this really chemistry? Where are the details about chemical reactions, acids and bases, gas laws, and so forth? Not to worry—we have approached the topics in this order so that you have a strong conceptual foundation before you proceed to the nuts and bolts of chemical reactions. Without this foundation, you would just memorize whatever equations we presented, without making the connections between seemingly disparate reactions. Many of these reactions are complex and overwhelming even for the most devoted student of chemistry. The topics we have covered so far will serve as a tool kit for understanding the behavior of increasingly complex chemical systems. We will continue to reinforce these basic ideas and their application as we move on to the types of reactions that are relevant to most chemical systems.

6.1 What Is a Solution?

The first type of complex system that we will consider is a solution. You almost certainly already have some thoughts about what a solution is and you might want to take a moment to think about what these are. This will help you recognize your implicit assumptions if they “get in the way” of understanding what a solution is scientifically. The major difference between a solution and the systems we have previously discussed is that solutions have more than one chemical substance in them. This raises the question: what exactly is a solution and what does it mean to dissolve? You are probably thinking of examples like sugar or salt dissolved in water or soda. What about milk? Is it a solution? Do solutions have to be liquid or can they also include gases and solids? What is the difference between a solution and a mixture?

Let us take a closer look at what we mean by a solution, starting with a two-component system. Typically, one of the components is present in a smaller amount than the other. We call the major component the solvent and the minor component(s) the solute(s). The most familiar solutions are aqueous solutions, in which water is the solvent. For example, in a solution of the sugar glucose in water, glucose molecules are the solute and water molecules are the solvent. In hydrogen peroxide, which you may find in your medicine cabinet, it is typically 3% hydrogen peroxide and the rest is water. So hydrogen peroxide is the solute and water is the solvent. Once they are thoroughly mixed, solutions have the same composition throughout—they are homogeneous at the macroscopic scale, even though at the molecular level we still find different types of molecules or ions. This is an important point: Once mixed, they remain mixed! If you take a sample from the top of a solution, it has the same composition as a sample from elsewhere in the solution. Solutions, when viewed at the molecular level, have the solute particles evenly (and randomly) dispersed in the solute. Also, because the solute and solvent are in contact with each other, there must be some kind of interaction between the two types of particles. This is not true for simple mixtures. For example, we tend to describe air as a mixture of gases (N_2, O_2, H_2O, etc.), rather than a solution because the gas molecules do not interact aside from the occasional collision with each other.

It turns out that we can make solutions from a wide range of materials. Although it is common to think of solutions in terms of a solid dissolved into a liquid, this is not the only type of solution. Other examples of solutions include: gas in liquid (where molecular oxygen, or $O_{2,}$ dissolves in water – important for fish); solid in solid (the alloy brass is a solution of copper and zinc); gas in solid (hydrogen can be dissolved in the metal palladium); and liquid in liquid (lemonade is a solution of lemon juice and water and a few other things).

Molecular Formation of Solutions

Let us consider a solution of hydrogen peroxide and water. Hydrogen peroxide and water are soluble in each other (what is known as “miscible”) in all proportions. For example, the hydrogen peroxide that you find in your medicine cabinet is typically 3% but the hydrogen peroxide that you find in a pool supply store is typically 30%. How do they dissolve into each other at the molecular level, and why?

So what happens when we add a drop of hydrogen peroxide to a volume of water? The hydrogen peroxide molecules rapidly disperse and the solution becomes homogeneous. However, we know that not everything is soluble in water. For example, oil is not soluble in water and neither are diamonds, although for very different reasons. We will concern ourselves chiefly with energetic (enthalpic involving ΔH) contributors to solubility in this course though there are other factors beyond the scope of our discussion.

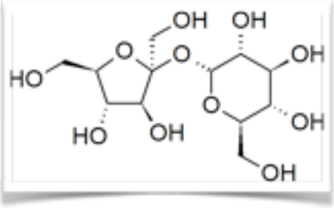
Questions to Answer

- Make a list of some common solutions you might encounter in everyday life. How do you know they are solutions and not mixtures?
- Consider a solution formed from 100 g of water and 5 g sodium chloride:
    - What would you expect the mass of the solution to be? Why?
    - What would you expect the volume of the solution to be? Why?
    - How would you test your hypotheses? What experiments would you do?
    - What evidence would you collect?

6.2 Solubility: why do some things form solutions and others not?

Let us say you have a 100-mL graduated cylinder and you take 50 mL of ethanol and add it to 50 mL of water. You might be surprised to find that the volume of the resulting solution is less than 100 mL. In fact, it is about 98 mL, assuming good technique (no spilling). How can we explain this? Well, we can first reassure ourselves that matter has not been destroyed. If we weigh the solution, it weighs the same as 50 mL of water plus 50 mL of ethanol. As the solution has the mass of the two components added together, but a lesser volume, therefore the density of the solution must be greater than the density of either the water or ethanol alone. At the molecular level, we can immediately deduce that the molecules are closer together in the ethanol and water mixture than they were when pure (before mixing) –try drawing a molecular level picture of this to convince yourself that this is possible. Now, if you took 50 mL of oil and 50 mL of water, you would find that they do not mix—no matter how hard you tried. They will always separate away from one another into two layers. What factors determine whether or not substances form solutions?

First, we need to be aware that solubility is not an all-or-nothing property. Even in the case of oil and water, a very small number of oil molecules are present in the water (the aqueous phase), and a small number of water molecules are present in the oil. There are a number of ways to describe solubility. The most common way is to define the number of moles of solute per liter of solution. This is called the solution's molarity (M, mol/L). If no more solute can dissolve at a given temperature, the solution is said to be saturated; if more solute can dissolve, it is unsaturated.



If we look at the structure of compounds that dissolve in water, we can begin to see some trends: hydrocarbons are not very soluble in water (remember from Chapter 4 that these are compounds composed only of carbon and hydrogen), whereas alcohols (hydrocarbons with an —O–H group attached) with up to 3 carbons are completely soluble. As the number of carbon atoms increases, the solubility of the compound in water decreases. For example, $CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol), is only very slightly soluble in water (0.4 g/L). So perhaps the hydroxyl (—O–H) group is responsible for the molecule's solubility in water. Evidence supporting this hypothesis can be found in the fact that diols (compounds with 2 —O–H groups) are more soluble than similar alcohols. For example, $HOCH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$ (1,6-hexanediol) is quite soluble in water. More familiar water-soluble compounds such as the sugars glucose, fructose, and sucrose (a dimer of glucose and fructose – shown in the figure) are, in fact, polyalcohols. Each of their six carbons is attached to a hydroxyl group.

Compound	Molar Mass (g/mol)	Structure	Solubility (g/L) 20 °C
Propane	44	$CH_3CH_2CH_3$	0.07g/L

Compound	Molar Mass (g/mol)	Structure	Solubility (g/L) 20 °C
Ethanol	46	CH_3CH_2OH	Completely miscible
Dimethyl ether	46	CH_3OCH_3	328 g/L
Pentane	72	$CH_3CH_2CH_2CH_2CH_3$	0.4 g/L
Butanol	74	$CH_3CH_2CH_2CH_2OH$	80 g/L
Diethyl ether	74	$CH_3CH_2OCH_2CH_3$	69 g/L
Hexanol	102	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	0.4 g/L
1,6 Hexanediol	226	$HOCH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$	500 g/L
Glucose	180	$C_6H_{12}O_6$	910g/L

Questions to Answer

- Make a list of substances that you know dissolve in water.
- Which of these dissolve: metals, ionic compounds, molecular compounds (polar, non-polar), network solids (diamond graphite)?
- Can you make any generalizations about which things dissolve and which don't?
- What must happen in order for something to dissolve in water?
- How would you design an experiment to determine the solubility of a solute?
- How would you determine whether or not a solution was saturated?
- Draw a molecular level picture of a solution of ethanol and water showing why the solution is more dense than the separate liquids.
- Draw a molecular level picture of an oil and water mixture.
- Draw a molecular level picture of the process of solution
- When you try mixing oil and water, which layer ends up on top? Why?

Question to Ponder

- You have a saturated solution, with some solid solute present.
- Do you think the solute particles that are in solution are the same ones over time?
- How would you determine whether they were the same?

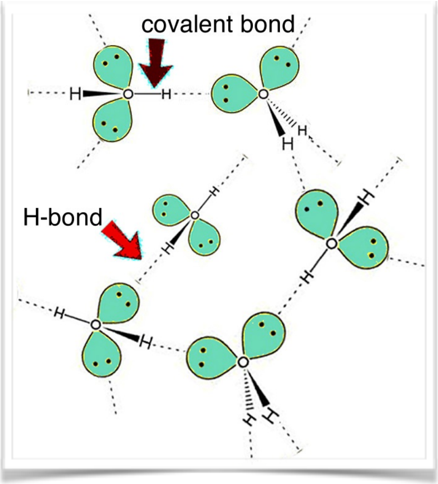
Questions for Later

- What would you predict for the sign of ΔH upon the formation of any solution? Why?

6.3 Hydrogen Bonding Interactions and Solubility

How does adding –OH groups increase the solubility of a hydrocarbon in water? To understand this, we must return to ΔH (enthalpy). For a solute to dissolve in a liquid, the solute molecules must be evenly distributed in that liquid. Solubility depends on how many solute molecules can be present within a volume of solution before they begin to associate preferentially with themselves rather than the solvent molecules. When the solute molecules are dispersed, whatever bonds or attractions holding the particles together in the solute are replaced by interactions between solvent and solute molecules. One reason diamonds are not soluble in water is that the C—C bonds holding a carbon atom within a diamond are much stronger (take more energy to break) than the possible interactions between carbon atoms and water molecules. For a diamond to dissolve in water, a chemical reaction must take place in which multiple covalent bonds are broken. Based on this idea, we can conclude that the stronger the interactions between the solute particles, the less favorable it is for the solute to dissolve in water. At the same time, the stronger the interactions between solute and solvent molecules, the greater the likelihood that solubility will increase.

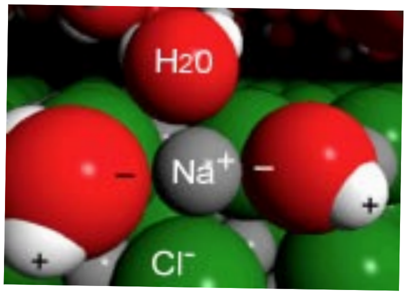
So do intermolecular interactions explain everything about solubility? Do they explain the differences between the solubility of sugar and oil in water? Sugar (with many -OH groups) is readily soluble, and if we consider its structure we can see that interactions between sugar molecules include hydrogen bonding (involving the two hydroxyl groups) and van der Waals interactions (LDFs and dipole-dipole). We can also approach this from a more abstract perspective. If we indicate the non-hydroxyl (—O–H) part of a molecule as R (R just represents the **R**est of the molecule that isn't the –OH group), then an alcohol molecule can be represented as R—O—H, and a diol can be represented as H–O—R—O–H. All alcohols have the ability to form hydrogen bonding interactions with each other as well as with water. So when an alcohol dissolves in water, the interactions between the alcohol molecules are replaced by interactions between alcohol and water molecules—an interaction similar to that between water molecules. Like water molecules, alcohols have a dipole (unequal charge distribution), with a small negative charge on the oxygen(s) and small positive charges on the hydrogen (bonded to the oxygen atoms). It makes sense that molecules with similar structures interact in similar ways. Thus, small molecular-weight alcohols can dissolve in water. But if you look again at the previous table, notice that hexanol (a 6-carbon chain with one —O–H group) is much less soluble than hexanediol (a 6-carbon chain with two —O–H groups—one at each end). As the non-polar carbon chain lengthens, the solubility typically decreases. However, if there are more —O–H groups present, there are more possible interactions with the water. This is also why common sugars, which are really polyalcohols with large numbers of —O–H groups (at least 4 or 5 per molecule), are very soluble in water. Their –O–H groups form hydrogen-bonds with water molecules to form stabilizing interactions. As the length of the hydrocarbon chain increases, the non-polar hydrocarbon part of the molecule starts to become more important and the solubility decreases. This phenomenon is responsible for the "like-dissolves-like" statements that are often found in introductory chemistry books (including this one, apparently).



6.4 Solubility of Ionic Compounds: Salts

Polar compounds tend to dissolve in water, and we can extend that generality to the most polar compounds of all—ionic compounds. Table salt, or sodium chloride (NaCl), the most common ionic compound, is soluble in water (360 g/L). Recall that NaCl is a salt crystal composed not of discrete NaCl molecules, but rather of an extended array of Na^+ and Cl^- ions bound together in three dimensions through electrostatic interactions. When NaCl dissolves in water, the electrostatic interactions within the crystal must be broken. By contrast, when molecular compounds dissolve in water, it is the intermolecular forces between separate molecules that are disrupted. As dissolving ionic compounds requires the breaking of strong ionic interactions, you would think this requires a lot of energy (we have already seen that diamonds do not dissolve in water because actual covalent bonds have to be broken). But we know that substances like NaCl dissolve readily in water, so clearly there is something else going on. The trick is to consider the whole system when NaCl dissolves, just like we did for molecular species. We need to consider the interactions that are broken and those that are formed. These changes in interactions are reflected in the ΔH.

When a crystal of NaCl comes into contact with water, the water molecules interact with the Na^+ and Cl^- ions on the crystal's surface, as shown in the figure. The positive ends of water molecules (the hydrogens) interact with the chloride ions, while the negative end of the water molecules (the oxygen) interacts with the sodium ions. This results in each ion in solution being surrounded by water molecules interacting through ion–dipole interaction between ions and water molecules. The formation of these interactions releases energy and can be very strongly stabilizing ($-\Delta H$). The process by which solvent molecules interact with and stabilize solute molecules in solution is called solvation. When water is the solvent, the process is known as hydration.



VisChem animation from depicting the hydration of a Na+ ion on a NaCl surface.

Questions to Answer

- Draw a molecular-level picture of a solution of NaCl. Show all the kinds of particles and interactions present in the solution.
- When we calculate and measure thermodynamic quantities (such as ΔH), why is it important to specify the system and the surroundings?
- When a substance dissolves in water, what is the system and what are the surroundings? Why? What criteria would you use to specify the system and surroundings?
- For a solution made from NaCl and water, what interactions must be overcome as the NaCl goes into solution? What new interactions are formed in the solution?
- If the temperature goes up when the solution is formed, what can we conclude about the relative strengths of the interactions that are broken and those that are formed? What can we conclude if the temperature goes down?
- When you measure the temperature of a solution, are you measuring the system or the surroundings?

Questions to Ponder

- Why is the water shell around an ion not stable?
- What are the boundaries of a biological system?

6.5 Solutions of Solids in Solids: Alloys

Another type of solution occurs when two or more elements, typically metals, are melted and mixed together so that their atoms can intersperse, forming an alloy. Upon re-solidification, the atoms become fixed in space relative to each other and the resulting alloy has different properties than the two separate metals. Bronze was one of the first known alloys. Its major component is copper (~90%) and its minor component is tin (~10%), although other elements such as arsenic or phosphorus may also be included.

The Bronze Age was a significant leap forward in human history.[89] Before bronze, the only metals available were those that occurred naturally in their elemental form—typically silver, copper, and gold, which were not well suited to forming weapons and armor. Bronze is harder and more durable than copper because the tin atoms substitute for copper atoms in the solid lattice. Its structure has stronger metallic bonding interactions, making it harder and less deformable, with a higher melting point than copper itself. Artifacts (weapons, pots, statues, etc.) made from bronze are highly prized. Before bronze, the only metals available were those that occurred naturally in their elemental form– typically silver, copper, and gold.

Steel is another example of a solid–solid solution. It is an iron solvent with a carbon solute. The carbon atoms do not replace the iron atoms, but fit in the spaces between them; this is often called an interstitial alloy. Because there are more atoms per unit volume, steel is denser, harder, and less metallic than iron. The carbon atoms are not in the original lattice, so they affect the metallic properties more and make it harder for the atoms to move relative to each other. Steel is more rigid, less malleable, and conducts electricity and heat less effectively than iron.

Questions to Answer

- Why do you think silver, copper, and gold often occur naturally as elements (rather than compounds)?
- Draw an atomic-level picture of what you imagine bronze looks like and compare it to a similar picture of steel.
- Use these pictures to explain the properties of bronze and steel, as compared to copper and iron.

Questions to Ponder

- Why do you think the Iron Age followed the Bronze Age? (Hint: Does iron normally occur in its elemental form? Why not?)
- How did the properties of bronze and steel influence human history?

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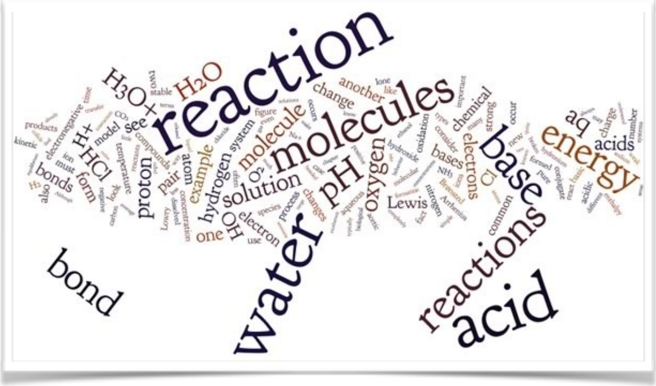
[89] http://en.wikipedia.org/wiki/Bronze_Age

Chapter 7: A Field Guide to Chemical Reactions



At last we have arrived at the place where many chemistry courses begin: chemical reactions. In this chapter we will examine what a chemical reaction is, which processes are not chemical reactions, how chemical reactions occur, and how they are characterized. We will also look at how molecules come to be reorganized during a chemical reaction. (In Chapter 8, we will look at reaction behaviors in greater detail.)

There are a bewildering array of possible reactions, but the truth is that most chemical reactions fall into a rather limited number of basic types. Recognizing types simplifies our task greatly, and enables us to achieve a greater level of confidence with predicting and explaining the outcomes of chemical reactions. Although each particular reaction differs in its specific molecules and conditions (e.g., temperature, solvent, etc.), some common rules apply. Rather than bombard you with a lot of seemingly unrelated reactions, we will introduce you to the two most common reaction types: acid–base and oxidation-reduction. Keep in mind that whatever the reaction type, reactions are systems composed of reactants, products, and the environment in which the reaction occurs. Reactants behave quite differently in the gas phase than in an aqueous or non-aqueous system. High or low temperatures also affect behavior. In the next chapter, we will consider how thermodynamics and kinetics come into play in particular reactions, under specific conditions. This will then lead us to consider equilibrium and non-equilibrium systems.

7.1 Collisions and Chemical Reactions

First we will state the obvious: chemical reactions are linked to change but not all change involves a chemical reaction. When liquid water boils or freezes, it undergoes a change of state (a phase change) but the water molecules are still discrete H_2O molecules. In ice, they remain more or less anchored to one another through H-bonding interactions, whereas in liquid and water vapor they are constantly moving with respect to one another and the interactions that occur between the molecules are transient. We can write out this transition in symbolic form as:

$$H_2O \text{ (solid)} \rightleftarrows H_2O \text{ (liquid)} \rightleftarrows H_2O \text{ (vapor)}$$

The double arrows mean that the changes are reversible. In this case, reversibility is a function of temperature, which controls whether the interactions between molecules are stable (as in ice), transient (as in liquid water), or basically non-existent (as in water vapor). What you notice immediately is that there are water molecules present in each phase. This helps shed light on the common misconception that bubbles found in boiling water are composed of oxygen and hydrogen. Boiling does not break the bonds in a water molecule, so the bubbles are actually composed of water vapor. That said, within liquid water there is actually a chemical reaction going on: the disassociation of water into ^{-}OH and H^+ (which we will discuss in more detail shortly). However a naked proton (that is, H^+ as discrete entity) does not exist in water. Therefore, this reaction is more accurately written as:

$$H_2O + H_2O \rightleftarrows H_3O^+ + {}^{-}OH$$

Here we see the signature of a chemical reaction. The molecules/ions on the two sides of the equation are different; covalent bonds are broken (an O—H bond in one water molecule) and formed (a H—O bond in the other.) All chemical reactions can be recognized in this way. The water dissociation reaction also illustrates how reactions can vary in terms of the extent to which they occur. In liquid water, which has a concentration of about ~55 M, very few molecules undergo this reaction. In fact, in pure water the concentration of H_3O^+ is only 10^{-7} M, which is eight orders of magnitude less than the concentration of water molecules. Another interesting feature of this reaction is that it is going in both directions, as indicated by the double arrows $\rightleftarrows$.

Water reacts with itself to form $H_3O^+ + {}^{-}OH$, and at the same time $H_3O^+ + {}^{-}OH$ are reacting to generate water molecules. The reaction is at equilibrium, and in this case the position of the equilibrium indicates that the majority of the species in water are actually water molecules.

In contrast, other reactions essentially go to completion (proceed until essentially all the reactants are used up).[90] For example, pure ethanol (CH_3CH_2OH), is ~17.1 M and it will burn in air (which contains O_2). We can write the reaction going to completion as:

$$CH_3CH_2OH + 3\ O_2 \rightleftarrows 2\ CO_2 + 3\ H_2O$$

There is very little ethanol left if this reaction occurs in the presence of sufficient O_2.[91] In the real world, the reaction is irreversible because the system is open and both CO_2 and H_2O escape and are therefore not able to collide with each other – which would be a prerequisite for the reverse reaction to occur. Another interesting feature of the ethanol burning reaction is that pure ethanol can be quite stable in contact with the atmosphere, which typically contains ~20% O_2. It takes a spark or a little heat to initiate the reaction. For example, vodka, which is about 50% ethanol, will not burst into flames without a little help! Most reactions need a spark of energy to get them started, but once started, many of them release enough energy to keep them going. As we saw in our discussion of solutions, some reactions release energy (are exothermic) and some require energy (are endothermic). It is important to note that this overall energy change is not related to the spark or energy that is required to get some reactions started. We will return to these ideas in chapter 8.

Another feature of reactions is that some are faster than others. For example, if we add hydrogen chloride gas to water, a reaction occurs almost instantaneously:

$$HCl(g) + H_2O(l) \rightleftarrows H_3O^+(aq) + Cl^-(aq)$$

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[90] That said, one might argue that 10^{-7} M is complete

[91] Although slight traces of ethanol are still detectable; forensic scientists can detect the presence of substances such as hydrocarbons at the scene of a fire, even though the amounts are extremely small.

Very little time elapses between dissolving the HCl and the reaction occurring. We say the rate of the reaction is fast or instantaneous (in Chapter 8, we will look more closely at reaction rate and what affects it.) In contrast, when iron nails are left out in the weather, they form rust. This reaction is slow and can take many years, although in hot climates the reaction goes faster. Similarly, when we cook food, the reactions that take place occur at a faster rate than they would at room temperature.

As we have seen previously, bonded atoms are typically more stable than unbonded atoms. For a reaction to occur, some bonds have to break and new ones have to form. What leads to a bond breaking? Why are new bonds formed? What are the factors that affect whether reactions occur, how much energy is released or absorbed, where they come to equilibrium, and how fast they occur? All these questions and more will be addressed in Chapter 8.

But first things first, in order for a reaction to occur, the reacting molecules have to collide. They have to bump into each other to have a chance of reacting at all. An important point to remember is that molecules are not sitting still. They may be moving from one place to another (if they are in liquid or gaseous phase) and/or they are vibrating and rotating. Remember that the temperature of a system of molecules is a function of the average kinetic energy of those molecules. Normally, it is enough to define the kinetic energy of a molecule as $1/2\ mv^2$, but if we are being completely rigorous this equation applies only to monatomic gases. Molecules are more complex because they can flex, bend, rotate around bonds, and vibrate. Many reactions occur in solution where molecules are constantly in contact with each other—bumping and transferring energy, which may appear as either kinetic or vibrational energy. Nevertheless, we can keep things simple for now as long as we remember what simplifications we are assuming. Recall that although temperature is proportional to the average kinetic energy of the molecules, this does not mean that all the molecules in the system are moving with the same velocity. There is typically a broad range of molecular velocities, even if all the molecules are of the same type. There is an even broader range in reaction mixtures, which have more than one type of molecule in them. Since the system has only a single temperature, all types of molecules must have the same average kinetic energy, which means that the more massive molecules are moving more slowly, on average, than the less massive molecules. At the same time, all the molecules are (of course) moving so they inevitably collide with one another and the walls of the container holding the molecules. We have previously described the distribution of velocities found in the system in terms of a distribution of velocity (or speed) and the percent or even absolute number of molecules with that speed, the Boltzmann distribution. At any particular temperature, there are molecules that move much faster (have higher kinetic energy) and other molecules that move much slower (have less kinetic energy) than the average kinetic energy of the population. This means that when any two molecules collide with one another, the energetics of that interaction can vary dramatically. Some collisions involve relatively little energy, whereas others involve a lot!

These collisions may or may not lead to a chemical reaction, so let's consider what happens during a chemical reaction. To focus our attention, we will consider the specific reaction of hydrogen and oxygen gases to form water:

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

This is, in fact, a very complex reaction, so let's simplify it in a way that may seem cartoonish but is accurate. If we have a closed flask of pure oxygen, and we add some hydrogen (H_2) to the flask, the two types of gas molecules quickly mix, because the mixed system is more probable. Some of the molecules collide with each other, but the overwhelming majority of these collisions are unproductive. Neither the hydrogen molecule (H_2) nor the oxygen molecule (O_2) are altered, although there are changes in their respective kinetic energies. However, when we add kinetic energy (say, from a burning match, which is itself a chemical reaction), the average kinetic energy of the molecules in the heated region increases, thus increasing the energy that can be transferred upon collision. When molecules collide with more energy it increases the probability that a particular collision will lead to a bond breaking. This in turn increases the probability of the $H_2 + O_2$ reaction. In addition, because the stability of the bonds in H_2O is greater than those of H_2 and O_2, the reaction releases energy to the surroundings. This energy can take the form of kinetic energy (which leads to a further increase in the temperature) and electromagnetic energy (which results in the emission of photons of light.) In this way, the system becomes self-sustaining. It no longer needs the burning match because the energy released as the reaction continues is enough to keep new molecules reacting. The reaction of H_2 and O_2 is explosive (it rapidly releases thermal energy and light), but only after that initial spark has been supplied.

We can plot out the behavior of the reaction, as a function of time, beginning with the addition of the burning match. It is worth keeping in mind that the reaction converts H_2 and O_2 into water. Therefore, the concentrations of H_2 and O_2 in the system decrease as the reaction proceeds while the concentration of H_2O increases. As the reaction proceeds, the probability of productive collisions between H_2 and O_2 molecules decreases simply because there are fewer H_2 and O_2 molecules present. We can think of it this way: the rate at which the reaction occurs in the forward (to the right) direction is based on the probability of productive collisions between molecules of H_2 and O_2. This in turn depends upon their relative concentration (this is why hydrogen will not burn in the absence of O_2). As the concentrations of the two molecules decrease, the reaction rate slows down. Normally, the water molecules produced by burning disperse and the concentration (molecules per unit volume) of H_2O never grows very large. But if the molecules are in a container, then their concentrations increase, and eventually the backward reaction could begin to occur. The reaction will reach equilibrium, at which point the rate of forward and backward reactions would be equal. Because the forward reaction is so favorable, some (but very little) H_2 and O_2 would remain at equilibrium. The point is to recognize that reactions are dynamic and, depending on the conditions, the exact nature of the equilibrium state will be determined by concentrations, temperatures, and the nature of the reaction.

Questions to Answer

- In your own words, define the term chemical reaction. How can you tell when a chemical reaction has occurred?
- Give some examples of reactions that you already know about or have learned about in previous courses.
- What do we mean by rate of reaction? How might you determine a reaction rate?
- What conditions must exist in order for something to react?
- How does the concentration of reactants and products influence the rate of a reaction?
- Are chemical reactions possible in the solid phase?
- What factors are required for a reaction to reach a stable (albeit dynamic) equilibrium?
- Why is a burning building unlikely to reach equilibrium?
- Assuming you have encountered them before, define the terms acidic and basic in your own words.

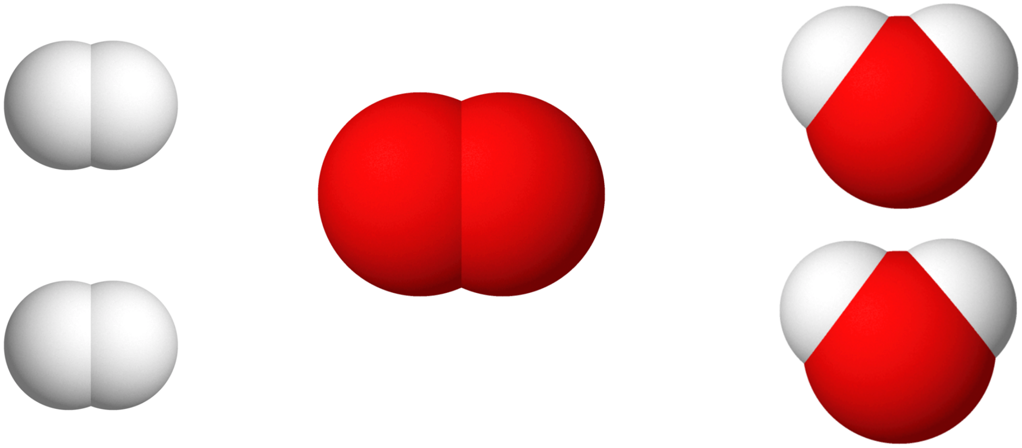
Questions to Ponder

- What reactions are going on around you right now?
- What is required in order for a reaction to go backwards?

7.2 Expressing Conservation of Mass in Chemical Reactions: Stoichiometry

Keen-eyed observers may have noticed that H_2O contains twice as many atoms of hydrogen as it does atoms of oxygen. Recall that matter is neither created nor destroyed in chemical reactions and thus reaction products must result from rearrangements of atoms input into the system as reactants. As both hydrogen and oxygen exist as diatomic molecules (H_2 and O_2) under normal conditions, and not individual atoms, water has to arise from the combination of a set number of oxygen molecules with twice that number of hydrogen molecules. The ratio of reactants to products for a given reaction are represented by coefficients in front of the atomic symbols in a chemical equation. These coefficients are written as whole numbers and thus generation of water from diatomic hydrogen and oxygen is written as follows:

$$2H_2 \quad + \quad O_2 \quad \rightleftarrows \quad 2H_2O$$



The function of equations such as that shown above is to specify the identity of reactants and products in a reaction as well as the ratio of chemical species involved in forming a particular product. The number of each type of atom in a chemical equation must be the same on both sides (as matter is conserved). Additionally, it is important to note that in writing a balanced chemical equation we can change the coefficients (e.g., put a 2 in front of H_2) but cannot change the subscripts (e.g., we CANNOT say H_2 + O), as changing the subscript changes the chemical species. Such expressions, however, tell us little about what is occurring at the molecular level (where hydrogen and oxygen atoms are occasionally colliding in productive ways provided they have sufficient kinetic energy).

Despite giving little molecular-level detail about how reactions work, chemical equations are useful things for working chemists. For example, many employed in the chemical sciences are interested in making compounds important in modern life such as plastics or pharmaceuticals. The reactants for producing a good portion of these materials are often rather expensive and thus process chemists invest a great deal of time and energy into ensuring reactions are as efficient as possible. Of fundamental importance to such chemists is the ratio of reactants that must be combined to form the desired products. To meaningfully discuss how chemists think about setting up reactions, we must shift our discussion towards more useful units. Until now we have thought of the ratio of reactants to products in a reaction in terms of atoms (e.g. “twice as many atoms of X as Y”). As you might imagine, it is not possible to weigh out and work with a single atom so we must now think about converting quantities of atoms to grams.

The concept of the mole, first introduced back in Chapter 3, will be of great use to us in thinking of the combination of reactants in quantitative terms. Recall that a mole is simply a very large number ($6.02*10^{23}$ particles/mole). The atomic or molecular mass of any element or compound, expressed in grams, contains one mole of particles. Thus 12 grams of carbon contains approximately $6.02*10^{23}$ atoms of carbon and 18 grams of water contains that same number of water molecules. As one mole of *anything* is equal to $6.02*10^{23}$ of that thing, we can express the ratios contained within chemical equations in terms of moles. Instead of saying “two molecules of hydrogen can combine with one molecule of oxygen to form two molecules of water” we can say “two moles of hydrogen can be combined with one mole of oxygen to produce one mole of water”. This second statement comes about from multiplying the numbers in the first statement by $6.02*10^{23}$ (and could be re-written “$12.04*10^{24}$ molecules of hydrogen can be combined with $6.02*10^{23}$ molecules of oxygen to produce $12.04*10^{24}$ molecules of water”).

As a mole of any substances is equal to the atomic or molecular mass of that substance in grams, we can now think of reactions in terms that are more useful to working chemists. Given that the atomic mass of H_2 is approximately 2g/mol, the atomic mass of O_2 is approximately 32g/mol, and the atomic mass of H_2O is approximately 18g/mol, we can express the statement “two moles of hydrogen can be combined with one mole of oxygen to produce one mole of water” as “4g of hydrogen can be combined with 32g of oxygen to produce 36g of water”. Note that mass is conserved in this process (as 4g +32g = 36g), which is what we ought to expect in a world where reactions are 100% efficient.

Let us now turn to a practical scenario of producing a certain amount of a useful compound: ammonia. Ammonia (NH_3) is an extremely important fertilizer worldwide and over 100 million tonnes are used for agricultural purposes each year. These vast quantities of ammonia are supplied by a process conceived of by chemists Fritz Haber and Carl Bosch in the early 20th century. The so-called Haber-Bosch process involves combining nitrogen and hydrogen in the presence of a catalyst[92] under high temperatures and pressures to produce ammonia. The chemical equation for the Haber-Bosch process can be found below:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

From this equation you can see that one nitrogen molecule must be combined with three hydrogen molecules to produce two molecules of ammonia. Expressed in terms of moles, 1 mole of N_2 can be combined with 3 moles of H_2 to produce 2 moles of NH_3. Now that you know how to convert between moles and grams, can you determine how many grams of hydrogen and nitrogen would be needed to produce 36g of ammonia? How about 1000000 grams (1 tonne) of ammonia?

Up to this point we have been assuming that all reactants combine with 100% efficiency to produce desired products. Sadly, this is essentially never the case. As discussed in section 7.1, at the molecular level reactions occur due to atoms or molecules colliding in productive orientations with sufficient kinetic energy to drive the desired process forward. Collisions between molecules are random and may thus result in the formation of undesired products. It is further possible that the point at which a forward and reverse reaction are proceeding at the same rate (equilibrium) will occur prior to the consumption of all reactants for the process. The efficiency of a reaction is usually expressed as a percent yield. Percent yield is a measure of how much of desired product is produced as compared to the maximum amount that could be expected to be produced for a given chemical reaction. For example, in the Haber-Bosch process when 1 mole of N_2 is combined with 3 moles of H_2, only 1 mole of $NH_3$is produced. To calculate the percent yield for this reaction we take the actual yield, divide by the theoretical yield (what the balanced chemical equation tells us) and multiply by 100 as follows:

$$\%\, Yield = \frac{actual\ yield}{theoretical\ yield} x\ 100$$

$$\%\, Yield = \frac{1\ mole}{2\ moles} x\ 100$$

$$\%\, Yield = 50\%$$

One of the major tasks of process chemists is to devise strategies for maximizing reaction yield. Impressively, some processes are able to yield very close to 100% of a desired product at tonne scale.

As a final point regarding quantitative relationships between reactants and products, we will consider what happens if one (or more) reactants is in excess of what is needed. For instance, what would happen if you were to combine 2 moles of N_2 with 3 moles of H_2 under Haber-Bosch conditions? Looking at the ratios in the balanced chemical equation for this process, we can see that 3 moles of H_2 (the amount we have) would react with 1 mole of N_2 (half the amount we have) to produce ammonia. This then leaves us with an extra mole of N_2. Thus, the amount of product

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[92] A substance which lowers the energy barrier between reactants and products

formed is limited by the amount of hydrogen (in this case). Hydrogen is therefore the "limiting reagent". In a scenario where 1 mole of N_2 was combined with 6 moles of H_2, two moles of NH_3 would again be produced (assuming 100% yield, of course) but we would be limited by nitrogen, not hydrogen.

Questions to Answer

- Calculate the amount of ammonia produced if 80g of N_2 were combined with 65g of H_2 assuming the process was 100% efficient.
- Assume the above process is 50% efficient and calculate the amount of ammonia produced.
- Why is it necessary to express the ratios of reactants to products in terms of grams?
- How does the mole enable conversion from the number of atoms to the grams of a given element?

Questions to Ponder

- Why might you want to include one reactant in excess? Think about this from the point of view of probable collisions.

7.3 Acid–Base Reactions: A Guide for Beginners

Let us begin our discussion of specific reaction types with the hydrogen chloride and water reaction from the last chapter, a classic acid–base reaction. To understand how these types of reactions are related, we need to learn how to identify their essential and common components. Our first hurdle is the fact that the terms acid and acidity, and to a lesser extent, bases and basicity, have entered the language of everyday life. Most people have some notion of acids and acidity. Examples of common usage include: acid rain, stomach acid, acid reflux, acid tongue, etc. You might hear someone talk about juice that tastes acidic, by which they probably mean sour, and most people would nod their heads in comprehension. You have also probably heard of or even learned about measurements of acidity that involve pH, but what is pH exactly? What is an acid, and why would you want to neutralize it? Are acidic things bad? Do we need to avoid them at all costs and under all circumstances? Although the term base is less common, you may already be familiar with materials that are basic in the chemical sense. Bases are often called alkalis, as in alkaline batteries and alkali metals. They are slippery to the touch, bitter tasting.

Not surprisingly, many definitions of acid–base reactions have been developed over the years. Each new definition has been consistent, that is it produces similar conclusions when applied to a particular system, to the ones that have come before, but each new definition has also furthered the evolution of the idea of acids and bases. Later definitions encompass original ideas about acids and bases, but also broaden them and make them more widely applicable, covering a large array of reactions with similar characteristics. We will start with the simplest model of acids and bases—the Arrhenius model.[93] This is the most common introduction to acid–base chemistry. Although the Arrhenius model is of limited usefulness, we will examine its simple structure as the foundation for more sophisticated and useful models. Our model-by-model consideration should help you appreciate how acid–base chemistry has become increasingly general, and powerful over time. As

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[93] Arrhenius proposed these ideas in 1888 and won a Nobel Prize for his discovery of ionization reactions in solution in 1903.

we progress, keep this simple rule in mind: All acid–base reactions begin and end with polarized molecules. As we go through the various models for acid–base reactions, see if you can identify the polar groups and how they interact with each other.

Arrhenius Acids and Bases

In the Arrhenius model, an acid is defined as a compound that dissociates when dissolved in water to produce a proton (H^+) and a negatively-charged ion (an anion). In fact, naked protons (H^+) do not roam around in solution. They always associate with at least one, and more likely multiple, water molecules.[94] Generally, chemists use a shorthand for this situation, either referring to the H^+ in aqueous solution as a hydronium ion (denoted as H_3O^+) or even more simply as H^+, but do not forget, this is a short-hand. An example of an Arrhenius acid reaction is:

$$HCl(g) + H_2O \rightleftarrows H_3O^+ (aq) + Cl^- (aq)$$

or, more simply (and truer to the original theory):

$$HCl(g) \rightleftarrows H^+ (aq) + Cl^- (aq$$

But this is really quite a weird way to present the actual situation, because the HCl molecule does not interact with a single water molecule, but rather interacts with water as a solvent. When hydrogen chloride (HCl) gas is dissolved in water, it dissociates into $H^+(aq)$ and $Cl^-(aq)$ almost completely. For all intents and purposes, there are no HCl molecules in the solution. An aqueous solution of HCl is known as hydrochloric acid, which distinguishes it from the gas, hydrogen chloride. This complete dissociation is a characteristic of strong acids, but not all acids are strong!

An Arrhenius base is defined as a compound that generates hydroxide (^-OH) ions when dissolved in water. The most common examples of Arrhenius bases are the Group I (alkali metal) hydroxides, such as sodium hydroxide:

$$NaOH(s) + H_2O \rightleftarrows Na^+(aq) + {}^-OH(aq)$$

Again, this is a reaction system that involves both NaOH and liquid water. The process of forming a solution of sodium hydroxide is just like the one involved in the interaction between sodium chloride (NaCl) and water: the ions (Na^+ and ^-OH) separate and are solvated (surrounded) by the water molecules.

As we will see shortly, some acids (and bases) do not ionize completely; some of the acid molecules remain intact when they dissolve in water. When this occurs we use double-headed arrows $\rightleftharpoons$ to indicate that the reaction is reversible, and both reactants and products are present in the same reaction mixture. We will have much more to say about the duration and direction of a reaction in the next chapter. For now, it is enough to understand that acid–base reactions (in fact, all reactions) are reversible at the molecular level. In the case of simple Arrhenius acids and bases, however, we can assume that the reaction proceeds almost exclusively to the right.

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[94] http://www.nature.com/nature/journal/v397/n6720/abs/397601a0.html

An Arrhenius acid–base reaction occurs when a dissolved (aqueous) acid and a dissolved (aqueous) base are mixed together. The product of such a reaction is usually said to be a salt plus water and the reaction is often called a neutralization reaction: the acid neutralizes the base, and vice versa. The equation can be written like this:

$$HCl(aq) + NaOH(aq) \rightleftarrows H_2O(l) + NaCl(aq)$$

When the reaction is written in this molecular form it is quite difficult to see what is actually happening. If we rewrite the equation to show all of the species involved, and assume that the number of HCl and NaOH molecules are equal, we get:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + {}^-OH(aq) \rightleftarrows H_2O(l) + Na^+(aq) + Cl^-(aq)$$

$Na^+(aq)$ and $Cl^-(aq)$ appear on both sides of the equation; they are unchanged and do not react (they are often called spectator ions because they do not participate in the reaction). The only actual reaction that occurs is the formation of water:

$$H^+(aq) + {}^-OH(aq) \rightleftarrows H_2O(l)$$

The formation of water (not the formation of a salt) is the signature of an Arrhenius acid–base reaction. A number of common strong acids, including hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3), react with a strong base such as NaOH or KOH (which, like strong acids, dissociate completely in water) to produce water..

Such acid–base reactions are always exothermic and we can measure the temperature change and calculate the corresponding enthalpy change (ΔH) for the reaction. Regardless of which strong acid or strong base you choose, the enthalpy change is always the same (about 58 kJ/mol of H_2O produced). This is because the only consistent net reaction that takes place in a solution of a strong acid and a strong base is:

$$H^+ (aq) + {}^-OH (aq) \rightleftarrows H_2O(l)$$

One other factor to note is that the overall reaction involves a new bond being formed between the proton (H^+) and the oxygen of the hydroxide (${}^-OH$.) It makes sense that something with a positive charge would be attracted to (and bond with) a negatively-charged species (although you should recall why the Na^+ and Cl^- do not combine to form sodium chloride solid in aqueous solution.) Whether or not bonds form depends on the exact nature of the system. We will return to this idea later in chapter 8.

Questions to Answer

- What would be the reaction if equal amounts of equimolar HNO_3 and KOH were mixed?
- How about equal amounts of equimolar H_2SO_4 and KOH? What would the products be?
- How about equal amounts of equimolar H_3PO_4 and KOH?
- How many moles of NaOH would be needed to react fully with one mole of H_3PO_4?
- Draw a molecular level picture of Arrhenius acid base reaction.

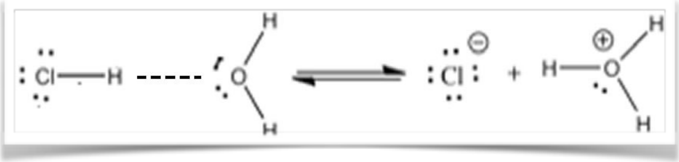
Brønsted–Lowry[95] Acids and Bases

The Arrhenius acid–base model is fairly easy to understand but its application is limited to certain kinds of reactions. Rather than continue down this road, chemists found that they needed to expand their model of acids and bases and how they react. The first of these expansions was the Brønsted–Lowry model. In the Brønsted–Lowry model, an acid is characterized as a proton (H^+) donor and a base as a proton acceptor. If we revisit the reactions we looked at earlier in the context of the Brønsted–Lowry acid-base model, we see that HCl is the proton donor; it gives away H^+ and water is the proton acceptor. In this scheme, HCl is the acid and water is the base:

$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{H_2O(l)} \rightleftarrows \underset{\text{conjugate acid}}{H_3O^+ (aq)} + \underset{\text{conjugate base}}{Cl^-(aq)}$$

The resulting species are called the conjugate acid (so H_3O^+ is the conjugate acid of H_2O) and the conjugate base (Cl^- is the conjugate base of HCl). This is because H_3O^+ can and generally does donate its H^+ to another molecule (most often another water molecule) and Cl^- can accept an H^+.

A major (and important difference) between the Brønsted–Lowry and Arrhenius acid–base models is that a Brønsted–Lowry acid must always have an accompanying base to react with—the two are inseparable. A proton donor must have something to donate the protons to (a base)—in this case, water. Remember that bond breaking requires energy, whereas bond formation releases energy. Some energy input is always required for a reaction in which the only thing that happens is the breaking of a bond (for example the Cl–H bond in HCl). Acid–base reactions are typically exothermic; they release energy to the surroundings and the released energy is associated with the interaction between the H^+ and the base. In other words, the proton does not drop off the acid and then bond with the base. Instead, the acid–H bond starts to break as the base–H bond starts to form. One way that we can visualize this process is to draw out the Lewis structures of the molecules involved and see how the proton is transferred.



As shown in the figure, we use a dotted line to show the growing attraction between the partial positive charge on the H of the H—Cl molecule and the partial negative charge on the oxygen. This interaction results in the destabilization of the H—Cl bond. Because the Cl is more electronegative than the H, the electrons of the original H—Cl bond remain with the Cl (which becomes Cl^-) and the H^+ forms a new bond with a water molecule. Essentially, a Brønsted–Lowry acid–base reaction involves the transfer of a proton from an acid to a base, leaving behind the original bonding electrons.

Another example of an acid–base reaction is the reaction of ammonia with water:

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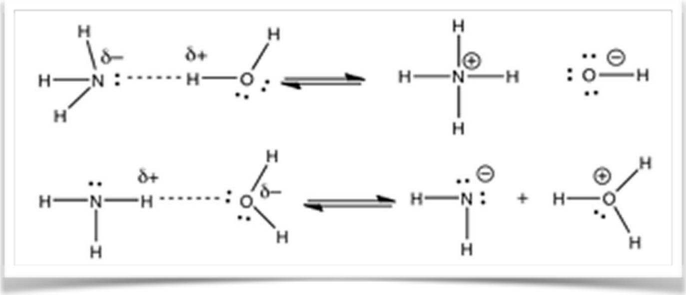
[95] This theory was postulated simultaneously by both Brønsted and Lowry in 1923.

$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + {}^-OH(aq)$
base acid conjugate acid + conjugate base

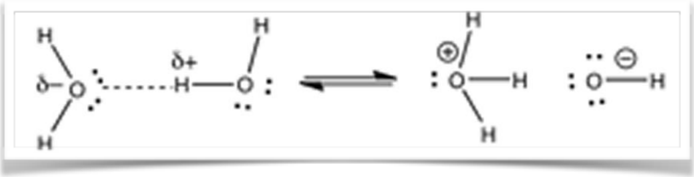
In this case, oxygen is more electronegative than nitrogen. The proton is transferred from the oxygen to the nitrogen. Again, the dotted line in the figure represents the developing bond between the hydrogen and the nitrogen. As the H—O bond breaks, a new H—N bond forms, making the resulting NH_4^+ molecule positively-charged. The electrons associated with the original H—O bond are retained by the O, making it negatively-charged. So, water is the acid and ammonia is the base!



An important difference between this and the preceding HCl–H_2O reaction is that H_2O is a much weaker acid than is HCl. In aqueous solution, not all of the NH_3 reacts with H_2O to form NH_4^+. Moreover, the reaction between NH_3 and water is reversible, as indicated by the ⇄ symbol. The next chapter will consider the extent to which a reaction proceeds to completion. You may be wondering why the water does not act as a base in the reaction with NH_3, like it does with HCl. If you draw out the products resulting from a proton transfer from nitrogen to oxygen, you will see that this process results in a mixture of products where the more electronegative atom (O) now has a positive charge, and the less electronegative atom (N) has a negative charge. It does not make sense that the most electronegative atom would end up with a positive charge, and indeed this process does not happen (to any measurable extent).

We will soon return to a discussion of what makes a compound acidic and/or basic. At the moment, we have two acid–base reactions: one in which water is the acid and the other in which water is the base. How can this be? How can one molecule of water be both an acid and a base, apparently at the same time? It is possible because of the water molecule's unique structure. In fact, water reacts with itself, with one molecule acting as an acid and one as a base:

$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + {}^-OH(aq)$
acid base conjugate acid + conjugate base



As shown in the figure, we can again visualize this process by drawing out the Lewis structures of the water molecules to see how the proton is able to move from one water molecule to another, so that it is never "alone" and always interacting with the lone pairs on the oxygens.

Questions to Ponder

- Between the Arrhenius model and the Brønsted–Lowry model of acids and base, which is more useful? Why?

Questions to Answer

- Which do you think is more likely to happen? The reaction $H_2O + H_2O \rightarrow H_3O^+ + {}^-OH$? Or the reverse process $H_3O^+ + {}^-OH \rightarrow H_2O + H_2O$? Could they both happen at once?
- What do you think the relative amounts of H_2O, $H_3O^+ + {}^-OH$ might be in a pure sample of liquid water? How would you measure the relative amounts?
- Now that you know HCl is an acid and ammonia is a base, can you predict the reaction that occurs between them?
- Is water a necessary component of a Brønsted–Lowry acid–base reaction? How about for an Arrhenius acid–base reaction?

Strong, Weak, Concentrated, and Dilute Acids and Bases

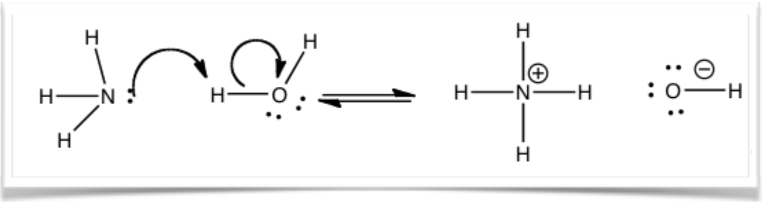
It can be very confusing when words have a different meaning in the scientific context than they do in everyday life. The words we use to describe solutions of acids and bases fall into this category of easily mixed-up definitions. We use the term strong to refer to acids that ionize completely in water, and weak for those acids that are only partially ionized (see Chapter 8 for more information on why). Strong and weak are used to describe an intrinsic property of the acid or base. The terms dilute and concentrated are used to describe the concentration of the acid in water. We could have a dilute solution (say 0.1 M) of the strong acid hydrochloric acid, or a concentrated solution (say 10 M) of the weak acid acetic acid. By contrast, when we refer to strong versus weak liquids in the everyday sense, we are referring to the concentration of the solution. For example, if you say, “This tea is very weak” or “I like my coffee strong” what you are really saying that you like a lot of tea or coffee dissolved in the solution you are drinking. It is important to remember this difference and understand that the scientific context can change the meaning of familiar words.

Questions to Answer

- Draw out molecular-level pictures of a dilute solution of a strong acid and a weak acid.
- Draw out molecular-level pictures of a concentrated solution of a strong acid and a weak acid.
- What are the similarities and differences between all the representations you have drawn?
- Consider what you have learned about the energy changes associated with the reaction of a strong acid with water. From a safety point of view, which of the following actions makes more sense when diluting a concentrated solution of a strong acid with water? Why?
- A. Add water slowly (dropwise) to the concentrated strong acid or
- B. Add the concentrated strong acid dropwise to water

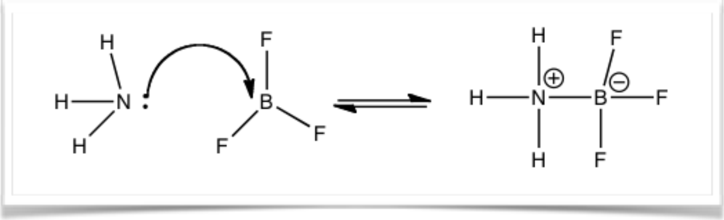
7.3 Lewis Acid–Base Reactions

Although chemists use the Brønsted–Lowry model for any reaction in which a proton is transferred from one atom to another, there is an even broader model. The Lewis model incorporates reactions where there is no proton transfer. Instead of seeing the reaction as a proton transfer, we can look at it from the vantage point of the electron pair that eventually becomes part of the new bond. That is: we can consider an acid-base reaction as the donation of

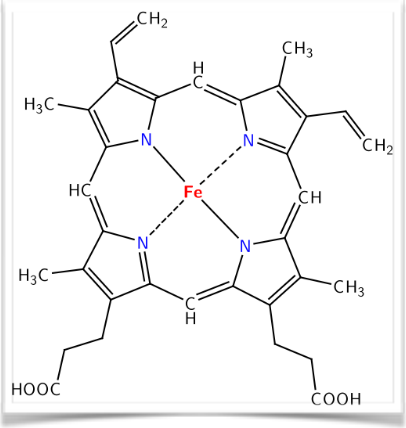


an electron pair (from a base) to form a bond between the donor atom and the proton (or the acid). So, instead of saying water transfers a proton to ammonia, the Lewis model would view the process as ammonia donating a lone electron pair to form a new bond with a proton from a water molecule. This process results in the transfer of a hydrogen from the water to the ammonia molecule (a bond formation event, as shown in the figure).

The electrons that were originally bonded to the hydrogen do not disappear. Rather, they are left behind on the oxygen, leading to the generation of a hydroxide (^-OH) ion. The Lewis acid–base model allows us to consider reactions in which there is no transferred hydrogen, but where there is a lone pair of electrons that can form a new bond.



This figure shows an example of the Lewis acid–base model in the reaction between boron trifluoride (BF_3) and ammonia (NH_3). In this case, the base is the electron pair donor and the acid is the electron pair acceptor. The lone electron pair from NH_3 is donated to boron, which has an empty bonding orbital that accepts the pair of electrons, forming a bond between the N and the B. Even though we use the term “donate”, the electron pair does not leave the NH_3 molecule; it changes from a non-bonding pair to a bonding pair of electrons. BF_3 is a Lewis acid, but note that it has no H to donate. It represents a new class of acids: Lewis acids. These include substances such as BF_3 or $AlCl_3$, compounds of periodic table Group III atoms, which have only six electrons in their bonding orbitals. This electron deficiency leaves empty, energetically-accessible orbitals open to accept an electron pair from the Lewis base, the electron pair donor. Other examples of Lewis acids are metal ions, like Fe^{2+}, Fe^{3+}, Mg^{2+}, and Zn^{2+}. All of these elements play a critical role in biological systems via their behavior as Lewis acids. An important example is the heme group of hemoglobin. In the center of this group is a positively-charged iron (Fe) atom. Such positively-charged ions (cations) have empty orbitals that can interact with the lone pair electrons from Lewis bases and form Lewis acid–base complexes. In the case of hemoglobin, the Lewis bases (O_2, CO_2, and CO) interact with Fe to move oxygen into the body from the lungs and move CO_2 from the body to the lungs. It takes a little practice to gain confidence in recognizing Lewis acid–base reactions, but this skill can help us understand many biological and chemical systems.



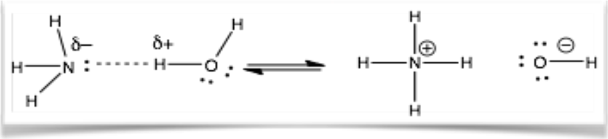
If we look back over the acid–base theories about acids, we see that the theories become increasingly complex as each subsequent theory subsumes the previous one and extends the range of reactions that can be explained. Neither the Arrhenius nor Brønsted–Lowry theories explain why iron in the heme complexes and oxygen to form the oxygen transport system in our bodies. The Lewis acid–base model, on the other hand, can help explain this as well as the simple reaction between HCl and NaOH (where ^{-}OH is the Lewis base and H^+ is the Lewis acid).

Questions to Answer

- For the reaction: $HCl(g) + H_2O(l) \dashrightarrow H_3O^+(aq) + Cl^-(aq)$, write out (in words and molecular level pictures) what is going on during the reaction in terms of:
    - Arrhenius acid–base theory
    - Bronsted–Lowry acid–base theory
    - Lewis acid–base theory
- Now do the same activity for the reaction of NH_3 and HCl.
- Now do the same activity for the reaction of R_2NH and $AlCl_3$.
- Why do you think we use different models of acid–base reactions?
- Can you describe what would dictate the use of a particular model?

7.4 Nucleophiles and Electrophiles

The Lewis acid–base model is more inclusive than the Brønsted–Lowry model, but we often use the Brønsted–Lowry model because it is easier to follow the proton transfer from one molecule (the acid) to another (the base). In aqueous solutions, the Brønsted–Lowry theory also allows us to use the concept of pH to quantify acidity (as we will see shortly). Both the Lewis and Brønsted–Lowry models capture the overarching principle that most chemical reactions are initiated by an electrostatic interaction between a positively-charged portion of a molecule to a negatively-charged portion of the same, or another, molecule.[96] As we will see in the next chapter, molecules must collide with one another in order for reactions to occur between them—they do not react at a distance. When the reacting particles collide, there has to be some continuous pathway through which bonds rearrange and produce products. The first step in this pathway often involves Coulombic (electrostatic) interactions between specific regions of the molecules involved. Of course, whether or not such Coulombic interactions are stable depends upon the kinetic energies of the colliding molecules and exactly how they collide with one another. Catalysts often speed reactions by controlling how molecules collide with or interact with one another. This figure (→) shows the reaction of H_2O and NH_3, in which the positive end of one molecule interacts with the negative end of the other. If we consider this as a Lewis acid–base reaction, the same principle holds true. It turns out that we can profitably consider a wide range of reactions using the principle of Coulombic



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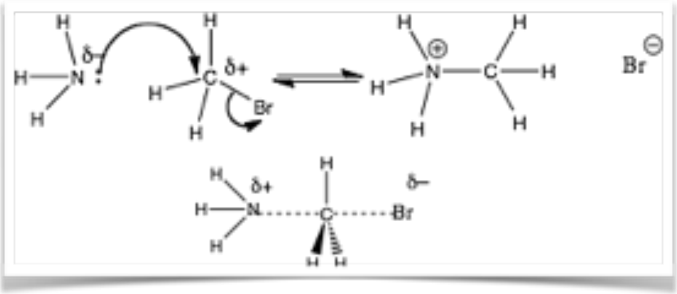
[96] Note reactions between molecules are intermolecular reactions; those that involve a single molecule are intramolecular.

attraction. For example, ammonia (and other nitrogen compounds) can react with carbon-containing molecules if the appropriate conditions are met.

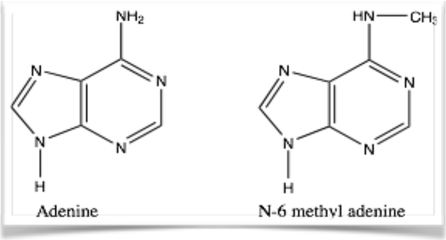
In the figure (→) the nitrogen is behaving as a Lewis base, donating its lone pair of electrons to the carbon. However, it is a little more difficult to see the analogy with a Lewis acid at the carbon site. What we can see is that there is an electronegative, polarizing group (in this case a bromine atom) bonded to the carbon. The presence of a bromine atom polarizes the C—Br bond, giving the carbon a slight positive charge. This makes the carbon susceptible to attack by the lone pair of the nitrogen. Since carbon does not have an empty orbital to accept the lone pair into, and carbon can never form more than four bonds, something has to give. What gives is the C—Br bond, which breaks, and the bromine carries away the electrons from the bond with it, producing a bromide ion, Br^-.



This type of reaction, while is essentially a Lewis acid-base reactions, is usually described using yet another set of terms, probably because these reactions usually belong in the realm of organic chemistry, which was once considered a distinct chemical discipline. For organic chemists, the species with the lone pair (in this case the NH_3) is called the nucleophile (literally, "nucleus-loving") and is attracted to a positive center of charge. The species that accepts the lone pair of electrons, in this case the CH_3Br molecule, is called the electrophile (literally, "electron-loving"). The species that is released from its bond with the carbon is called the leaving group. Leaving groups must be relatively electronegative (as in the case of Br) or stable when associated with an extra pair of electrons. So, good leaving groups are weak bases. Conjugate bases of strong acids are excellent leaving groups because they are stable.

If we analyze the reaction in the figure further, we see the nitrogen nucleophile approaching the carbon electrophile: as the bond forms between the C and N, the bond breaks between the C and the Br. The bond-breaking and bond-making occur simultaneously. Given what we know about water and aqueous solutions, we might even be so brave as to predict that the product ($^+NH_3CH_3$ Br^-) will rapidly lose a proton in aqueous solution to produce $CH_3—NH_2$ and H_3O^+. This kind of reaction is often referred to as a methylation (a $–CH_3$ group is a methyl group). The product is an N-methylated derivative of ammonia.

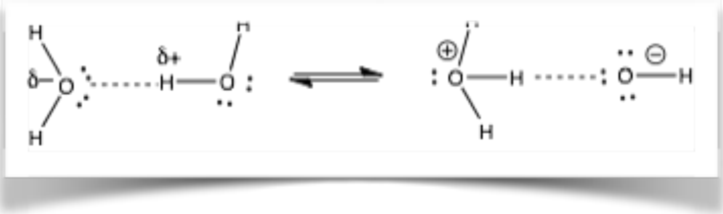
As we have already seen, nitrogen compounds are common in biological systems. We now see how these compounds can also act as nucleophiles, and how methylation of nitrogen is a fairly common occurrence with a range of effects. For example, methylation and demethylation of the nitrogenous bases in DNA adenine and cytosine is used to influence gene expression and mark newly synthesized DNA strands from older, preexisting DNA strands. At the same time, various methylated sequences (such as CpG) are much less stable than the unmethylated form, and so more likely to to mutate.[97] Methylation reactions are quite common in other biological reactions as well. For example, epinephrine (also known as adrenaline, the fight-or-flight hormone) is synthesized in the body by methylation of the related molecule norepinephrine.



Considering Acid–Base Reactions: pH

It is almost certain that you have heard the term pH, it is another of those scientific terms that have made it into everyday life, yet its scientific meaning is not entirely obvious. For example: why does an increase in pH correspond to a decrease in "acidity" and why does pH change with temperature?[98] How do we make sense of pH and use that information to better understand chemical systems?

The key idea underlying pH is that water undergoes an acid–base reaction with itself. Recall that this reaction involves the transfer of a proton from one water molecule to another. The proton is never free or "alone"; it is always bonded to an oxygen within another water molecule. Another important point about pH is that the reaction is readily reversible. Under normal conditions (room temperature), the reaction proceeds in both directions. If we look at the reaction, it makes intuitive sense that the reactants on the right (H_3O^+ and ^-OH) can react together to give two H_2O molecules simply because of the interaction of the positive and negative charges, and we have already seen that the forward reaction does occur. This is one of the first examples we have seen of a reaction that goes both forward and backward in the same system. As we will see, all reactions are reversible at the nanoscale (we will consider the implications of this fact in detail in the next chapter). In any sample of pure water, there are three different molecular species: water molecules (H_2O), hydronium ions (H_3O^+), and hydroxide ions (^-OH), as shown in the figure (→). These three species are constantly interacting with each other through the formation of relatively weak H-bonding interactions, which are constantly forming and breaking. Remember, in liquid water, the water molecules are constantly in motion and colliding with one another. Some of these collisions have enough energy to break the covalent H—



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[97] http://www.springerlink.com/content/n274g10812m30107/

[98] In fact K_w increases with temperature due to Le Chatelier's principle, about which we will have more to say shortly.

O bond in water or in the hydronium ion. The result is the transfer of H^+ and the formation of a new bond with either another water molecule (to form hydronium ion) or with a hydroxide ion (to form a water molecule). To get a feeling for how dynamic this process is, it is estimated that the average lifetime of an individual hydronium ion is on the order of 1 to 2 picoseconds (1×10^{-12} ps), an unimaginably short period of time. In pure water, at 25 °C, the average concentration of hydronium ions is 1×10^{-7} mol/L. We use square brackets to indicate concentration, so we write this as:

$$[H_3O^+] = 1 \times 10^{-7} \text{ M}$$

Note that this is a very, very, very small fraction of the total water molecules, given that the concentration of water molecules $[H_2O]$ in pure water is ~55.4 M.

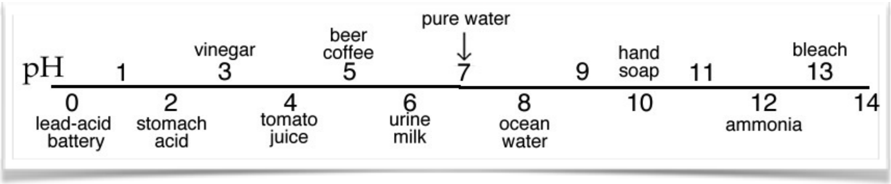
In pure water, every time a hydronium ion is produced, a hydroxide ion must also be formed. Therefore, in pure water at 25 °C, the following equation must be true:

$$[H_3O^+] = [^-OH] = 1 \times 10^{-7} \text{ M}$$

It must also be true that the product of the hydronium and hydroxide ion concentrations, [H3O+][–OH], is a constant at a particular temperature. This constant is a property of water. At 25 ºC, this constant is 1 x 10–14 and given the symbol Kw,25ºC. So why do we care? Because when we add an acid or a base to a solution of water at 25 ºC, the product of [H3O+][–OH] remains the same: 1 x 10–14. We can use this fact to better understand the behavior of acids, bases, and aqueous solutions.

For many people, dealing with negative exponents does not come naturally. Their implications and manipulations can be difficult. Believe it or not, the pH scale[99] was designed to make dealing with exponents easier, but it does require that you understand how to work with logarithms (perhaps an equally difficult task). pH is defined as: $\text{pH} = -\log [H_3O^+]$ [100]

In pure water (at 25 ºC), where the $[H_3O^+] = 1 \times 10^{-7}$ M, pH = 7 (pH has no units). A solution with a higher concentration of hydronium ions than pure water is acidic, and a solution with a higher concentration of hydroxyl ions is basic. This leads to the counter-intuitive fact that as acidity $[H_3O^+]$ goes up, pH goes down. See for yourself: calculate the pH of a solution with a $[H_3O^+]$ of 1×10^{-2} M (pH = 2), and of 1×10^{-9} M (pH = 9). Moreover, because it is logarithmic, a one unit change in pH corresponds to a change in $[H_3O^+]$ of a factor of 10.



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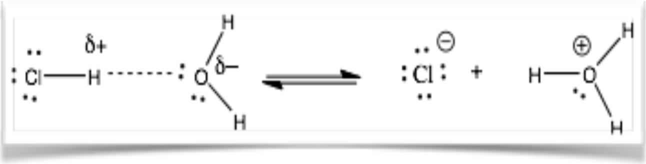
[99] The pH scale was first developed in 1909 by Danish biochemist Soren Sorensen.

[100] In fact, pH is better defined as pH = $\{H_3O^+\}$, where the { } refer to the activity of the species rather than the concentration. This is a topic better left to subsequent courses, although it is important to remember that any resulting calculations on pH using concentrations provide only approximations.

The pH scale is commonly thought of as spanning units 1–14, but in fact many of the strongest acid solutions have pH < 1. Representations of the pH scale often use colors to indicate the change in pH. This convention is used because there are many compounds that change color depending on the [H_3O^+] of the solution in which they are dissolved. For example, litmus[101] is red when dissolved in an acidic (pH < 7) solution, and blue when dissolved in a basic (pH > 7) solution. Perhaps you have noticed that when you add lemon juice (acidic) to tea, the color changes. Do not get confused: solutions of acids and bases do not intrinsically differ in terms of color. The color change depends on the nature of molecules dissolved in the solution. Think about how changes in pH might affect molecular structure and, by extension, the interactions between molecules and light (a topic that is more extensively treated in the spectroscopy supplement).

It is important to note that at 37 °C the value of K_w is different: $[H_3O^+][^-OH] = 2.5 \times 10^{-14}$ and therefore the pH = 6.8. Weirdly, this does not mean that the solution is acidic, since $[H_3O^+] = [^-OH]$. The effect is small, but it is significant; it means that a pH of 7 does not always mean that a solution is neutral (it depends on the temperature). This is particularly important when the concept of pH is applied to physiological systems, since the body is usually not at room temperature.

Now let us consider what happens when we add a Brønsted–Lowry acid to water.



For example, if we prepare a solution of 0.10 M HCl (where we dissolve 0.10 mol HCl(g) in enough water to make 1 liter of solution), the reaction that results (see figure) contains more hydronium ion (H_3O^+). Now if we measure[102] the pH of the solution of 0.10 M HCl, we find that it is 1.0 pH units. If we convert back to concentration units from pH (if $pH = -\log [H_3O^+]$, then $[H_3O^+] = 10^{-pH}$), we find that the concentration of H_3O^+ in 0.10 M HCl is 0.10 M. This makes sense, in light of our previous discussion about how HCl completely dissociates into Cl^- and H^+ (associated with water molecules).

	[HCl] M	[H_2O] M	[H_3O^+] M	[OH] M	[Cl–] M
Before reaction	0.10	~55.5	1.0×10^{-7}	1.0×10^{-7}	0
After Reaction	~0	~55.4	$\sim 1.0 \times 10^{-1}$	1.0×10^{-13}	1.0×10^{-1}

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[101] Litmus is a water-soluble mixture of different dyes extracted from lichens, especially Roccella tinctoria— Wikipedia!

[102] pH is typically measured by using a pH meter that measures the differences between the electrical potential of the solution relative to some reference. As the concentration of hydronium ion increases, the voltage (potential between the solution and the reference) changes and can be calibrated and reported as pH.

This table gives the concentrations of all the species present both before and after the reaction. There are several things to notice about this table. Because the measured pH = 1 and we added 0.1 M (or 10^{-1} M) HCl, it is reasonable to assume that all the HCl dissociated and that the vast majority of the H_3O^+ came from the HCl. We can ignore the H_3O^+ present initially in the water. Why? Because it was six orders of magnitude (0.0000001)(10^{-7}) smaller than the H^+ derived from the HCl (10^{-1}). It is rare to see pH measurements with more than three significant figures, so the H_3O^+ originally present in the water does not have a significant effect on the measured pH value. Although we are not generally concerned about the amount of hydroxide, it is worth noting that $[H_3O^+][^-OH]$ remains a constant (K_w),and therefore when $[H_3O^+]$ increases the $[^-OH]$ decreases.

Although a number of substances dissolve in water, not all ionize, and not all substances that ionize alter the pH. For example, NaCl ionizes completely when dissolved in water, yet the pH of this solution is still 7. The Na^+ and Cl^- ions do not affect the pH at all. However, if we make a 1 M solution of ammonium chloride (NH_4Cl), we find that its pH is around 5. Although it might not be completely obvious why the pH of this solution is 5 and the pH of a 1M NaCl solution is 7, once you know that it is (and given what you know about pH), you can determine the concentrations of H_3O^+, NH_4^+, NH_3, ^-OH and Cl^- present (see Chapter 8). The question is: Why are NH_4Cl and HCl so different? (We consider this point in Chapter 9.)

7.5 Oxidation–Reduction Reactions

In contrast to acid–base reactions, oxidation–reduction (or redox) reactions obey a different pattern. In the simplest kinds of redox reactions, polar products are generated from non-polar reactants. You may have run into such reactions already (even if you did not know what they were called!) When iron is left in contact with oxygen (in air) and water, it rusts. The iron is transformed from a hard, non-polar metallic substance, Fe (solid), into a powdery substance, $Fe_2O_3.nH_2O(s)$. Rusting is mechanistically similar to the reactions that occur when copper turns green, when silver tarnishes and turns black, or (in perhaps the favorite reaction of chemists everywhere[103]) when sodium metal explodes in water.[104]

All of these reactions start with a metal in its elemental form. Pure metals have no charge or permanent unequal distribution of charge (which makes them different from salts like NaCl). In fact we can use the synthesis of sodium chloride (NaCl) from its elements sodium (Na) and chlorine (Cl_2) to analyze what happens during a redox reaction. The reaction can be written as:

$$2Na(s) + Cl_2(g) \rightleftarrows 2NaCl(s)$$

We have already looked at the structure of ionic compounds in Chapter 4 and know that the best way to think about them is to consider NaCl as a three-dimensional lattice of alternating positive (Na^+) and negative (Cl^-) ions. That is as the reaction proceeds the metal atoms becomes cations,

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[103] This is based on the personal memories of one (and only one) of the authors.

[104] Visit http://www.youtube.com/watch?v=eCk0lYB_8c0 for an entertaining video of what happens when sodium and other alkali metals are added to water (yes, they probably faked the cesium).

and the chlorine molecules become anions. We could write this as two separate reactions: The Na loses an electron – a process that we define as oxidation.

$$Na \rightleftarrows Na^+ + e^- \text{ (an oxidation reaction)}$$

The electrons must go somewhere (they cannot just disappear) and since chlorine is an electronegative element, it makes sense that the electrons should be attracted to the chlorine. We define the gain of electrons as a reduction.

$$Cl + e^- \rightleftarrows Cl^- \text{(a reduction reaction).}$$

It turns out that all reactions in which elements react with each other to form compounds are redox reactions. For example, the reaction of molecular hydrogen and molecular oxygen is also a redox reaction:

$$2H_2(g) + O_2(g) \rightleftarrows 2H_2O(l)$$

The problem here is that there is no obvious transfer of electrons. Neither is there an obvious reason why these two elements should react in the first place, as neither of them has any charge polarity that might lead to an initial interaction. That being said, there is no doubt that H_2 and O_2 react. In fact, like sodium and water, they react explosively.[105] When we look a little more closely at the reaction, we can see that there is a shift in electron density on individual atoms as they move from being reactants to being products. The reactants contain only pure covalent (H—H and O—O) bonds, but in the product (H_2O) the bonds are polarized: $H^{\delta+}$ and $O^{\delta-}$ (recall that oxygen is a highly electronegative atom because of its highly effective nuclear charge.) There is a shift in overall electron density towards the oxygen. This is a bit subtler than the NaCl case. The oxygen has gained some extra electron density, and so been reduced, but only partially – it does not gain the whole negative charge. The hydrogen has also been oxidized by losing some electron density. We are really talking about where the electron spends most of its time.

Questions to Answer

- For the reaction $CH_4(g) + O_2(g) \rightleftarrows CO_2(g) + H_2O(g)$, which atoms are oxidized and which are
- reduced?
- For the reaction $CH_3CO_2H + H_2(g) \rightleftarrows CH_3CH_2OH$ which atoms are oxidized and which are reduced?
- Write an explanation to a friend who has no chemistry background to explain the difference between these two reactions that give the same product:
  $2H_2(g) + O_2(g) \rightleftarrows 2H_2O(l)$ and $H^+(aq) + {}^-OH(aq) \rightleftarrows H_2O(l)$

Questions for Later

- Is it possible to separate out the oxidation reaction (where electrons are lost) and the reduction reaction (where electrons are gained)? What would happen?
- What if you separate the two reactions but join them by an electrical connection? What do you think would happen?

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[105] Hydrogen and oxygen can be used as rocket fuel, and the so-called "hydrogen economy" is based on the energy released when hydrogen reacts with the oxygen from the air.

7.6 Energy Changes and Chemical Reactions

All chemical reactions are accompanied by energy changes. Under most circumstances, particularly when the pressure and volume are kept constant, these changes can be ascribed to changes in enthalpy ΔH. For example, combustion reactions (redox reactions involving oxygen) are a major source of energy for most organisms. In warm-blooded organisms, the energy released through such reactions is used to maintain a set body temperature. Within organisms, combustion reactions occur in highly-controlled stages (which is why you do not burst into flames), through the process known as respiration (different from breathing, although breathing is necessary to bring molecular oxygen to your cells).

Not all biological forms of respiration use molecular oxygen.[106] There are other molecules that serve to accept electrons; this process is known as anaerobic (air-free) respiration. All known organisms use the molecule adenosine triphosphate (ATP) as a convenient place to store energy. ATP is synthesized from adenosine diphosphate (ADP) and inorganic phosphate. As two separate species, ADP and inorganic phosphate are more stable than ATP and the energy captured from the environment use to drive the synthesis of ATP can be released again via the formation of ADP and inorganic phosphate:

$$\text{ADP} + \text{Pi} + \text{energy} \rightleftarrows \text{ATP} + H_2O$$

If we looked closely at the molecular level mechanism of ATP synthesis, we would see that it is another example of an acid-base interaction. But regardless of the type of reactions, we can ask the same question: Where (ultimately) does the energy released in an exothermic reaction come from? When an exothermic reaction occurs and energy is transferred from the system to the surroundings, the result is a temperature increase in the surroundings and a negative enthalpy change $-\Delta H$.) What is the source of that energy? Of course, you already know the answer—it has to be the energy released when a bond is formed!

The defining trait of a chemical reaction is a change in the chemical identity of the reactants: new types of molecules are produced. In order for this to occur, at least some of the bonds in the starting material must be broken and new bonds must be formed in the products, otherwise no reaction occurs. So to analyze energy changes in chemical reactions, we look at which bonds are broken and which are formed, and then compare their energies. As we will discuss later, the process is not quite so simple, given that the pathway for the reaction may include higher energy intermediates. As we will see it is the pathway of a reaction that determines its rate (how fast it occurs), whereas the difference between products and reactions determines the extent to which the reaction will occur. The following analysis will lead to some reasonable approximations for estimating energy changes during a reaction.

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[106] When O_2 is used, the process is known as aerobic respiration.

As we have already seen, bond formation releases energy and bond breaking requires energy. Tables of bond dissociation energies are found in most chemistry books and can be easily retrieved from the Internet.[107] One caveat: these measurements are typically taken in the gas phase and refer to a process where the bond is broken homolytically (each atom in the original bond ends up with one electron and the species formed are known as radicals).[108] The bond dissociation energy for hydrogen is the energy required to drive the process:

$$H{-}H(g) \rightleftarrows 2H$$

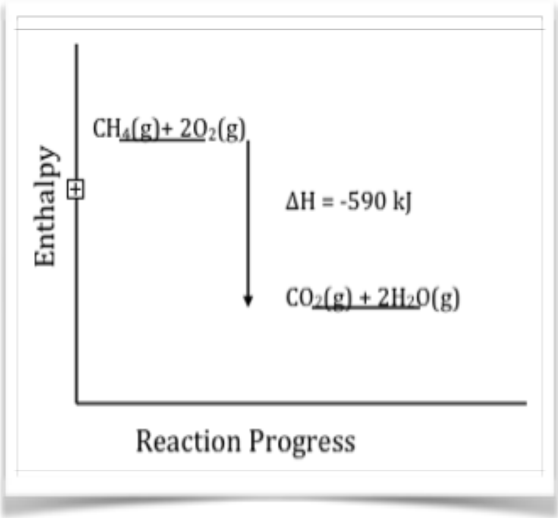
where the dot represents an unpaired electron. The enthalpy change for this process is $\Delta H = +436$ kJ/mol. Note that tables of bond energies record the energy required to break the bond. As we noted earlier, enthalpy is a state function – its value does not depend on the path taken for the change to occur, so we also know what the enthalpy change is for the reverse process. That is, when a hydrogen molecule forms from two hydrogen atoms the process is exothermic:

$$2H \rightleftarrows H{-}H(g) \quad \Delta H = -436 \text{ kJ/mol.}$$

We have tables of bond energy values for most common bond types, so one way to figure out energy changes (or at least the enthalpy changes) for a particular reaction is to analyze the reaction in terms of which bonds are broken and which bonds are formed. The broken bonds contribute a positive term to the total reaction energy change whereas bond formation contributes a negative term. For example, let us take a closer look at the combustion of methane:[109]

$$CH_4(g) + 2O_2(g) \rightleftarrows CO_2(g) + 2H_2O(g)$$

In the course of this reaction, four C—H bonds [4 x C—H (436kJ/mol)] and two O=O bonds (498 kJ/mol) are broken. The new bonds formed are 2 x C=O (803 kJ/mol) and 4 x O—H (460 kJ/mol). If you do the math, you will find that the sum of the bond energies broken is 2740 kJ, whereas the sum of the bond energies formed is –3330 kJ. In other words, the bonds in the products are 706 kJ more stable than the bonds in the reactants. This is easier to see if we plot the progress of enthalpy versus reaction; it becomes more obvious that the products are lower in energy (more stable).



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[107] Although bond dissociation energy and bond energy are often used interchangeably, they are slightly different. Bond dissociation energy is the energy required to break a particular bond in a molecule; bond energy is the average energy required to break a bond of that type. For our purposes, the difference is not important. Tables of bond energies usually refer to average bond energies.

[108] Species with unpaired electrons

[109] To begin this calculation, you must be able to figure out what bonds are present in the molecule; you must be able to draw the Lewis structure.

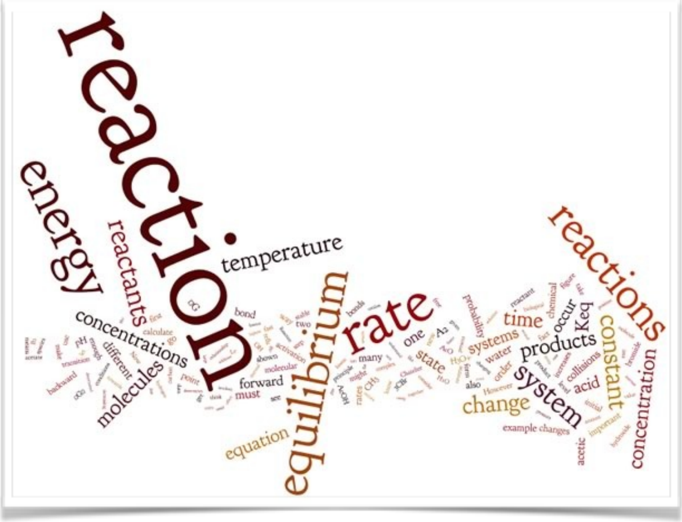
There are several important aspects to note about this analysis:

1. This is only an estimation of the enthalpy change, because (as noted above) bond energies are averages and are measured in the gas phase. In the real world, most reactions do not occur in the gas phase. In solutions, there are all kinds of other interactions (intermolecular forces) that can affect the enthalpy change, but for an initial approximation this method often gives surprisingly good results.
2. Remember, every reaction must be considered as a part of the system. Both the reactants and products have to be included in any analysis, as well as the direction of energy transfer between the reaction system and the surroundings.
3. An exothermic reaction occurs when the bonds formed are stronger than the bonds that are broken. If we look closely at this calculation, we can see that combustion reactions are so exothermic because they produce carbon dioxide. The bond energy of the carbon—oxygen double bond is very high (although not two times the C—O single bond—can you think why?) The production of CO_2 is very favorable from an energy standpoint: it sits in a deep energy well because it has such strong bonds. This point has important ramifications for the world we live in. Carbon dioxide is quite stable; although it can be made to react, such reactions require the input of energy. Large numbers of us expel CO_2 into the atmosphere from burning fossil fuels and breathing, at a higher rate than is currently being removed through various types of sequestration processes, including chemical reactions and photosynthesis. You have certainly heard of the greenhouse effect, caused by the build-up of CO_2. CO_2 is difficult to get rid of because strong bonds give it stability. (Given the notoriety of CO_2 in terms of climate change, we will come back to this topic later.)

Questions to Answer

- Many biology texts refer to energy being released when high-energy bonds in ATP are broken. In light of what you know, is this a reasonable statement? What do these texts really mean?

Chapter 8: How Far? How Fast?



After our overview of common chemical reactions in Chapter 7, the next questions on your mind may well be what determines whether or not a reaction will happen, how fast it will go, how far it will go, or whether it will go in the forward or reverse direction? What causes gasoline to suddenly combust in a violent explosion whereas an iron nail slowly rusts over many years? Are these mysteries of the universe, or can we untangle them in some coherent way?

Once again, it turns out that the universe behaves in an orderly way, and by paying attention to various experimental observations, chemists over the last few centuries have come to understand the factors that control the rate, extent, and direction of reactions. The subject of rate and extent will lead us back to thermodynamics, as we work out the molecular reorganizations that occur during the forward and reverse reactions. In this chapter, we introduce concepts that will allow us to consider how fast a reaction occurs and predict how far it will go.

8.1 What Factors Control Reactions?

The key to understanding the behavior of chemical reactions is to remember that: (a) chemical reactions are systems in which reactants and products interact with their environment and (b) at the molecular level, all reactions are reversible, even though some reactions may seem irreversible. For example, once a log starts burning, we cannot easily reassemble it from carbon dioxide (CO_2), water (H_2O), and energy. But in fact, we can reassemble the log in a fashion by allowing a tree to grow, and by using CO_2 from the air, H_2O from the ground, and energy from the sun (photosynthesis). However, this type of reverse (or backward) reaction is far more complex and involved than the simple forward reaction of burning.

There are, however, a number of factors that we can use to predict how fast and how far a particular reaction will go, including the concentration of the reactants, the temperature, the type of reaction, and the presence of a catalyst. The concentrations of molecules and the temperature of the system are important because all reactions involve collisions between molecules (except for reactions driven by the absorption of light—and you could view those as collisions of a sort). The concentration of reactants determines how often various types of collisions take place (i.e., the more molecules per unit volume, the more frequently collisions occur), whereas the temperature determines the energetics of the collisions: recall that there is a distribution of kinetic energies of molecules at a particular temperature, so not all collisions will lead to a reaction. Molecular structure also matters because it determines whether or not collisions are productive. The only collisions that work are those in which molecules hit each other in particular orientations and with particular energies.

At the beginning, because you have mainly reactants, the forward reaction occurs and very little backward occurs but as the reaction proceeds more there more products formed so more of the backwards reactions occurs. That is the rate of the forward reaction slows down and the rate of the reverse reaction speeds up. This will continue until the rates of the forward reaction and the backward reaction are equal, and the system reaches equilibrium: the point at which no more macroscopic changes occur and the concentrations of reactants and products remain constant at the macroscopic scale.[110] However, as we will discuss further, the forward and back reactions have not stopped, and if we could see the molecules we would see both forward and back reactions still occurring, although there is no overall change in concentration.

As an example, Brønsted–Lowry acid–base reactions are very fast because the probability that the reaction occurs per unit of time is high. When an acid and a base are mixed together, they react immediately with no waiting and without the addition of heat. For example, if we dissolve enough hydrogen chloride gas (HCl) in water to make a 0.1 M solution of hydrochloric acid, the pH immediately drops from 7 (the pH of water) to 1.[111] This measurement tells us that all the HCl has ionized, to give: $[H^+] = 0.1$ and $[Cl^-] = 0.1$.

Now let us take the case of acetic acid (CH_3COOH). If we dissolve enough acetic acid in water to make a 0.1-M solution, the pH of the solution immediately changes from pH 7 (pure water) to 2.9 (not 1). Even if you wait (as long as you want) the pH stays constant, around 3. You might well ask, “What is going on here?” The acid–base reaction of acetic acid and water is fast, but the pH is not as low as you might have predicted. We can calculate the $[H^+]$ from the pH, again using the relationship $pH = -\log [H^+]$ and $[H^+] = 10^{-pH}$, giving us a value of $[H^+] = 1.3 \times 10^{-3}$ M. Thus, the concentration of H^+ is more than two orders of magnitude less than you might have expected! If you think about this, you will probably conclude that the amount of acetic acid (AcOH)[112] that actually reacted with the water must have been very small indeed. In fact we can calculate how much acetic acid reacted using the relationships from the equation:

$$AcOH + H_2O \rightleftarrows H_3O^+ + AcO^-$$

If the concentration of acetic acid started at 0.10 M, and after the ionization reaction 1.3×10^{-3} M of H^+ are present, then the final concentration of acetic acid must be (0.10 minus 1.3×10^{-3}) M. If we use the appropriate number of significant figures, this means that the concentration of acetic acid is still 0.10 M (actually 0.0986 M).

There are two important conclusions here: first, the reaction of acetic acid is fast, and second, most of the acetic acid has not, in fact, reacted with the water. But wait—there is more!

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[110] The rate of reaction is discussed in the next section.

[111] Recall that the $pH = -\log [H^+]$, so $[H^+] = 10^{-pH}$, if the pH is = 1 then the concentration of $H^+ = 10^{-1}$, or 0.1 M.

[112] We write acetic acid in this condensed formula for clarity, remembering that the actual structure of acetic acid is $CH_3C{=}O(O\text{-}H)$, and it is the H on the terminal O that is donated to a base (water).

Even if the reaction appears to have stopped because the pH is not changing any further, at the molecular level things are still happening. That is, the reaction of acetic acid with water continues on, but the reverse reaction occurs at the same rate. So the bulk concentrations of all the species remain constant, even though individual molecules present in each population are constantly changing.[113] The questions of how far a reaction proceeds (towards products) and how fast it gets there are intertwined. We will demonstrate the many factors that affect these two reaction properties.

Questions to Answer

- Draw out a general Brønsted–Lowry acid–base reaction that might occur in water.
- Why do you think the reaction occurs so fast (as soon as the molecules bump into each other)?
- Do you think the water plays a role in the reaction? Draw out a molecular-level picture of your acid–base reaction, showing the solvent interactions.

Question to Ponder

- How do you think the reaction would be affected if it took place in the gas phase instead of an aqueous solution?

8.2 Reaction Rates

In science, when we talk about a rate we mean the change in a quantity over time. A few non-chemical examples include: certain investments with an interest rate, which is the increase in the principle over time (if the rate is negative, then it means that the amount of principle is decreasing over time—not a good investment!); your speed, which is the rate at which you travel down the road, given in miles per hour (or kilometers per hour); a child's growth rate, which might be an inch or two per year (while the elderly might shrink at a different rate); and the growth rate of some plants, like kudzu, which can grow at a rate of 12 inches per day. The units of rate are an amount divided by a period of time. This might seem too obvious to dwell on, but it is worth noting that most real processes do not have a constant rate of change; rates themselves can and do change. This is one reason why calculus is useful in chemistry: it provides the mathematical tools needed to deal with changing rates, like those associated with planetary motions, falling bodies, and (it turns out) chemical reactions.

If we apply the idea of an amount divided by a period of time to the speed of a chemical reaction, what can we measure to determine a reaction's rate? What units tell us the amount present, in the same way that miles and meters measure distance? We can't use mass, because reactions occur between particles (atoms, molecules, ions), which have different masses. We must use the unit that tells us how many particles of a particular type there are—moles. Furthermore, because most reactions (particularly the ones involved in biological and environmental systems) occur in aqueous solutions or in the atmosphere, we usually use units of concentration—molarity (M, mol/L)—to describe the amount of a substance taking part in or produced by a reaction.

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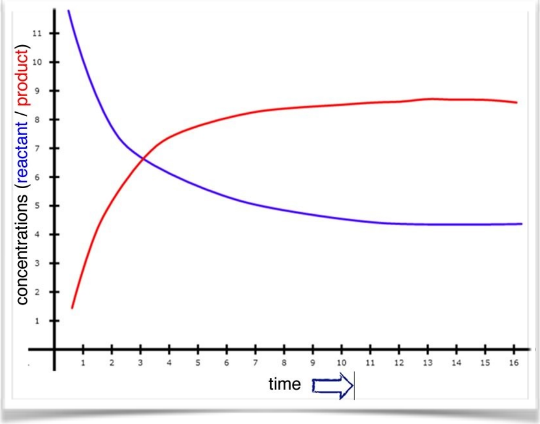
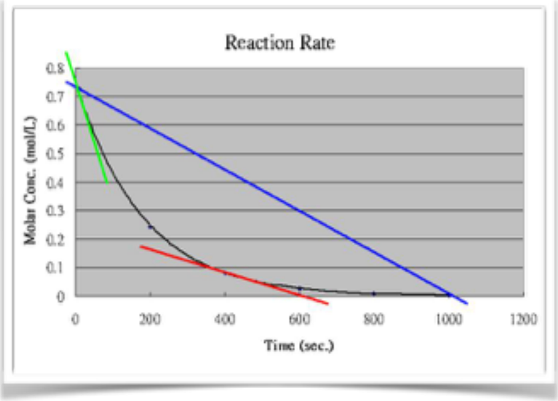
[113] This is true provided that we are talking about reasonably large numbers of molecules - the smaller the number of molecules, the "noisier" the process. You can think about the molecular movements of a single molecule compared to the movement of many molecules, as an example.

Typically, the concentration of substance A_2 is written $[A_2]$, and the rate of a reaction can be described as the change in concentration of a reactant or product over a unit of time. So, $\Delta[A_2]/\Delta t$ or $[A_2]_2 – [A_2]_1 / t_2 – t_1$, where $[A_2]_2$ is the concentration at time t_2, and $[A_2]_1$ is the concentration at time t_2 (assuming that t_2 occurs later in time than t_1).

Reaction Rates and Probabilities



Let us now step back and think about what must happen in order for a reaction to occur. First, the reactants must be mixed together. The best way to make a homogeneous mixture is to form solutions, and it is true that many reactions take place in solution. When reactions do involve a solid, like the rusting of iron, the reactants interact with one another at a surface. To increase the probability of such a reaction, it is common to use a solid that is very finely divided, so that it has a large surface area and thus more places for the reactants to collide.[114]



We will begin with a more in-depth look at reaction rates with a simple hypothetical reaction that occurs slowly, but with a reasonable rate in solution. Our hypothetical reaction will be $A_2 + B_2 \rightleftarrows 2AB$. Because the reaction is slow, the loss of reactants ($A_2 + B_2$) and the production of product (AB) will also be slow, but measurable. Over a reasonable period of time, the concentrations of A_2, B_2, and AB change significantly. If we were to watch the rate of the forward reaction ($A_2 + B_2 \rightleftarrows 2AB$), we would find that it begins to slow down. One way to visualize this is to plot the concentration of a reactant versus time (as shown by the black line in the graph). We can see that the relationship between them is not linear, but falls off gradually as time increases. We can measure rates at any given time by taking the slope of the tangent to the line at that instant (green and red lines).[115] As you can see from the figure, these slopes decrease as time goes by; the tangent at time = 0 (green line) is much steeper than the tangent at a later time (red line). On the other hand, immediately after mixing $A_2 + B_2$, we find that the rate of the backward reaction (that is: $2AB \rightleftarrows A_2 + B_2$) is zero, because there is no AB around to

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[114] One very unfortunate consequence of this is that flour stored in grain silos can explode without warning, if exposed to a spark or other energy source. http://en.wikipedia.org/wiki/Grain_elevator#Elevator_explosions

[115] The slope of the tangent is the change in concentration/change in time or the rate of the reaction. The slope of the tangent is the derivative of the curve at that point (calculus!).

react, at least initially. As the forward reaction proceeds, however, the concentration of AB increases, and the backward reaction rate increases. As you can see from the figure, as the reaction proceeds, the concentrations of both the reactants and products reach a point where they do not change any further, and the slope of each concentration time curve is now 0 (it does not change and is "flat").

Let us now consider what is going on in molecular terms. For a reaction to occur, some of the bonds holding the reactant molecules together must break, and new bonds must form to create the products. We can also think of forward and backward reactions in terms of probabilities. The forward reaction rate is determined by the probability that a collision between an A_2 and a B_2 molecule will provide enough energy to break the A—A and B—B bonds, together with the probability of an AB molecule forming. The backward reaction rate is determined by the probability that collisions (with surrounding molecules) will provide sufficient energy to break the A—B bond, together with the probability that A–A and B–B bonds form. Remember, collisions are critical; there are no reactions at a distance. The exact steps in the forward and backward reactions are not specified, but we can make a prediction: if these steps are unlikely to occur (low probability), the reactions will be slow.

As the reaction proceeds, the forward reaction rate decreases because the concentrations of A_2 and B_2 decrease, while the backward reaction rate increases as the concentration of AB increases. At some point, the two reaction rates will be equal and opposite. This is the point of equilibrium. This point could occur at a high concentration of AB or a low one, depending upon the reaction. At the macroscopic level, we recognize the equilibrium state by the fact that there are no further changes in the concentrations of reactants and products, though this does not mean that the concentration of the reactants and the products are equal. It is important to understand that at the molecular level, the reactions have not stopped. For this reason, we call the chemical equilibrium state a dynamic equilibrium. We should also point out that the word equilibrium is misleading because in common usage it often refers to a state of rest. In chemical systems, nothing could be further from the truth. Even though there are no macroscopic changes observable, molecules are still reacting.[116]

Questions to Answer

- What does linear mean (exactly) when referring to a graph?
- Imagine you are driving at a constant speed of 60 miles per hour. Draw a graph of distance versus time, over a time period of four hours.
- How would you determine your speed from the graph (assuming you did not already know the answer)?
- Now imagine you take your foot off the accelerator and the car coasts to a stop over the course of one hour. What is the average speed over the last hour? How would you figure that out?
- What is the speed exactly 30 minutes after you take your foot off the brake? How would you figure that out?

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[116] You might ask yourself: How do we know the molecules are still reacting if we can only observe the macroscopic level? There are a number of ways of tracking what happens at the molecular level. For example, there are spectroscopic techniques such as NMR that can be used, but they are beyond the scope of this book.

- How does the rate of the forward reaction change over time? Does it increase, decrease or stay the same? Why?
- What does a probability of “0” mean?

Questions to Ponder

- Why can a macroscopic reaction be irreversible, even though at the molecular level reaction is reversible?
- Under what conditions (if any) would a reaction stop completely?
- Why are molecular level and macroscopic behaviors different?

Questions for Later

- Why do you think the amounts of products and reactants do not change after a certain time?
- What is the observable rate of reaction after the time when the concentrations of products and reactants change?

8.3 Temperature and Reaction Rates

Temperature is another important factor when we consider reaction rates. This makes sense if you remember that the vast majority of reactions involve collisions and that the effects of collisions are influenced by how fast the colliding objects are moving. We know intuitively that heating things up tends to make things happen faster. For example, if you want something to cook faster you heat it to a higher temperature (and cooking, as we know, is just a series of chemical reactions). Why is this so? If we consider the reaction of hydrogen and oxygen, discussed in Chapter 7, which is a highly exothermic reaction—explosive, in fact. Yet a mixture of hydrogen and oxygen is quite stable unless energy is supplied, either by heating or a spark of electricity. The same is true of wood and molecular oxygen. The question is: What is the initial spark of energy being used for?

The answer lies within one of the principles that we have returned to over and over again: When atoms form bonds, the result is a more stable system, compared to the energy of non-bonded atoms. But not all bonds are equally stable; some are more stable than others. Nevertheless, energy is always required to disrupt a bond—any bond. If a reaction is to take place, then at least one of the bonds present in the reactants must be broken, and this requires energy.

Imagine two reactants approaching each other. As the reaction starts to occur, the first thing that happens is that at least one bond in a reactant molecule must start to break. It is the initial, partial-bond-breaking step that requires an input of energy from the molecule's surroundings, and the amount of energy required and available will determine if the reaction occurs. If the amount of energy in the environment is not enough to begin the breaking of bonds in the reactants (for example, in the burning of wood, large amounts of energy are required for the initial bond breaking), then the reaction will not occur without an energy "push". Wood does not just burst into flames (at least at standard temperatures)—and neither do humans.[117] The burning wood reaction, wood + $O_2 \rightleftarrows H_2O + CO_2$, does not occur under normal conditions, but if the temperature increases enough, the reaction starts. Once the reaction starts, however, the energy released from the formation of new bonds is sufficient to raise the local temperature and lead to the breaking of more bonds, the formation of new ones, and the release of more energy. As long as there is wood and oxygen available, the system behaves as a positive and self-sustaining feedback loop. The reaction will stop if one of the reactants becomes used up or the temperature is lowered.

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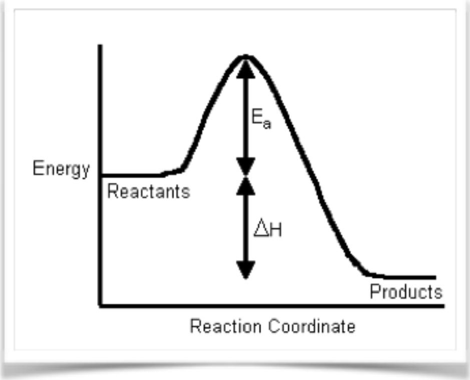
[117] http://en.wikipedia.org/wiki/Spontaneous_human_combustion

It is the activation energy associated with reactions that is responsible for the stability of our world. For example, we live in an atmosphere of ~20% oxygen (O_2). There are many molecules in our bodies and in our environment that can react with O_2. If there were no energy barriers to combustion (i.e., reaction with O_2), we would burst into flames. Sadly, as Salem witches and others would have attested (if they could have), raise the temperature and we do burn. And once we start burning, it is hard to stop the reaction. As we have said before, combustion reactions are exothermic. Once they have produced enough thermal energy, the reaction doesn't need that spark any more. But that initial spark needs the addition of energy (such as the kind provided by a detonator) for explosions to occur.



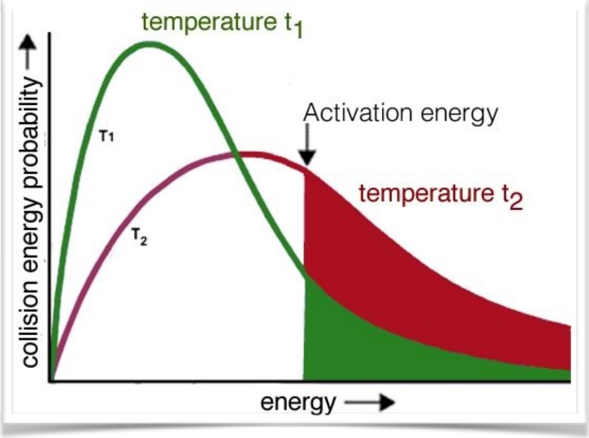
If we plot energy versus the progress of the reaction, we can get a picture of the energy changes that go on during the reaction. Remember that the reaction coordinate on the x-axis is not time; we have seen that reactions go backwards and forwards all the time. For a simple one-step reaction as shown in the figure, the highest point on the energy profile is called the transition state. It is not a stable entity and only exists on the timescale of molecular vibrations (femtoseconds). The energy change between the reactants and the transition state is called the activation energy. This is the energy that must be supplied to the reactants before the reaction can occur. This activation energy barrier is why, for example, we can mix hydrogen and oxygen and they will not explode until we supply a spark, and why we can pump gasoline in an atmosphere that contains oxygen, even though we know that gasoline and oxygen can also explode. The amount of energy that must be supplied to bring about a reaction is a function of the type of reaction, some reactions (acid base) have low activation energies and correspondingly high rates, and some (rusting) have high activation energies and low rates.

Now it should be easier to understand how increasing temperature increases the reaction rate—by increasing the average kinetic energy of the molecules in the environment. Recall that even though individual molecules have different kinetic energies, all of the different populations of molecules in a system have the same average kinetic energy. If we consider the effect of temperature on the distribution of kinetic energies, we see right away that at higher temperatures there are relatively more molecules with higher kinetic energy. Collisions between these high-energy molecules provide the energy needed to overcome the activation energy barrier, that is, the minimum energy required to start a chemical reaction. As the temperature rises, the probability of productive collisions between particles per unit time increases, thus increasing the reaction rate. At the same time, it is possible that raising the temperature will allow other reactions to occur (perhaps reactions we have not been considering). This is particularly likely if we are dealing with complex mixtures of different types of molecules.

The activation energy for a reaction also depends upon the type of reaction that is occurring. For example, a Brønsted–Lowry acid–base reaction has a very low activation energy barrier. In these reactions the only thing that is happening is that a proton is being transferred from one electronegative element to another:

$$H—Cl + H—O—H \rightleftarrows Cl^- + H_3O^+$$

(draw this out to better see what is happening).



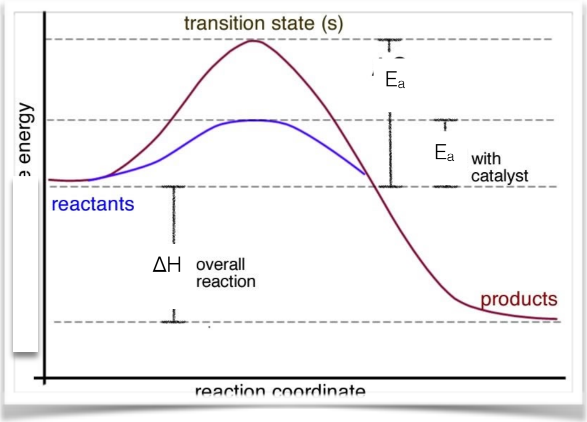
The reaction is rapid because the Cl—H bond is highly polarized and weak. In a sense, it is already partially broken. Also, these reactions usually take place in water, which interacts with and stabilizes the growing charges. Low-energy collisions with water molecules are sufficient to finish breaking the Cl—H bond. We say that acid–base reactions like this are kinetically controlled because they occur upon mixing and do not require heating up or extra energy to proceed. Essentially all collisions involving the HCl molecule provide sufficient energy to break the H—Cl bond. This is also true for almost all proton-transfer reactions. However, for most other types of reactions, simply mixing the reactants is not enough. Energy must be supplied to the system to overcome this energy barrier, or we have to wait a long time for the reaction to occur. In fact, most organic reactions (those in which carbon is involved) are quite slow. Why the difference? The answer should be reasonably obvious. There is simply not enough energy in the vast majority of the collisions between molecules to break a C—H, C—C, C—N, or C—O bond. If you take organic chemistry lab, you will discover that large portions of time are spent waiting as solutions are heated to make reactions happen faster. As we mentioned before, this is quite fortunate. As we mentioned before, this is quite fortunate, since we are (basically) organized by chance and natural selection, from collections of organic reactions. If these reactions occurred spontaneously and rapidly, we would fall apart and approach equilibrium (and equilibrium for living things means death!). You may already see the potential problem in all of this: it is generally not advisable to heat up a biological system, but we certainly need biological systems to undergo reactions. Biological systems need different reactions to proceed in different places and at different rates, without being heated up. For this, biological systems (and many other types of systems) use a wide range of catalysts, the topic of our next section.

Questions to Answer:

- When a reaction releases energy, where does the energy come from?
- Explain why the reaction rate increases when the temperature increases.

8.4 Catalysis

A catalyst provides an alternate pathway for a reaction to occur. More importantly, this pathway usually involves a lower activation energy than the uncatalyzed pathway, as shown in the graph. This means that the rate of the reaction can increase. It can do so because at a given temperature, collisions with enough energy to overcome the new lower activation energy barrier occur more frequently. But because the catalyst is neither a reactant nor a product of the reaction, it does not influence the reaction's overall energy change. In biological systems, there are protein and RNA-based catalysts (enzymes and ribozymes); in non-living systems, minerals and metals often act as catalysts. Even simple species such as protons can be considered catalysts. Anything that is unchanged at the start and at the end of the reaction can be considered a catalyst. There are many different mechanisms through which catalysts can act. Biological catalysts are generally very selective in terms of the reactions they catalyze and very effective in speeding reactions up. It is not uncommon for the rate of a catalyzed reaction to be millions of times faster than the uncatalyzed reaction. In a complex reaction system, speeding up one reaction at the expense of others can have profound effects. However, there are also many examples where enzymes catalyze "off-target" reactions of the same or different types (although these reactions are generally accelerated to a much lesser extent). This ability to catalyze a range of reactions occurs because the surfaces of enzyme molecules are complex and often accommodate and bind a range of molecules. In other words, they are promiscuous.[118] The common analogy of an enzyme as a lock and the reactant molecules are viewed as the unique key, but this is far too simplistic. In reality, there are many molecules that can bind to a specific active site in an enzyme with greatly varying affinities. Although the mode of action of enzymes varies, in many cases the active site holds the two reactive molecules in close juxtaposition, which can speed their reaction. Can you imagine why?[119]



An organic chemical reaction that requires a catalyst is the addition of hydrogens across a C=C bond. Without the catalyst, this reaction would not occur on a human timescale. It is an important reaction in many pharmaceutical syntheses and in the production of fat (solid) from oil (liquids). For example, margarine is produced by adding hydrogen to the C=C bonds of oils extracted from plants, as shown in the figure. The removal of the C=C bond makes the molecules pack better together. This is because London dispersion forces can now act upon the whole length of the molecule, increasing the strength of the van der Waals interactions between the molecules. Thus, the hydrogenated oil is a solid at room temperature. The catalyst is usually a transition metal,

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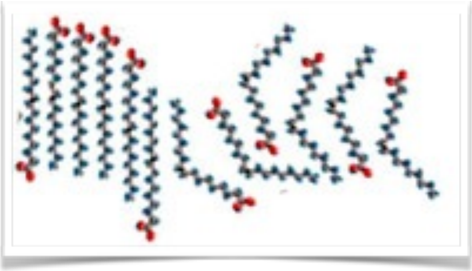
[118] http://www.ncbi.nlm.nih.gov/pubmed/21332126

[119] Here is an example: http://www.febsletters.org/article/S0014-5793(07)00971-4/abstract

palladium (Pd) or platinum (Pt), finely divided and adsorbed onto the surface of an inert substance like charcoal (carbon), as shown in the figure. The transition metal has empty d orbitals that interact with the C=C bond's pi orbital, destabilizing the pi bond and making it more susceptible to reaction. H_2 molecules also adsorb onto (interact with) the surface of the transition metal and insert themselves between the C and the catalyst, forming a fully-hydrogenated fat. Unfortunately, in many cases the hydrogen does not add across the double bond. Instead, the bond isomerizes from cis to trans, forming the unnatural trans isomer which has been implicated in the development of heart disease.[120]



Questions to Answer

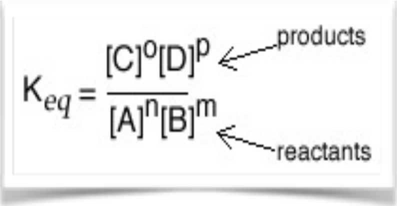
- Draw a representation of an enzyme active site. What kinds of interactions do you think hold the substrate molecule in the active site?
- Why do you think binding two reactants in close proximity will increase the reaction rate?

8.5 Equilibrium

Now that we have a good idea about the factors that affect how fast a reaction goes, let us return to a discussion of what factors affect how far a reaction goes. As previously discussed, a reaction reaches equilibrium when the rate of the forward reaction equals the rate of the reverse reaction, so the concentrations of reactants and products do not change over time. The equilibrium state of a particular reaction is characterized by what is known as the equilibrium constant, K_{eq}. We can generalize this relationship for a general reaction:

$nA + mB \rightleftarrows oC + pD$.

Note that each concentration is raised to the power of its coefficient in the balanced reaction. By convention, the constant is always written with the products on the numerator, and the reactants in the denominator. So large values of K_{eq} indicate that, at equilibrium, the reaction mixture has more products than reactants. Conversely, a small value of K_{eq} (typically <1, depending on the form of K_{eq}) indicates that there are fewer products than reactants in the mixture at equilibrium. The equilibrium constant for any reaction at a particular temperature is a constant. This means that you can add reactants or products and the constant does not change.[121] You cannot, however, change the temperature, because that will change the equilibrium constant as we will see shortly. The


$$K_{eq} = \frac{[C]^o[D]^p}{[A]^n[B]^m}$$

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[120] http://www.webmd.com/diet/features/trans-fats-science-and-risks

[121] Strictly speaking, it is not concentrations that appear in the expression for K. Rather, it is another property called the activity (a)—often called the effective concentration. The activity takes into account the interactions between molecules and ions and solvents, but for our purposes it is acceptable to use concentrations in the expressions for K_{eq}. One outcome of this is that activity is a dimensionless quantity, so equilibrium constants are one of the few places where we don't have to worry about getting the right units!

implications of this are quite profound. For example, if you add or take away products or reactants from a reaction, the amounts of reactants or products will change so that the reaction reaches equilibrium again—with the same value of K_{eq}. And because we know (or can look up and calculate) what the equilibrium constant is, we are able to figure out exactly what the system will do to reassert the equilibrium condition.

Equilibrium and Non-Equilibrium States

Let us look at a chemical system macroscopically. If we consider a reaction system that begins to change when the reactants are mixed up (that is, it occurs spontaneously), we will eventually see that the change slows down and then stops. It would not be unreasonable to think that the system is static and assume that the molecules in the system are stable and no longer reacting. However, as we discussed earlier, at the molecular level we see that the system is still changing and the molecules of reactants and products are still reacting in both the forwards and reverse reactions. In the case of our acetic acid example, there are still molecules of acetic acid, (AcOH), acetate (AcO^-), and hydronium ion (H_3O^+) colliding with solvent water molecules and each other. Some of these reactions will have enough energy to be productive; molecules of acetate will transfer protons to water molecules and the reverse reaction will also occur. What has changed is that the rate of acetate (AcO^-) and hydronium ion (H_3O^+) formation is equal and opposite to the rate of acetic acid deprotonation (transfer of the proton to water). Although there is no net change at the macroscopic level, things are happening at the molecular level. Bonds are breaking and forming. This is the dynamic equilibrium we discussed earlier.

Now what happens when we disturb the system. At equilibrium, the acetic acid–water system contains acetic acid (AcOH), protons (H_3O^+), and acetate ion ($AcO^–$). We know that a 0.10-M solution of acetic acid has concentrations of $[H_3O^+] = [AcO^–] = 1.3 \times 10^{–3}$ M. Now we add enough acetate[122] to make the acetate concentration 0.10 M? One way to think about this new situation is to consider the probabilities of the forward and backward reactions. If we add more product (acetate), the rate of the backward reaction must increase (because there are more acetate ions around to collide with). Note that to do this, the acetate must react with the hydronium ion, so we predict that the $[H_3O^+]$ will decrease and the acetate will increase. But as we saw previously, as soon as more acetic acid is formed, the probability of the forward reaction increases and a new equilibrium position is established, where the rate of the forward reactions equal the rate of the backward reactions. Using this argument we might expect that at the new equilibrium position there will be more acetic acid, more acetate, and less hydronium ion than there was originally. We predict that the position of equilibrium will shift backwards towards acetic acid.

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[122] Of course, there is no such thing as acetate ($CH_3COO^–$) alone. There must also be a counter-ion present. Typically, we use ions such as Na^+ or K^+, stable monovalent cations that will not participate in any further reaction. So when we say we add acetate to the solution, we really mean we add sodium acetate—the sodium salt of acetic acid (just like sodium chloride is the sodium salt of hydrochloric acid).

Le Chatelier's Principle

You may recognize the preceding discussion as a rather well-known idea articulated by Henry Louis Le Chatelier: "If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established." Le Chatelier's principle is one of the best-known and most widely applicable heuristics (a rule of thumb that helps you predict an outcome) in science. However, it is important to understand why this principle works. Le Chatelier's principle is yet another reminder that the second law of thermodynamics is always in force.

Le Chatelier's principle specifically mentions different kinds of changes that can affect the position of equilibrium, yet we have only discussed changes in concentrations. What about temperature, volume, and partial pressure? How do they affect equilibrium? We have also not specifically addressed equilibrium reactions that take place in the gas phase. As an example, important atmospheric reactions such as the formation and depletion of ozone take place in the gas phase. There is nothing particularly special or different about calculating the equilibrium constant for gas phase reactions. We can use either partial pressures of each gas or concentrations (mol/L), although the value of K_{eq} differs depending on which units you choose. Also, you can't mix and match; you must use either all pressures or all concentrations. The effect of increasing the volume is the same as decreasing the concentration, and increasing the pressure has the same effect as increasing the concentration. Note, however, that adding a gas that is not a participant in the reaction has no effect even though the total pressure is increased.

Temperature, Equilibrium, and Reaction Rates

The effect of changing the temperature on the position of equilibrium is a little more complex. At first guess, you might predict that increasing the temperature will affect the rates of both the forward and backward reactions equally. However, if we look more closely, we see that this is not true. Cast your mind back to the discussions of temperature and thermal energy. If the temperature of the system is raised, it means that thermal energy has been added to the system from the surroundings. We can treat the addition of energy to the system as a perturbation and according to Le Chatelier's principle, if something in the system is changed (concentration, volume, pressure, temperature), then the system shifts to a new equilibrium state. In order to predict the effect of adding energy to the system, we need to have more information about the energy changes associated with that system. As we saw earlier, the enthalpy change (ΔH) tells us about the thermal energy change for systems under constant pressure (most of the systems we are interested in). We can measure or calculate enthalpy changes for many reactions and therefore use them to predict the effect of increasing the temperature (adding thermal energy). For example, take the reaction of nitrogen and hydrogen to form ammonia.[123] This reaction is:

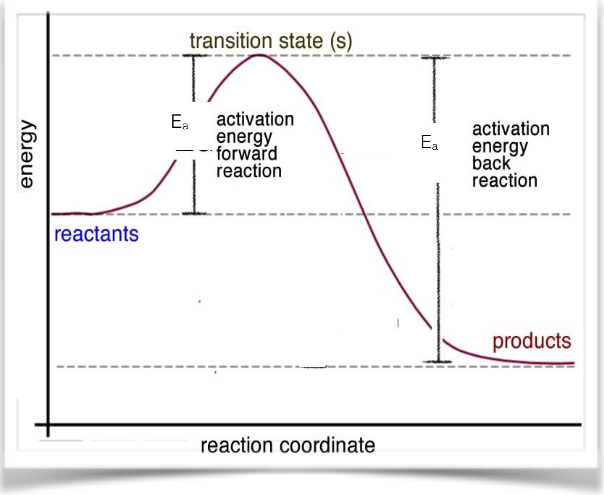
$$N_2\,(g) + 3\,H_2\,(g) \rightleftarrows 2\,NH_3\,(g)\ (\Delta H = -92.4\ \text{kJ/mol})$$

The reaction is exothermic because for each mole of ammonia (17g), 92.4 kJ of thermal energy is produced and transferred to the surroundings (as indicated by the negative sign of the enthalpy change). Now, if we heat this reaction up, what will happen to the position of equilibrium? Let us rewrite the equation to show that thermal energy is produced:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftarrows 2\,NH_3\,(g) + 184.8\ \text{kJ}$$

(2 x 92.4 kJ since two moles of ammonia are produced). If thermal energy is a product of the reaction, Le Chatelier's principle tells us that if we add more product, the reaction should shift towards the reactants. Sure enough, if we heat this reaction up, the position of equilibrium shifts towards ammonia and hydrogen—it starts to go backward! This is actually quite a problem, as this reaction requires a fairly high temperature to make it go in the first place. The production of ammonia is difficult if heating up the reaction makes it go in the opposite direction to the one you want.

It is important to remember that Le Chatelier's principle is only a heuristic; it doesn't tell us why the system shifts to the left. To answer this question, let us consider the energy profile for an exothermic reaction. We can see from the graph → that the activation energy for the reverse (or back) reaction (Ea reverse) is larger than that for the forward reaction (Ea forward). Stated in another way: more energy is required for molecules to react so that the reverse (back) reaction requires more energy to occur than for the forward reaction. Therefore, it makes sense that if you supply more energy, the reverse reaction is affected more than the forward reaction.[124]



There is an important difference between disturbing a reaction at equilibrium by changing concentrations of reactants or products, and changing the temperature. When we change the concentrations, the concentrations of all the reactants and products change as the reaction moves towards equilibrium again, but the equilibrium constant stays constant and does not change. However, if we change the temperature, the equilibrium constant changes in value, in a direction that can be predicted by Le Chatelier's principle.

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[123] The production of ammonia is a commercially-important process because nitrogen is an important element necessary for plant growth (it is commonly added to fertilizers). However, the major source of nitrogen is "locked up" in the air as molecular nitrogen, - a substance that is quite unreactive and inaccessible to most plants.

[124] By analogy, consider the NCAA basketball tournament: if the field is widened to allow more participants, it helps the weaker teams because the stronger teams would have made it into the tournament anyway.

Questions to Answer

- What does it mean when we say a reaction has reached equilibrium?
- What does the magnitude of the equilibrium constant imply about the extent to which acetic acid ionizes in water?
- For the reaction N_2 (g) + 3 H_2 (g) ⇄ 2 NH_3 (g) ($\Delta H = -92.4$ kJ/mol), predict the effect on the position of equilibrium, and on the concentrations of all the species in the system, if you:
    - add nitrogen
    - remove hydrogen
    - add ammonia
    - heat the reaction up
    - cool it down
- Draw a reaction energy diagram in which the reverse reaction is much faster than the forward reaction (and vice versa).