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Helium The Disappearing Element



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Helium

The Disappearing Element



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For my boys Walker, Harrison, and Henry

Preface

When I told my friends and colleagues that I was writing a book about Helium I was met primarily with wrinkled evebrows and comments like, "Why would you write a book about Helium?" I pondered the question for quite some time before deciding to sit down and start typing. I mean, why is helium interesting? I would speculate that a vast majority of the population only thinks that helium is used in toy balloons and blimps. Thus, to them, it *would* be quite boring I assume. That's when it hit me. There needs to be some education about the element that is fundamentally critical to an abundance of high-technology applications in order to help prevent its wastage. You see, helium is the second most abundant element in the Universe but it is actually quite rare here on Earth. I will explain this supply polarity in the subsequent chapters but the point is we currently have a global shortage of the stuff and without it, many facets of industry and scientific research would screech to a halt. There are arguments that toy balloons, which normally sell for a dollar or so should actually sell for higher than US\$50 each to essentially prevent its wastage in the balloon industry. All of that helium inside the latex or foil balloons found in countless birthday parties ultimately finds its way out of the balloon and into the atmosphere where it is lost forever. That helium formerly in the balloon will find a home in our atmosphere for a year or two, mixing with air currents, before it ultimately leaves our atmosphere and enters space.

This book is about the most common isotope of helium, Helium-4 (⁴He). When you hear anything about helium, they are more than likely talking about this common isotope which has two protons and two neutrons in its nucleus and orbited by two electrons. Every balloon you see, for instance, contains Helium-4. The same goes for any other helium used in its abundant array of commercial and scientific uses. Helium does, however, have a lighter and stable isotope called Helium-3 (³He). Although any detailed explanation about Helium-3 is beyond the scope of this book, it is important to note that it is also a very valuable and exceedingly rare commodity that is very important for use in neutron detectors, for example, which are able to detect radioactive materials crossing country borders. In addition, if you Google "Helium-3", you will find an abundance of information about mining the moon for

Helium-3 for use as a clean nuclear fuel. Whether Helium-3 lunar mining becomes a reality or not is also beyond the scope of this book so it will not be discussed.

The chances are that if you bought this book, you are aware that there is a helium (Helium-4 which I will simply call "helium" from now on) shortage. Hold on, if helium is the second most abundant element in the Universe, how could there be a shortage of it? That's a great question and one that I am frequently asked. Although the explanation will be discussed in greater detail in subsequent chapters, the short answer is that the Earthly inventory of helium has a different origin than the cosmic inventory. All of the helium found in the Universe was created in the Big Bang, or the birth of our universe, whereas the helium we use here on Earth is a product of the radioactive decay of the two heaviest natural elements, uranium and thorium. Indeed if Earth had no supply of these heavy radioactive elements, we would have no helium to harvest. In fact, if there were no uranium and thorium, life on Earth would be very different than it is today, if life existed at all.

As I go back to my balloon example, every helium atom in that balloon was a product of the radioactive decay of the elements mentioned above. This radioactive decay occurs in both the Earth's crust and mantle and in rare cases, helium can migrate up through the crust and collect to form commercial deposits. This process will be discussed in great detail in Chap. 4. Interestingly, if I were to look at any balloon at any party in any state in the United States, all of that helium was produced in the United States. You see, the United States has been the primary source of helium worldwide since the industry began after World War I. As I am writing this, however, the paradigm is shifting and the United States will soon be a net importer of helium unless new reserves are discovered. In fact, Qatar has just replaced the United States as the largest exporter of helium in the world.

This book is about Helium and its industry. Although many important aspects and properties are mentioned, helium is a very complex atom with some very amazing properties. However, due to the somewhat macro scope of this book, more micro information such as transition phases between Helium I and II, for example, will not be discussed. In addition, there are other property terms like "polarizability" and "diamagnetic susceptibility", while important when studying the nature of the helium atom, will not be discussed here. The main objective of this book is to provide the reader with a general, albeit thorough, text of the primary industrial aspects of helium without delving too deeply into the heavy details of the element.

I hope this book satisfies your curiosity about this fascinating element. Although I tend to use "balloons" as examples, it is merely because they are the most visible use of helium and something that most can relate to. In the subsequent chapters we will discuss what helium is and why it is so important across various industrial and scientific applications. Next we will learn about the cosmic abundances of helium and from there move into the history of helium's discovery. Lastly, we will delve into how it is formed and produced here on Earth, discuss its industry, and visit briefly the future of the helium industry. There is simply no other element like it. Preface

This book was written to provide a full and comprehensive piece on all aspects of helium from its cosmic and terrestrial abundance all the way to its end usage. This text was designed to allow readers to choose what is of interest. Some portions are highly scientific and thus can be skipped if the reader simply wants to better understand a specific chapter of the text.

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Author Biography

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Chapter 1 What Is Helium?

If you look at a periodic table, you will notice helium on the opposite side, but the same row as hydrogen. Helium and hydrogen alone sit at the top of the entire spectrum of elements. Why is that? Although this will be discussed in greater detail in Chap. 2, quite simply, they were the first elements formed during the birth of our Universe but also the two simplest atoms in the periodic table. Hydrogen has a single proton in its nucleus while helium has two. Each sequential element has an additional proton in its nucleus all the way up to the heaviest natural element, uranium. Interestingly, uranium (and thorium) is extremely important in helium generation which will also be discussed in greater detail in Chap. 4. All of the elements in the periodic table have isotopes which are defined by the number of neutrons in the nucleus. The number of neutrons is what defines the type of isotope an element it is while the number of protons identifies the type of atom it is. Helium-4, which is the most common isotope of helium has two protons and two neutrons in its nucleus. A common hydrogen atom has no neutrons although hydrogen does have isotopes where neutrons are part of the nucleus.

When I talk to people about what I do (I'm in the helium exploration business), I would speculate that around 90 % of the folks I talk to think helium is a fabricated product; something made synthetically. Most of the remaining people know that helium is a natural element but have no idea where it comes from or how it is collected. They would see a balloon and not even think twice about where the helium inside comes from. Who could blame them? Party balloons are everywhere so it is easy to see why the gas inside is taken for granted. It is (or was) so easy to go to a supermarket and buy helium balloons for a birthday party that any thoughts of appreciation of what goes into that balloon are quickly forgotten, if considered at all.

So, what is helium? Helium is a colorless and odorless gas that has some amazing properties. It is a noble gas and thus completely inert. A noble gas is a very stable atom whose electron shells are completely filled and are unable to easily form compounds. The other noble gases include (in order), neon, argon, krypton,

xenon, and radon. Helium, in particular, has two electrons around its nucleus called the 1s orbital and these electrons have opposite spins and thus chemically labeled as $(1s)^2$. To help understand how helium is so unreactive, take hydrogen for example. Hydrogen only has a single electron and is thus particularly prone to combine with something to fill the void of the extra electron that it wants. Hydrogen combines with many things but the most common example here on Earth is H₂O, or water. The combination of a diatomic molecule of hydrogen (H₂) with oxygen is crucially important to life on Earth and once hydrogen combines with oxygen, it is stable and happy in its new atomic structure. In essence, once hydrogen combines with oxygen, it effectively becomes "inert" in its natural state because their electron shells are filled. It is this reason why hydrogen is so abundant on Earth while helium is so rare. Helium, on the other hand, has its outer electron shell completely filled so it does not seek or need electrons thus making it completely inert. Helium, due to its inability to form compounds, is unable to latch onto anything and will ultimately escape Earth's gravity and be lost into space forever.

Helium is the second lightest element, behind hydrogen. It is this property that became the first application for helium ultimately ushering in a new industry after World War I (which will be discussed in greater detail in Chap. 5). The primary reason why helium was used for lighter-than-air craft after World War I was because of its inertness. Hydrogen, being so reactive, can easily ignite and burn rapidly. The most notable example of this effect was Germany's Hindenburg whose hydrogen ignited upon mooring at Lakehurst, New Jersey on May 6, 1937. That event alone effectively sealed the deal on ending hydrogen's use in dirigibles (or blimps) ever again. If the Hindenburg were filled with helium, the airship would most certainly have landed safely with no fatalities. Interestingly, the Hindenburg *was* built to use helium but as this was a period just before German aggression in World War II, the United States would not sell Germany any helium. At the time and through most of the history of the helium industry, the United States was the only producer of helium in the world. More about this will be discussed in Chap. 5 (Fig. 1.1).

Helium is lighter than air because it has an atomic weight (mass) of 4.003 g/mol (grams per mol) while ambient dry air has a molecular weight of 28.966 g/mol making helium 86.2 % lighter (or less dense) than air. The composition of air is roughly 78 % nitrogen (molecular nitrogen, N₂), 20.9 % oxygen (molecular oxygen, O₂), 0.9 % argon, and 0.04 % of trace elements such as carbon dioxide, neon, helium, methane, krypton, and hydrogen (Fig. 1.2). When we add these atomic and molecular weights weighted by their percentage of composition, we reach a molecular weight (dry air) of 28.966 g/mol. So, any element or compound that has a weight of less than 28.966 is less dense than air. If we were to look at the periodic table, theoretically all of the elements up to Silicon, which has an atomic weight of 28.085 g/mol are lighter than air. Why can't any of these elements be used to lift an airship or balloon? The answer is that most of these elements simply are not light enough nor are they commonly found outside of molecular compounds. In addition, elements such as magnesium, sodium, and aluminum are solid metals and would

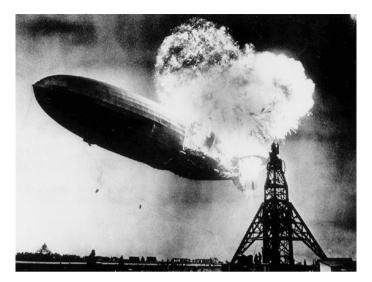


Fig. 1.1 Germany's Hindenburg whose hydrogen ignited upon mooring at Lakehurst, New Jersey on May 6, 1937

Fig. 1.2 Composition of atmosphere

Average composition of the atmosphere, by volume, in parts per million (Mason, 1966)						
N ₂	780,900	78.08776%				
0 ₂	209,500	20.94939%				
Ar	9,300	0.929973%				
CO2	300	0.029999%				
Ne	18	0.001799%				
He	5.2	0.000520%				
CH₄	1.5	0.000150%				
Kr	1.0	0.000100%				
N ₂ O	0.5	0.000050%				
H ₂	0.5	0.000050%				
0 ₃	0.4	0.000040%				
Xe	0.08	0.00008%				

thus have to be converted into a gas which would require energy and simply be too hot to fill any lifting device. For example, aluminum vapor (gaseous aluminum) is actually slightly lighter than air but it is found as a solid in its natural ground state. Some examples of elements or compounds that are lighter than air include (from light to heavy) neon, water vapor, ammonia (NH₃), methane (CH₄), and nitrogen. Neon, which is 30 % lighter than air, will actually lift a balloon but it is very rare and we would not be able to produce enough to use commercially.¹ Even if we could, however, helium is 80 % lighter than neon and is far better for lifting. Evaporation is a good example of how water vapor is lighter than air which ultimately condenses into clouds upon reaching colder temperatures. Ammonia and methane will both lift balloons and have been used before but they are both dangerous compounds to work with. Lastly, nitrogen (molecular nitrogen, N₂) is only 3 % lighter than air and is not able to lift anything with any weight. Hot air, of course, is lighter than dry air because increased temperature reduces the density of the molecules causing it to rise.

Putting hydrogen against helium, hydrogen is only 7 % more buoyant than helium which is somewhat negligible when considering other lighter-than-air gases. When we factor in the danger of using hydrogen as previously demonstrated using the Hindenburg example, helium is really the only real and safe option for use as a lifting medium. Thus, it is helium that we are seeing when we look at the Goodyear blimp flying above a ballgame or when we look at birthday party balloon. These examples are the most visible uses of helium and are generally what people think about when they hear the word "helium."

Ever since the start of World War II, helium has been used as the primary lifting gas for dirigibles, blimps, and balloons. As a matter of fact, nearly all of the helium produced from 1918 to 1950 was used as a lifting gas. During this time, there were "other" applications for helium such as a deep-sea diving gas but its overall consumption in this role was very small. In addition, the production of high purity helium (>99.0 % pure) was not available until 1949. Other uses for helium such as arc welding accelerated when higher purities became available in the 1950s.

Today, helium is still used as the primary lifting medium for applications such as weather balloons, strategic and advertising blimps, and party balloons. Although hydrogen can be substituted for weather balloons, helium is still the most preferred gas due to its inertness. According to the National Academies Press', *Selling the Nations Helium Reserve* (2010), weather balloons are the largest consumer of gaseous helium as a *lifting gas* consuming roughly 140 million cubic feet of helium per year as hundreds of weather balloons are released every day worldwide. Although helium's use as a lifting medium is its most visible application, its lifting applications as a whole represents only a small portion of its overall consumption.

Helium's use as a lifting medium is obviously found in gaseous form and is the preferred gas because it is unreactive (inert), unlike hydrogen, and far less dense than air. These properties alone account for helium's use as a lifting gas. Other

¹ Neon is produced by air distillation. It is a very small component of ambient air only representing 0.001799 % of the atmosphere (18 parts per million).

properties of helium such as its low boiling point, small atomic radius, and high thermal conductivity make it useful in gaseous form in many more applications such as pressurizing and purging rocket engines, welding, semiconductor and fiber optic manufacturing, chromatography, leak detection, breathing mixtures, and next-generation nuclear power facilities. These uses are listed in rough order of overall helium consumption with pressurizing and purging representing the largest user of gaseous helium while breathing mixtures represents a mere 2 % of gaseous consumption.

In the United States, the National Aeronautics and Space Administration (NASA) and the U.S. Department of Defense (DOD) are large consumers of gaseous helium for use in rocket propulsion systems. Although the Space Shuttle program shut down in 2011 and represented a large portion of domestic helium consumption in this category, helium is still used in other rockets, for example, such as the Delta IV's rocket propulsion system. Helium, due to its inertness and low boiling point, is critical in pressurizing and purging rocket engines that use liquid hydrogen and liquid oxygen as fuel. Gaseous helium, which will not liquefy at hydrogen and oxygen temperatures, is the only element that can effectively push these fuels into the rocket propulsion system while maintaining the pressure of the fuel tanks as the fuel is burned. Without helium, as the rocket fuel is used in the rocket engines, the canisters would crumple like a soda can due to the vacuum created in the void of these canisters. Even in interstellar space, for example, the Cassini spacecraft which was launched in 1997 to study Saturn's moon, Titan, uses helium to pressurize fuel tanks for trajectory adjustments.² In the United States alone, pressurizing and purging represents roughly 26 % of domestic helium consumption. It should be noted here that all of the gaseous helium that is mentioned here and from now on is very high purity helium. Any contaminants could have severe impacts on its usefulness in this and other applications.

The next largest user of gaseous helium, welding, relies on helium's chemical inertness, high thermal conductivity, and ionization potential. When we talk about welding, however, we are not talking about brazing or soldering which simply join two metals together. Rather, we are talking about arc welding, for example, that actually fuses two materials together using very high heat caused by an electric arc to melt and fuse two adjoining materials in a metallurgical bond. The result of this type of weld is a product where the joined materials are as strong as the two individual parts. In these types of welds, any contamination could have dire consequences on the integrity of the metallurgical bond which is where helium comes in. Helium is pushed into the weld creating a shield so that any elements in the air are unable to contaminate the weld and reduce its efficacy. Although argon is commonly used as a replacement to helium in arc welding, there are some processes where the heating is so intense that helium is the only element with the thermal conductivity high

² Helium was also used to pressurize the fuel system during the launching of the Titan IVB/ Centaur rocket which launched the Cassini spacecraft into space.

enough to handle these processes. Using only United States figures, helium usage for welding accounts for roughly 20 % of total consumption.

Other important users of high purity gaseous helium are optic fiber manufacturing and semiconductor processing. In both processes, helium is used as the controlling environment to prohibit exposure to ambient air which might compromise the efficacy of both products. In fiber optic manufacturing, helium's high thermal conductivity and inertness is essential for cooling the glass fibers when drawn from the furnace and is also a crucial component when adding the coating to the glass fibers. Without helium, the probability of forming gas bubbles would render the fiber useless. Similarly, all of these atomic properties are useful in semiconductor manufacturing where helium is needed to create an inert environment to prevent contamination of wafers and circuits.

In order to gain some perspective from the semiconductor industry itself, this excerpt from the Semiconductor Industry Association's testimony for the U.S. Congressional Hearing titled, "Helium: Supply Shortages Impacting our Economy, National Defense and Manufacturing" (2012), is a great example on its many uses in the industry: "Helium's unique physical and chemical properties have made it critical to the manufacture of semiconductors. The industry uses helium because it is very inert, has a very low boiling point (at 4 degrees K, near absolute zero), and due to its high thermal conductivity. Some of principle uses of helium in the semiconductor industry are as a carrier gas for deposition processes, as a dilutant gas in plasma etch processes, and in some specialized wafer cooling applications. It is also critical in leak detection. Helium is used to achieve ultraclean manufacturing and assembly environments that are essential for advanced semiconductor manufacturing. According to a report of the National Academy of Sciences, semiconductor and optical fiber manufacturing account for 13 percent of uses of helium; suppliers to the industry have indicated to us that semiconductor uses account for approximately 6 percent of helium usage. In some applications, alternatives such as argon or nitrogen may be used, but this typically results in a decrease in throughput."

There are other uses of gaseous helium such as chromatography which is used in various industries such as pharmaceutical, food, and environmental analysis to test for individual components in whatever is being tested. For example, a natural gas well that is tested for gas composition via a gas chromatograph is able to identify all of the constituents of the gas which would allow for the identification of a valuable commodity within the gas stream. Helium is used as a carrier gas in these applications because it is completely inert and thus purges the equipment of any impurities prior to and during analysis.

Leak detection is another important user of helium that spans across various manufacturing industries. Because helium has the smallest atomic radius and is completely inert, it is the ideal element to test for small leaks or micro cracks. Helium leak detection is used in numerous commercial applications such as locating small leaks in automotive and aircraft fuel tanks, fuel systems, engines, compressors in refrigerators, light bulbs, and many other uses where small leaks can have a detrimental effect on public safety. The method by which helium is used to detect leaks in these products is by utilizing a vacuum system where the product is either placed in a vacuum chamber or the device itself is injected with helium. A helium mass spectrometer is then used to detect any helium that might be present on the outside (or inside) of the system being analyzed. If helium is present where it is not supposed to be, there is a leak which can be quickly identified. Hydrogen is oftentimes a replacement for helium in many of these applications.

Helium can also be injected into water, natural gas, or oil pipelines to find any possible leaks. In these cases, if there is a leak in a pipeline, helium will find the leak and seep to the surface where surface equipment is able to pick up any anomalous helium readings. If there is an anomalously high reading of helium anywhere on the pipeline, the leak is easy to locate where repairs can take place. In water supply lines, helium is the ideal gas to test for leaks because of its inertness and thus eliminates any public health concern. Helium can be digested with absolutely no ill effect. The use of helium in water lines (and other pipelines) can enhance the deliverability of the product without any wastage whose cost is generally passed down to the consumer.

Rounding off the least abundant user of gaseous helium is for breathing mixtures in scuba diving. Most are aware of a condition called nitrogen narcosis, or "the bends" which results in nitrogen bubbles accumulating in the bloodstream which can be fatal for divers. Using compressed air is prohibitive for deeper and lengthy dives because of this condition. To help divers prevent this problem, helium is often a replacement for nitrogen because it does not diffuse quickly into the bloodstream thus reducing the possibility of the bends.

Lastly, many automobile owners are unaware their vehicles quite possibly contain small helium cannisters used to fill airbags in the event of an accident. Due to helium's small atomic radius, it is an ideal gas for an immediate filling of an airbag upon impact. Air, for example, is not used because of the differing (and larger) sizes of molecules in an air stream thus creating a bottleneck in the filling system resulting in a slower fill.

Gradually over the past sixty years, helium's primary use shifted from its gaseous to its liquid state thanks to the proliferation of superconducting applications. Helium is the only element in the periodic table which will not solidify at temperatures approaching absolute zero under standard atmospheric conditions. More importantly, it becomes a liquid at a far lower temperatures than any other element making it the only element available to achieve superconductivity. Superconductivity is, without question, the largest consumer of helium in the world. So, what is superconductivity and why is helium so important in its use?

In 1908, Heike Kamerlingh Onnes (1853–1926), a Dutch physicist, became the first person to liquefy helium and upon further experimentation on materials immersed in liquid helium temperatures discovered superconductivity three years later in 1911. Onnes' discovery would ultimately become one of the most important discoveries in the 20th century and provide later generations with powerful medical diagnostic tools that would save millions of lives but also help unlock the mysteries of the birth of our Universe. To understand what superconductivity is, it is helpful to understand general conductivity and resistivity (Fig. 1.3).

Fig. 1.3 Heike Kamerlingh Onnes (1853–1926)



Fig. 1.4 Johannes Diderik van der Waals (1837–1923)



Before we delve deeper into superconductivity, now is a good time to discuss just why helium has the lowest liquefaction temperature (boiling point) than any other element. There is no other element in the periodic table that boils at such a low temperature and it is this quality that makes helium crucial for superconductivity. Why is this? The reason is because of a phenomena called Van der Waals forces, named after Dutch scientist Johannes Diderik van der Waals (1837–1923) (Fig. 1.4).

Although there are three types of forces that make up Van der Walls forces, a good way to demonstrate Van der Waals forces is to think of water molecules in gaseous form about to condense into liquid form. In gaseous form, the large water molecules (two hydrogen and one oxygen atom) are moving rapidly when heated and are far apart. These molecules, when heated, have a high kinetic energy thus prohibiting any cohesion between the molecules. Although the water molecule is electrically neutral, the structure of the molecule is not symmetrical creating something called a dipole moment which is a slight separation of the negative and positive charges within the molecule. In the case of water, the Van der Waals force responsible for the attraction between the water molecules is called a Hydrogen bond (a Hydrogen bond is a Van der Walls bond). The water molecule, being

unsymmetrical, has a heavy positive and negative side in each molecule meaning that there is a strong attraction between the positive and negative side of an adjacent water molecule. As opposite charges attract, these hydrogen bonds between water molecules are stronger than the other Van der Waals forces making water liquefy at high temperatures.³ Very simply, Van der Waals forces are the intermolecular attraction between like molecules. Generally, the larger the molecule (or atom), the greater the Van der Waals force. This attractive force that takes advantage of these dipole (heavy positive and negative sides of the molecule) moments is called Van der Waals forces (or bonds). Luckily for life on Earth, the Van der Waals forces between water molecules are relatively strong allowing for vast stores of water on our planet. Van der Waals forces in water remain intact until a temperature of 100 °C at which point the Van der Waals forces break to create gaseous water.⁴

The helium atom, on the other hand, is perfectly symmetrical and is smaller than any other element in the periodic table. It is symmetrical because its electron shell is completely filled making the electrons very content in their position. Thus, unlike our water molecule example above, there is no side of the atom that is predominately negative or positive. All of the noble gases share this common trait and is the reason we call them noble gases; they are not willing to bond with each other or any other element. Because of this, noble gases have a very weak intermolecular attraction between them. Helium, being the smallest of all noble gases (and any other element) means the attraction is even weaker.

It may seem counterintuitive but the diameter of the helium atom with two protons, two neutrons, and two electrons is smaller than that of the simplest atom, hydrogen, which has only one proton and one electron.⁵ As a result, the tightly bound atom makes it highly stable, more so than any other atom. These properties of helium make the Van der Waals forces between the molecules very weak, weaker than any known substance. The Van der Waals force which is responsible for helium's liquefaction is called a London Dispersion Force⁶ which is the weakest of the Van der Waals forces. At extremely low temperatures, however, there arises in the helium atoms a fluctuating dipole moment which leads to an eventual attraction between the atoms allowing for liquefaction. That is, because electrons can be anywhere at any single moment, there are moments when a small positive and negative attraction can occur between the atoms which can only occur at extremely low temperatures. The London Dispersion Force seizes upon these rare moments which ultimately group the atoms together to form a liquid. The Van der Waals force (London Dispersion Force) between helium atoms occurs at the temperature of $-269 \,^{\circ}\text{C}$ (4 K), which is lower than any other element on the periodic

³ Although we mention "high" temperatures, high is a relative term. As helium is a liquid in its ground state, the temperature is high compared to other molecules, like helium.

⁴ The more specific name of the Van der Waals force between water molecules is Hydrogen Bonding, which is the strongest of the three Van der Waals forces.

⁵ Hydrogen, helium, and every other element has various isotopes but for the purposes of this chapter, only the primary isotope is used.

⁶ Named after the German-American physicist Fritz London.

table. It is this property of helium which makes it the only element available for cold temperature research and superconductivity. Every other element will solidify at these low temperatures because their Van der Waals forces are greater. As a matter of fact, helium will remain a liquid and will not solidify at temperatures approaching absolute zero (an unattainable temperature) at normal atmospheric pressure. Helium will solidify but only when significant pressure is added. Helium was first solidified by W.H. Keesom of the Kamerlingh Onnes laboratory on June 25, 1926.

Getting back to liquid helium and now that we know why helium liquefies at such low temperatures, we can see why liquid helium is so important in various applications where there is no substitute for helium's atomic properties. By far, the most common industrial use for liquid helium is superconductivity which is best represented by the countless MRI machines all over the world and large particle accelerators such as CERN's Large Hadron Collider. What exactly is superconductivity and why is it important for our modern society? Before we answer this question, it is important to understand the concept of conductivity and resistivity.

In general, conductivity and resistivity are polar opposites of the other. That is, if a material has low resistivity, it is a "good" conductor of electricity. Low resistivity = high conductivity; low conductivity = high resistivity. Resistivity means that a material *resists* the flow of an electric current and this resistance usually manifests itself as heat. A common example of a good conductor (and not very resistive) is copper, which is a commonly used material due to its low resistivity. Electrons can flow relatively easily through the copper lattice without bombarding into copper ions so little heat is lost (the heat is generated by the kinetic energy produced from the bombarding of electrons with the ions in the copper). If you touch a copper wire while it is transmitting an electric current, it will not be very hot. It is this quality which makes it such a good conductor. Silver is also a good and widely used conductor.

There are other materials which are good conductors but what is important to note is that these conductors allow for an efficient way to pass an electrical current. Power lines across the world rely on strands of a good conducting material sheathed in an insulating material. These power lines, however, rely on a steady source of power to continue the movement of an electrical current which is all too familiar when we see our power bills in the summer. Despite the use of these low resistivity materials, there is always "some" resistivity which results in a loss of energy down the transmission lines. This loss of energy is precisely what superconductivity eliminates.

When Kamerlingh Onnes liquefied helium in 1908, it was the coldest temperature ever reached in a laboratory, or anywhere on Earth for that matter. Prior to helium's liquefaction, a challenge was made by the Englishman Michael Faraday (1791–1867) in the mid 1800s to liquefy all known gases. Faraday was able to liquefy many various gases such as carbon dioxide, ammonia, and chlorine (to name a few) but quickly realized that gases such as hydrogen, nitrogen, and oxygen could not be liquefied due to the insufficient means available to him at the time. By the end of the century, however, every known permanent gas except for helium was liquefied as better equipment was made available to the new generation of scientists. Hydrogen, which was the second to last element to be liquefied was done so by James Dewar in 1898. Helium was the last on the list but it should be noted that at this time helium's existence on Earth was discovered only three years before hydrogen was liquefied. Once helium was able to be extracted with enough volumes to allow for experimental endeavors, the race was on to liquefy the last known permanent gas which was achieved by Kamerlingh Onnes in 1908.

After Onnes successfully liquefied helium, he wanted to better understand the behavior of materials when immersed in these extremely low temperatures. To be precise, he wanted to understand what happened to a materials *resistivity* when dropped to liquid helium temperatures. It was already known prior to his experiments that resistivity drops when temperatures are lowered thus his curiosity about resistivity in the coldest known substance was palpable. In 1911, Onnes discovered that when an electric current was passed through pure mercury (solid) bathed in liquid helium at precisely 4.19 K its resistivity abruptly dropped to zero. Surprised by this property, he repeated the experiment several times all with the same result. It wasn't until the temperature was raised above 4.19 K when there appeared some resistivity. Onnes called this phenomenon superconductivity because it was a "super" conductor. Its discovery was monumentally significant which would ultimately earn him a Nobel Prize (physics) two years later in 1913.

Superconductivity, quite simply, is when a material loses *all* resistivity to the flow of an electric current. To use a very common example of pushing a child on a swing, we all know that in order for the child to continue with their fun is to keep pushing. If you stop pushing, then several factors will slow the swing down where it will ultimately stop such as the friction on the hinges and simple gravity. Thus, a continuous amount of energy is required to keep the child swinging. The same is true in our current power transmission lines. In order for us to continue to have power in our homes, we need a continuous source of power, which in the United States, is principally coalfired generators. A superconductor, on the other hand and continuing to use our swing analogy, is when the child is able swing in perpetuity once set in motion.

In today's applications, some materials become superconductive when bathed in temperatures below 4.2 K. The reason for this phenomenon is purely a quantum effect because at these temperatures, free electrons that are flowing through material form pairs which then interact with other electron pairs resulting in a free flowing current that exhibits no resistivity. So, once the desired input (power) is achieved, the power can be turned off while electricity continues to flow as long as these low, liquid helium temperatures are maintained. Because no heat is released via resistivity, the superconducting wires can be packed very closely together resulting in a very tightly compacted and efficient method of electricity transmission.

If we look at a common example of an MRI (magnetic resonance imaging) device which utilizes superconductivity, we can see how useful superconductivity is in today's economy. For those who don't know, an MRI machine is a medical diagnostic device which allows for internal body images (particularly soft tissue) that are vastly superior to X-ray's which can be quite dangerous and are primarily



Fig. 1.5 MRI machine. Source U.S. Navy

used for bone images. An MRI works by using very powerful magnets which help hydrogen atoms in your body, which normally spin in random directions, to align themselves much like a compass points to north. As specific frequency radio waves (resonance frequency) tip some of these hydrogen atoms in your body to the opposite direction, they gain energy. When the radio waves are halted these atoms turn back to their original direction, releasing energy in the process which is picked up by antennas and processed in powerful computers to create an image.

The only way these devices are able to function is because of liquid helium. There is no substitute. Every MRI machine is comprised of very powerful magnets such as a titanium-niobium alloy that are literally submerged in a reservoir of liquid helium, thus bringing the magnets to a very cold 4.2 K. These magnets, by the way, are extremely powerful producing anywhere from 0.5 to 3.0 T^7 which require enormous amounts of power. At these temperatures, these powerful magnets become "superconducting" and have zero resistivity as mentioned above. No energy is lost but more importantly, as long as the temperatures remain at these there is absolutely no resistivity, the electric current can theoretically flow forever as long as the temperatures remain at temperatures 4.2 K or lower (Fig. 1.5).

Helium's use in its superconductive role is the largest single user of helium today and accounts for roughly 40 % of total helium consumed. Other

⁷ Tesla is a unit of measure for magnetic strength. One Tesla is equal to 10,000 Gauss. Earth's magnetic field equals roughly 0.5 Gauss. Thus, these MRI magnets have a very powerful magnetic field.

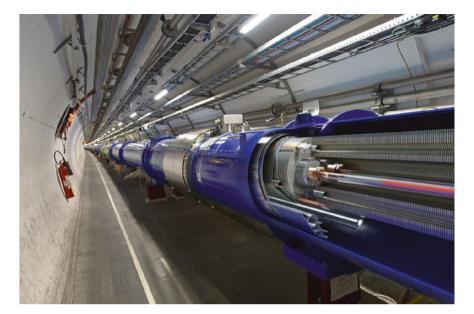


Fig. 1.6 3D cut dipole tunnel montage photo (CERN)

superconductive applications include particle accelerators such as CERN's Large Hadron Collider⁸ (Geneva, Switzerland) which use even more powerful magnets and tremendous power inputs to hurl subatomic particles together to help understand the nature of our Universe. Although particle accelerators are vastly larger, the principals of superconductivity are the same as the MRI devices mentioned above. Powerful magnets can handle enormous amounts of energy only as long as there is no resistivity (Fig. 1.6).

Readers may recall the helium leak at CERN's LHC in September 2008 which caused a temporary shutdown of the facility. This event is a good example of what happens when the temperature of helium rises to the point where superconductivity is no longer possible. Due to a "faulty electrical connection" between two magnets, a "quench" occurred resulting in the melting of some of the magnets which were normally cooled by liquid helium. Due to the tremendous amounts of power and the loss of liquid helium, resistivity manifested and magnets melted due to the incredible heat generated. Containing the liquid helium environment is extremely important to make sure that quenches do not occur thus rendering the superconducting equipment useless. The LHC finally became operational a year later in November of 2009.

⁸ CERN's Large Hadron Collider (LHC) uses approximately 120 tonnes of helium to cool powerful magnets down to 2.7 K (-271.3 °C). Helium at these even lower temperatures is called a superfluid which has even more amazing properties. For more information on helium's use in the LHC, please visit: http://home.web.cern.ch/about/engineering/ cryogenics-low-temperatures-high-performance.

In addition to liquid helium's use as a superconducting medium, it is also used in low-temperature physics laboratories around the world. Although it is impossible to reach absolute zero, scientists have been able to discover various quantum phenomenon at temperatures a mere fraction above absolute zero. For this application, there is also no substitute for helium because it is the only element that will never solidify at temperatures approaching fractions of a degree above absolute zero. Although applications and discoveries vary from laboratories around the world, helium is the only element that allows low-temperature research to flourish.

Another very important use for liquid helium is sensitive space telescopes which rely on liquid helium temperatures to operate. The Spitzer Space Telescope, for instance, which was launched in 2003, required a payload of liquid helium for proper telescope operation. The mission was designed to detect small doses of cosmic heat radiation which would not otherwise be detected due to the space-craft's own self-generated heat. The liquid helium supply ultimately depleted (as planned) and rendered the most sensitive part of the telescope useless. Other "warm" phase missions, however, which do not require liquid helium temperatures allow the spacecraft to continue to send valuable information back to Earth.

More recently (2014), helium was also used to cool the BICEP2 (Background Imaging of Cosmic Extragalactic Polarization) telescope at the South Pole which detected evidence of the early expansion of the Big Bang (Big Bang will be discussed in the following chapter). This equipment was designed, much like the Spitzer, to measure small amounts of cosmic radiation (CMB, Cosmic Microwave Background) which represents the leftover energy created from the Big Bang nearly 14 billion years ago. The BICEP2 was instrumental in enhancing our knowledge of the period called "inflation" after the Big Bang and was only made possible because of the cooling properties of liquid helium for which there is no other substitute.

The examples just mentioned where helium is used in its liquid state represent the primary consumer of all helium produced worldwide. Outside of these applications, helium has a very useful role in its gaseous state as well for which there are few to no substitutes. Now that we know most of the applications where helium is used, now is a good time to discuss where helium comes from both cosmically and terrestrially.

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Chapter 2 Where Does Helium Come from?

Cosmic Abundance

Hydrogen and helium are the two most abundant elements in the Universe. As a matter of fact, the entire cosmic inventory of hydrogen and helium make up over 98 % of all known matter in the Universe. The remaining 2 % amounts to every other element combined. Despite the fact that our Earth is a rocky planet and contains an abundance of additional elements like oxygen, silicon, and iron, for example, it is not representative of the entire Universe. Our planet Earth, in the grandest of grand schemes, is nothing more than a speck of cosmic dust revolving around a medium sized star. It is not until we take the Universe as a whole until we can understand just how much hydrogen and helium exists out there.

A hydrogen atom is the simplest element on the periodic table because its nucleus is nothing more than a single proton which is orbited by a single electron. It is number one on the periodic table and is, by far, the most abundant element in the Universe. If we break the hydrogen atom down we are left with a single, lonely proton. This single proton in the nucleus identifies the element as hydrogen because the number of protons equal the element's atomic number. It is this atomic number of two because it has two protons. As we add another proton to a nucleus, it becomes a different element. There are 92 naturally occurring elements from atomic numbers 1 (Hydrogen) to 92 (Uranium). Helium has two protons, two neutrons, and two electrons.

Leaving neutrons out for a moment, helium has two protons which are nothing more than two hydrogen nuclei. As we venture down the periodic table, every unique element has varying quantities of hydrogen nuclei in their own nucleus. Everything around us was born from the nucleus of hydrogen atoms (protons). Thus, everything starts with the simple proton and this is where we will begin the explanation of helium's abundance in the Universe. In order to see just how helium came to be, we need to start at the very beginning to an event called the Big Bang, or the birth of our Universe.

The Big Bang

The Big Bang is the prevailing theory about the birth of our Universe which theorizes that as we go back in time nearly 14 billion years, all energy and matter can be reduced to an infinitesimal point, called singularity. To clarify even further, when we think of this explosion, we are not talking about an explosion *in* time but rather *of* time. To ask the question what happened before the Big Bang would be meaningless because time did not exist before the event. In addition, this "point" was not in any specific location but it was everywhere at once. There was no medium in which the universe exploded in, rather it was the explosion of the medium itself. Although this is a difficult concept to grasp given our perceptions of such an event, it is nonetheless an important concept. Everything that we see today started from this single event of unparalleled proportions. All of the matter that ever existed and ever will be was created from this single event and as the Universe evolved, the matter from the initial Big Bang would transform into the elements we see today.

In order to understand the nature of singularity or the single point where space and time began, think of it this way: if we took the entire Earth, all of the other planets in our solar system, our Sun, our Milky Way galaxy containing hundreds of billions of stars, and every galaxy each containing hundreds of billions of stars, and hit the reverse button to nearly 14 billion years ago, everything would fit into a point the size smaller than an atom. Of course, this is no ordinary atom, it is the primeval atom which had infinite energy and temperature. It is the point from which everything we see today came from. From this infinitesimal point of energy, all matter was created.

After the Plank Era, or between 10^{-43} and 10^{-35} s, we know that the universe, which had already expanded and cooled dramatically (but still a very hot

 10^{32} – 10^{27} K), was principally full of radiation (energy). During this period, gravity was able to precipitate out as the temperature dropped and subatomic particles (and their anti-particles) were able to form via a process called pair production. Pair production, explained in an overly simplistic way, is how matter was created directly from energy. To understand how pair production works, it might be easier to explain by using a well known example.

We all know Einstein's equation, $E = mc^2$, which shows the relationship between mass and energy. This formula states that matter is energy and energy is mass. The mere fact that mass and energy are on opposite sides of the equal sign highlights this relationship. It is the "c" in c^2 that shows how much energy mass contains. c stands for the Latin word *celeritas* ("swiftness") and is the symbol for the speed of light. The speed of light is precisely 299,792,458 m/s (or about 671 million miles per hour). Thus, anything multiplied by this number squared is going to be a very large number. As you can see when we plug into the equation, then, the energy equivalent of a small amount of mass is fundamentally huge as is demonstrated, for example, by the explosion of an atomic bomb. Small amounts of matter contain vast amounts of energy.

Just as we see how the destruction of matter can produce massive amounts of energy by using this equation, we can also determine how much energy is required to produce mass. This is how the most fundamental building blocks of matter were created in the Big Bang and we call this process, pair production. Pair production occurs when two photons, which are discrete packets (packets of light) of electromagnetic radiation, merge to create a particle-antiparticle pair. In the case of the moments after the Big Bang, all of the energy in the form of high-energy gamma radiation could form actual matter and antimatter (we will discuss antimatter in a moment). So, from the very beginning, there was nothing more than energy from which we all spawned. This energy ultimately created all of the matter we see today from a galaxy all the way to the book you are holding in your hand.

Before we go on, it is important to understand the definition of energy as it relates to the events after the Big Bang. We are all familiar with the visible light spectrum which is made up of all of the colors of the rainbow. That is, and as will be discussed later in the book, if we took a beam of light and directed it through a prism, we would notice the constituent colors of this white light which range from red to violet. Each of these colors have different energy levels with red having the lowest energy (low frequency waves) and violet (high frequency waves) having the most. The entire rainbow makes up the visible spectrum which we see all around us. The energy levels above and below the visible spectrum like infrared and ultraviolet are outside of our visible range and we are not able to detect them without proper equipment. Beyond these immediate ranges, however, lie gamma rays which are the highest energy waves (highest frequency) and radio waves (lowest frequency) which are the lowest. Although humans can only see the narrow range of the visible spectrum, the entire electromagnetic spectrum, visible spectrum included, from radio waves to gamma rays are pure energy (light) and are emitted as photons which are discrete packets of light that have both wave and particle properties. They all move at the speed of light regardless of their frequency thus each can simply be called light rays. Gamma rays are high energy photons while radio waves are low energy photons. Immediately after the Big Bang, only highenergy gamma rays existed which, when the Universe cooled, began to lose energy and fall into other portions of the electromagnetic spectrum (Fig. 2.1).

All of the matter that was created during the Big Bang was formed from highenergy gamma radiation (photons) that was the only form of light (energy) created immediately after the Big Bang. It was these gamma ray photons with unfathomable energy which created the matter we see around us. As mentioned in the previous paragraphs, it takes an enormous amount of energy to create matter and it was these high-energy gamma ray photons which allowed this to happen. Any lower energy photon would not be able to create matter which is why all the matter in our Universe was created immediately after the Big Bang.

Getting back to the formation of matter from energy, we are now able to see how pair production occurs due to the incredible energies surrounding the moment of the Big Bang. In a moment we will discuss the types of particles created via pair production but first it is important to understand anti-particles (anti-matter) which created with equal quantities after the Big Bang.

For those who are unfamiliar, antimatter is the precise opposite of matter. For instance, an electron is a negatively charged form of matter and is the smallest elementary particle we know of. Its antimatter opposite is called a positron. Both an electron and positron are absolute mirror images of one another except that that a positron is positively charged. They are the same size, have the same mass, and are otherwise completely identical. Interestingly, when matter meets its antimatter opposite, they annihilate one another in a flash of energy to produce photons, or electromagnetic radiation (light). Put another way and in human form, we are all made up of matter. If we could somehow walk out the door and meet our antimatter opposite, we would look absolutely and completely identical in every way. If we were to shake hands with our antimatter opposite, however, we would both completely disappear and transformed into a burst of pure energy in the form of electromagnetic radiation.

The early universe created equal amounts of matter and antimatter. A question might arise, then, if matter and anti-matter annihilate one another, how is there any matter in the universe? It is a very good question and there is really no way to explain it other than somehow we ended up with a slight imbalance of more matter than antimatter and theories for this phenomenon are beyond the scope of this book. The fact that we are here means that matter prevailed over antimatter. One of the most amazing things about the Big Bang is that most of the matter and antimatter that were created in the moments after the Big Bang were annihilated. We are all products of that small amount of matter that somehow survived.

By the end of 10^{-35} s, the strong nuclear force (the force that binds an atomic nucleus together) began to precipitate out into its individual form but it is also in this time in which astronomers believe that dark matter became apparent. The subject of dark matter is also too vast to go into any great detail here but in the beginning of time, it was less important. As the universe aged, it has become much

Fig. 2.1 Electromagnetic spectrum. Source NASA





Microwave

Infrared







Control

Night vision goggles

AM radio

Amateur radio

Aircraft

Microwave oven

TV Remote



Ultraviolet

X-ray

Gamma-ray





UV light from the Sun

Airport security scanner

PET scan

Terrestrial gamma-ray flashes

communication

more important because it comprises the vast majority of density in the universe which holds our galaxies together but scientists have found very little evidence beyond theory.

In the period between 10^{-35} and 10^{-4} s after the Big Bang, the heavier elementary particles such as protons and neutrons, and their antimatter opposites, formed via the pair production process mentioned above. These heavier particles were the first to form because of the higher temperatures and higher energies of the photons. Greater energy resulted in more massive particles like protons which are 2,000 times more massive than electrons. Most of these particles created during this time were annihilated, however, converting their mass back into photons where the chain reaction would continue until there was nothing left but slightly more matter than antimatter. It was also during this time when both the weak nuclear force and the electromagnetic force precipitated out thus releasing the remaining individual components of the forces of nature.

By the time we fast forward to about one second after the birth of the universe, electrons and positrons (the electrons opposite) were formed by pair production and, once again, most of these particles were annihilated much like the earlier and heavier protons and neutrons. Electrons and positrons, which are elementary particles, required far lower temperatures and subsequently lower energy photons hence the low mass of the electron (and positron). After the end of this first second, all the matter formed through pair production resulted in all of the known matter in the universe. After the universe cooled below 10¹² K, pair production was no longer possible because there was not enough energy to produce matter as the temperature after expansion had dropped even further. Thus, the principal building blocks of matter were all manufactured within one second after the Big Bang.

After about 100 s (just over a minute and a half) after the Big Bang, protons and neutrons (the ones that were not annihilated) started to fuse into the heavier "nuclei" like helium (only the *nuclei* of protons and neutrons had formed by this time). This fusion process happened very quickly while the Universe was still hundreds of millions degrees Kelvin. Electrons could not attach to a nucleus until later due to the still extremely high temperatures that would otherwise tear off electrons from a nucleus. Within 15 min, however, conditions cooled to the point where the fusion process ended after which virtually all of the helium nuclei in the entire universe had already been formed.

From a minute until about 300,000 years after the Big Bang, radiation was still the predominant make-up of the early universe and this radiation (photons) would continue to break up nuclei as fast as they could form. The early universe was a soup of radiation, hydrogen and helium nuclei, and a vast array of electrons. Photons would break up nuclei and create more photons, which would go on to break more nuclei. Light (photons) could not travel a straight line because of the temperature and the state of the universe was still a radiation-filled plasma soup where photons would be absorbed by other photons only to be broken up again. After 300,000 years, however, the "radiation" era of the Universe ended and cooled to the point where electrons could latch on to nuclei and form

full-fledged atoms. Once full atoms were created after the radiation era, larger structures such as galaxies and stars (and ultimately planets) could form from the grouping of atoms.

On a cosmic scale, virtually all of the helium that was ever created was born in the Big Bang. The Universe is still predominantly hydrogen and helium that was created in the first moments of time and space. After the Universe was around 200 million years old, hydrogen and helium gas clusters would go on form large clumps of gas where gravity would take hold and form the first generation of stars and galaxies. Stars were born when large clusters of hydrogen and helium gas would fall under the weight of its own gravity and compress to the point where their core temperatures and pressures were high enough for perpetual hydrogen fusion reactions could occur. This reaction, as can be seen on our own Sun, is a process called the proton-proton exchange in which hydrogen is fused to produce helium. Thus, our Sun, along with virtually every star you see in the night sky is a giant nuclear, helium-producing, life-giving, furnace.

The Sun

Our Sun is a very important topic when considering helium for two reasons. First, enormous amounts of helium are created every second in the core of the Sun via hydrogen fusion and second, the Sun is where helium was first discovered many years before it was ever discovered on Earth. The purpose of this segment is to discuss the process by which the Sun produces helium but also give the reader a thorough understand as to *why* helium was detected on the Sun in the first place. Both points can be addressed by the process that occurs in the very hot and dense core of the Sun.

Breaking down the composition of our Sun by *mass*, ~75 % is hydrogen and ~25 % is helium which, as you learned in the segment about the Big Bang, is roughly the composition of our Universe (of course, we are only including visible matter and are not including dark energy or dark matter). The principal composition of our Sun is primarily the product of the material produced during the Big Bang. Interestingly, about 99.86 % of all of the mass of our solar system is housed completely in the Sun while the giant planet Jupiter has about 66 % of the rest of the mass. Everything else in our solar system, Earth included, only comprises 0.05 % of the entire mass in the solar system. Thus on a cosmic scale, our Earth is quite small indeed!

The Sun is a star, just like all of the stars visible to the naked eye on any clear night. Indeed, if you look at the stars at night, they all shine through the same process that occurs in our own Sun. This process, nuclear fusion, is at the heart of every star turning matter into energy much like energy creating matter in the moments after the Big Bang. Recall that energy and mass are on opposite sides of the $E = mc^2$ equation which highlights the relationship between mass and energy.

Our Sun is a second or third generation star that formed from the debris of stellar explosions before it. Although we will go into greater detail about these stellar explosions (supernova) and subsequent star formation later, what is important to understand that stars are born and die. There is a beginning and an end during the ever evolving state of our Universe. Our Sun was born roughly five billion years ago and will ultimately fade into existence in another five billion years.

What does a second or third generation star mean? About 200 million years after the Big Bang, large clusters of hydrogen and helium began to form creating large structures like stars and galaxies. These first clusters of gas which formed stars and galaxies were made from the only raw material the Universe had to offer in the early Universe, hydrogen and helium. These early stars were massive, hundreds of times more massive than our own Sun. The result of these larger sizes meant that these stars burned enormous amounts of hydrogen via nuclear fusion and consequently ran out of fuel faster than a smaller star. After these early stars ran out of hydrogen as their primary fuel source, the cores would become hotter resulting in the burning of helium created from the initial hydrogen fusion process (this process will be discussed in much greater detail later). Needless to say, once the helium fuel ran out, carbon was created. This process continues where the nuclear ash created in the previous reaction is used as fuel for the next stage of a stars life all the way up to the creation of iron when the fusion process ends. Once these early stars' cores contained iron in their core, they would explode in an event known as a supernova which is an event of unparalleled proportions scattering all of the elements up to iron into the Universe while creating new elements in the process. Thus, most of these "first generation" stars left material for second generation stars to form. When second generation stars explode, material is left for third generation stars.

Our Sun was formed from the debris left over from a previous supernova (or additional supernovas). We know this to be the case because when we analyze the composition of the sun via spectral analysis, many elements are present such as oxygen, carbon, nitrogen, silicon, magnesium, neon, iron, sulfur, and many others. However, the primary composition of our Sun is still hydrogen and helium (by far, the most abundant elements in the Universe) which represents 91.2 % and 8.7 % respectively from the standpoint of the total number of atoms in the Sun. The remaining 0.1 % represents everything else combined. There mere presence of these other elements means that our Sun was formed from the stellar debris of a previous supernova(s).

Although iron is the last element created via nuclear fusion in stars, once a star goes supernova (a very rare event with second and subsequent generation stars), all of the other elements up to the last natural element, uranium, are created in the explosion itself via *fission*. So, where elements are fused together (fusion) in the main portion of a stars life, fission (or the breaking up of atoms) is the process by which the heavier elements are formed. This topic will be discussed in greater detail later. These other heavier elements are also found in our Sun but in much lesser amounts as one would expect due to the rare event of a supernova. Our Sun, being an average sized star, will not go supernova but will rather simply fade away at the end of its life. Only massive stars go supernova and our Sun is a very average sized star.

Now that we know how our Sun (and by proxy all other stars) formed from the debris, we can begin the topic of how nuclear fusion takes place in the core of our Sun (and other stars). When our Sun formed from the debris of a previous stellar explosion, its mass gained by attracting other nearby material (again, with mostly hydrogen and helium). Once the gas cluster that formed our Sun became large enough, gravity began to pull the material in on itself creating a very dense and hot core. As soon as the pressures and temperature of the core were high enough, the fusion oven turned on and light (energy) was created. At this point, which happened about five billion years ago, our Sun was born.

How does our Sun work and how does it produce helium? Our Sun, on a cosmic level, is a very average star compared to all others in the Universe but as mentioned before, the process that drives our Sun is precisely the same as virtually every star you see in the night sky and, indeed, across the Universe. The nuclear furnace that produces helium from hydrogen in the Sun takes place in its core.

The hottest and densest part of our Sun is the core where the nuclear reactions take place that keep it shining. Inside the core, the temperatures (~15 million degrees Kelvin) and pressures are such that fusion can occur as hydrogen nuclei (protons) are moving fast enough to fuse together. How does that process work? In our Sun (and all stars), during the main period of life called the main sequence, it is a process called the Proton-Proton Chain (or P-P Chain). In larger stars, and in a small effect in our own Sun, there is another process called the C-N-O Cycle (Carbon-Nitrogen-Oxygen Cycle).

The P-P Chain is the predominant method of helium production in our own Sun. It starts with two hydrogen nuclei (or protons) that are moving fast enough to overcome the repulsion of the two positively charged protons and fuse together¹ to form a heavy hydrogen atom called deuteron (^{2}H) .² The collisions of these protons are nearly head-on and are actually very rare events. Only about one proton in one hundred million protons are even moving fast enough to be able to fuse together. Of that one in one hundred million protons which are moving fast enough to fuse, only about one in ten billion trillion (10^{22}) protons will actually fuse. This means that the average lifespan of a proton in the Sun is about 14 billion years before it will ever fuse with another proton.

The first stage of the P-P Chain is the fusion of two protons. To understand the formula below, we will call each proton "¹H" as it is noted scientifically (recall that the hydrogen nucleus is nothing more than a single proton). The one in front of the ¹H (Hydrogen) is the atomic weight of the element. As an example, the most common helium atom is written "⁴He" because the atomic weight of the nucleus is 4 (⁴He can also be written as Helium-4 and has two (2) protons plus two

¹ At very high speeds, when a proton has a head-on collision with another proton, they become a single nuclei because the strong nuclear force (the force that binds nuclei together) overpowers the electromagnetic repulsion between the two positively charged nuclei.

² Deuteron is an isotope of hydrogen that has one proton, one neutron, and one electron.

(2) neutrons thus having a weight of *roughly* 4). Getting back to the start of the P-P Chain, there exists two single protons, one of which turns into a neutron which fuse together to form a heavy hydrogen nuclei called deuteron (²H; one proton and one neutron) while releasing energy in the form of gamma radiation and a neutrino.³ The next step uses the product of the first stage to create a lighter isotope of helium. In this step, a single deuteron atom (²H) fuses with a proton to create the light isotope of helium (³He) and energy. In the third and final step, two ³He atoms fuse to create ⁴He plus two protons, two neutrons, and energy (gamma ray photons). In scientific notation, here are the steps:

- 1. ${}^{1}\text{H} + {}^{1}\text{H} \rightarrow {}^{2}\text{H} + \text{positron}^{4} + \text{neutrino}$
- 2. ${}^{2}\text{H} + {}^{1}\text{H} \rightarrow 3\text{He} + \text{energy}$
- 3. ${}^{3}\text{He} + {}^{3}\text{He} \rightarrow {}^{4}\text{He} + {}^{1}\text{H} + {}^{1}\text{H} + \text{energy}$

In short form, the equation is simply: $4(^{1}H) \rightarrow 4He + energy + 2$ neutrinos.

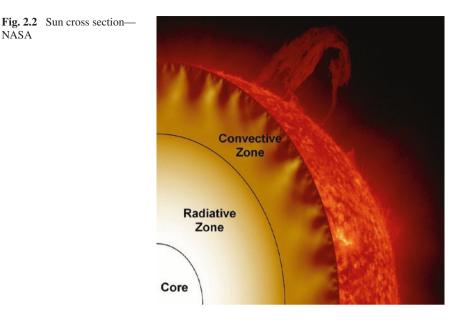
This reaction is the primary reaction for all stars you see in the night sky (and elsewhere in the universe) and is the principal reaction in our own Sun. There is another reaction that is common in larger stars (and to a much lesser extent in our own Sun) called the C-N-O (Carbon-Nitrogen-Oxygen) Cycle which utilizes carbon as a catalyst that ultimately produces helium (⁴He) and carbon. We won't bother going into any detail about this reaction because simply because it is not the primary fusion reaction in our own Sun.

The energy released by the P-P Chain is clearly very large but in order to understand just how much energy, we can break it down by looking at a single P-P Chain event listed above. As you learned from Einstein's famous equation $E = mc^2$ which showed how mass and energy are equivalent, we can use this equation to see how much energy is actually produced in this process. The mass of four individual protons (hydrogen nuclei) equals 6.6943×10^{-27} kg. However, the mass of the product, helium, equals 6.6466×10^{-27} kg meaning that a small amount of mass is lost when fusing hydrogen into helium. You may recall from chemistry class the Law of Conservation of Energy and Mass which, very simply states that the sum of energy and mass (matter) on one side of the equation must equal the sum of energy and mass on the other side of the equation. We can lose matter as exemplified by the loss of mass just mentioned in the P-P Chain above as long as this mass is converted to energy. This is precisely what happens in our Sun; the mass lost in a single reaction when multiplied by the

³ A neutrino (Latin for "little neutral one") is a particle that has no mass or charge and moves virtually undetected through matter. We are constantly bombarded by neutrinos produced by the Sun but they pass through the Earth (and us) as though it was not even there. They are very difficult to detect and can only be found in deeply buried neutron detectors.

⁴ Recall that a positron is the antimatter opposite of an electron. Immediately after a positron is emitted, it will interact with an electron (which are extremely abundant) and quickly annihilate in a burst of pure energy (gamma-ray photons). So, energy is released in this first phase of the P–P Chain albeit indirectly via the product of this first stage.

NASA



shear volumes of converted mass in the Sun produces an extraordinary amount of energy making life possible here on Earth. About 4.3 million tons of matter (the matter that is lost in the fusion process) is converted into energy every second in our Sun. The energy created in the P-P Chain is in the form of high-energy gamma ray photons.

The P-P Chain happens only the core of our Sun where temperatures and pressures are high enough to begin and perpetuate the nuclear reaction mentioned above. What about the rest of the Sun? This is where things get even more interesting and ultimately explains why we even have a visible spectrum which is the only form of light energy humans can detect without additional instrumentation. Surrounding the core of the Sun are several layers each with unique properties that ultimately transport the energy created in the core to the surface of the Sun. Although the detailed mechanisms that happen in these outer regions of the Sun are beyond the scope of this book, immediately surrounding the core is called the Radiation Zone. Other zones away from the Radiation Zone (in order from the core to the surface) include the Convection Zone, the Photosphere, the Chromosphere, and the Transition Zone. Each zone plays an important part in delivering the energy created in the core of our Sun to the surface and ultimately to the entire Solar System (Fig. 2.2).

What is important to note about our layered Sun is that the high-energy gamma ray photons created in the core of our Sun lose energy as these photons make their way to the surface. Gamma ray photons lose energy because most of these photons are absorbed by atoms in the outer layers. As soon as an atom absorbs some of the photons energy, the affected atoms electrons shift to a more excited state which takes some of the energy away from the gamma ray photons. The resulting lower energy photons are then absorbed by more atoms losing more energy along the way. Because of this phenomena, it can take 100,000 years for photons produced in the core to ever reach the surface of the Sun. By the time these photons reach the surface of the Sun to be disturbed across the solar system, the initial gamma ray photons have lost so much energy that the photons emitted are in the visible spectrum. In other words, the very high wavelength (high frequency) gamma rays are spread out to lower wavelength (lower frequency) visible light by the time it reaches our planet.

What happens to our Sun (and stars) when it runs out of hydrogen as its primary fuel? The answer to this question is crucial to understanding why we find helium on Earth which will be described briefly here and in much greater detail later in the book. As we discussed earlier, in about five billion years our Sun will leave what is called the main sequence of its life. The main sequence is the period between when the nuclear furnace begins until it runs out of hydrogen. Most stars are living in the main sequence of their lives because it is, by far, the longest period of a stars life. Our Sun, for example, will live in its main sequence for a total of about 10 billion years. After its main sequence, it will move into what is known as the Red Giant phase when the hydrogen fuel effectively runs out and is replaced by the leftover helium ash from the main sequence.⁵ Once the hydrogen runs out, a star (and our own Sun) is no longer in the main sequence of its life and it enters into its elderly years.

After our Sun's main sequence, gravity will pull the core in on itself making it much hotter. Immediately outside the inner core, left-over hydrogen will continue to fuse into helium making the layers beyond the core expand into the orbits of the inner planets of our Solar System. The energy production from helium burning is much lower thus creating a red surface appearance but it will shine about a hundred times brighter than our Sun in its main sequence. The product of helium fusion in the core of the Red Giant is carbon. Immediately outside the inner core, hydrogen fuses into helium no longer by the P-P Chain but rather shifts to the C-N-O Cycle mentioned earlier in the chapter which uses carbon as a catalyst to produce helium. The Red Giant phase of our Sun lasts only a fraction of the time of its main sequence, about 150 million years. After this, our Sun's life will effectively end because there will not be enough heat, due to its average size, to continue nuclear reactions and manufacture additional elements. The only elements that the Sun will produce is carbon, oxygen, and nitrogen. Our Sun will then cool down, lose much of its outer layer material into space, and retire as a cool white dwarf star and simply fade away into existence. The nuclear furnace stops resulting in no more light for our Solar System.

Although our Sun will fade away without providing many elements in the Universe, the same is not true for stars with a greater mass than our own Sun. Indeed, many *smaller* stars will not go beyond the hydrogen burning phase simply

⁵ Hydrogen burning will still occur in the outer core of a Red Giant star.

because there is not enough mass to allow gravity to pull itself into create heat required for helium burning. Larger stars, however, have a much different fate. Larger stars continue where our Sun left off creating even more elements because their mass allows gravity to pull in more material to generate more heat. Every sequential element created after hydrogen requires more heat for fusion. Helium fusion requires more heat than hydrogen fusion, carbon fusion requires even more heat, and so on. Thus, greater mass enables these additional reactions.

For stars larger than our Sun, this process continues dependent on the mass of the star but it should be noted that the larger the atomic mass of the element being consumed, the greater energy required to continue the fusion process. Although the actual processes by which this happens is beyond the scope of this book, the sequential products and fuels are as follows: hydrogen fuses to helium, helium fuses to carbon, carbon fuses to oxygen and magnesium,⁶ and oxygen fuses to sulfur and neon.⁷ After silicon, the primary method of fusion in stars is a process known as *helium capture* where helium fuses with the product of the last fused nuclei. For example, silicon fuses via helium capture to sulfur, sulfur fuses via helium capture to argon, argon to calcium, calcium to titanium, titanium to chromium, and finally chromium to the last elements produced via fusion, iron and unstable nickel which decays rapidly.

After iron, however, fusion can no longer continue because there can never be enough energy to fuse iron which is the most stable element. The internal nuclear reactor stops when the core fills with iron. Energy cannot be extracted either by fusion or fission meaning it is the end of the line for large stars. When a large star reaches this stage, the result is a gravitational inward pull that is so great that the star will ultimately explode in spectacular fashion in an event known as a supernova. The process of supernova will be discussed in greater detail later but these events are responsible for creating all of the other elements after iron and up to the last natural element, uranium.

This is not to say that other elements are not created in massive stars, they are. It is just that the last *fusion* product in a massive star is iron. Other elements up to Bismuth (specifically the isotope Bismuth-209) can be created in stars by process called neutron capture. More specifically, it is called the s-process (s stands for slow). Because there are an abundance of neutrons in these larger stars, neutrons are able to enter the nucleus of many elements without much fanfare. That is, neutrons are electrically neutral so there is no repulsive force from protons fighting

 $^{^{6}}$ In the carbon stage, two events occur. At extremely high temperatures (~600 million K) and pressures, carbon (12C) will fuse with another carbon nucleus to create magnesium. This process is known as carbon burning. Carbon can also fuse with helium (4He) to create oxygen (16O) and this process is called Helium Capture. Helium capture is far more common because it requires lower temperatures (~200 million K) than carbon burning.

⁷ Oxygen (16O) can fuse into another oxygen nuclei to form sulfur (32S) at the extremely high temperature of about 1 billion K. The more common oxygen reaction, however, is also via Helium Capture where oxygen fuses with helium to become neon (20Ne) which occur at lower temperatures.

against their entry. Recall that adding a neutron to an element does not change the element. Rather, it only changes the isotope of the same element. However, with the addition of several neutrons to a single nucleus can make it unstable, forcing it to break up into lighter nuclei. This process, specifically the s-process, is how elements like gold and silver are formed.

It is fascinating to know that all of the carbon in our bodies, the oxygen in our water, the iron in our blood, the nitrogen in our atmosphere, and indeed all of the elements that make up our bodies and the world around us were created in the cores of stars. Early stars used the only raw material available after the Big Bang, hydrogen and helium, and transformed it into the elements we see every day in our lives. Our Universe is a living, evolving machine.

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Chapter 3 Foundations of Discovery

The Prism

Helium's discovery is probably one of the most unique stories in elemental discovery. Its ultimate identification was the culmination of hundreds of years of scientific achievements by countless professional and amateur scientists. The most distinctive aspect of the discovery of helium lies in the fact that it was the first element to be detected on the Sun before it was identified on Earth. Helium was first detected through a device known as a spectrometer which at its very basic level is nothing more than an apparatus with a slit to allow the passage of light, a prism to refract the light, and an eyepiece (or display) to view the results. Although a very simple apparatus, the spectrometer became one of the most useful tools in atomic elemental identification and discovery for many years after its discovery in 1860. Although technology has certainly advanced since that time, the spectroscope is still used today to determine the composition of stars. At the very heart of spectroscopic analysis is the glass prism.

The effects of light passing through a prism had been known for centuries but it was Isaac Newton who first sought to understand the *nature* of white light. White light, or the most pure light, was believed to have no intrinsic color.¹ Newton, after receiving his bachelor's degree wrote:

In the beginning of the year 1666 (at which time I applied myself to the grinding of Optick glasses of other figures than Spherical) I procured me a Triangular glass-Prism, to try therewith the celebrated Phenomena of colours. And in order thereto having darkened my chamber, and made a small hole in my window shuts, to let in a convenient quantity of the Sun light, I placed my Prism at its entrance, that it might be thereby refracted to the opposite wall. It was at first a very pleasing divertissement, to view the vivid and intense colours produced thereby; but after a while applying myself to consider them more

¹ Isaac Newton, James Gleick, 2003, p. 66.

circumspectly, I became surprised to see them in an oblong form; which according to the received laws of Refraction I expected should have been circular...²

As Newton made calculations regarding the refraction (the bending of light as it passes through a prism or other medium) of light, he soon began to isolate a specific refracted colored beam in which to pass through a second prism. When a beam of sunlight would pass through the first prism, the light would separate into the colors by their degree of "refrangibility", with red being the least refrangible and violet being the most. Newton had subsequently discovered that isolating one particular beam of color and passing it through another prism would not be further dispersed, rather it would remain the same color. In order to confirm his findings he used a biconcave lens to gather the entire spectrum back to a single point, where the colors disappeared to produce the original white light.³ This information led Newton to finally uncover the nature of white light: "Light consists of Rays differently refrangible."⁴ Because a prism separates colors, not "creates" them, white light is a combination of all spectral colors. In Newton's words, "light itself is a Heterogeneous mixture of differently refrangible Rays."⁵

Recall from the previous chapter that the sunlight beam used by Newton was created first as gamma ray photons (packets of light) that have been absorbed by atoms for about 100,000 years inside the Sun before they leave the Sun's surface in the visible spectrum. Although we intuitively think of light as only what we see today, the entire electromagnetic spectrum from gamma rays to radio waves are considered "light". Despite the fact that they all have differing wavelengths, they all move at the speed of light. The visible light that Newton experimented with was the product of hydrogen fusing into helium as four protons lose mass to become helium.

Although Newtons work was, of course, monumentally significant, further spectral breakthroughs did not occur again for nearly 140 years. The next "break-through" occurred when Dr. William Hyde Wollaston (1766–1828) in 1802 made one simple adjustment to Newton's optical experiment: he used a narrow slit instead of a round hole to allow the passage of light. Amazingly, this very minor change (and a rectangular prism made of flint glass⁶) produced a spectrum which was vastly superior, both in quality and color. Wollaston's experiment further showed that the spectrum was not continuous as previously thought, rather the colors in the spectrum were interrupted by a series of dark lines. (Lesser quality prisms, like that used by Newton were not able to demarcate the solar spectrum. Rather, the colors would "blend" into one another much like a rainbow.) Unfortunately, Wollaston did not investigate these dark lines further and it would take twelve more years before these dark lines would gain significance.

In 1814, a brilliant German optician and producer of achromatic lenses (for use in telescopes), would use those dark spectral lines to create lenses of unparalleled

² <u>The Discoverers</u>, Daniel J. Boorstin, 1983, p. 404.

³ Ibid., pp. 404–405.

⁴ <u>The Discoverers</u>, Daniel J. Boorstin, 1983, p. 404.

⁵ The Discoverers, Daniel J. Boorstin, 1983, p. 404.

⁶ Spectrum of Belief, Myles W. Jackson, 2000, p. 31.



Fig. 3.1 Joseph von Fraunhofer demonstrating spectroscope (public domain)

quality. Germany had long been noted for creating the highest quality glass for use in achromatic lenses but it was Joseph von Fraunhofer (1787–1826), who through his glass-making achievements, was able to utilize these dark lines to make accurate measurements of the refractive and dispersive powers of particular glasses. These glasses were used for the manufacturing of achromatic lenses used in astronomical devises such as telescopes. Prior to Fraunhofer's work, "reflective" telescopes (invented by Isaac Newton), which use mirrors, were the most popular astronomical devise because "refracting" telescopes (which use achromatic lenses) would invariably have chromatic aberration,⁷ thus creating a blurred image. Chromatic aberration was eliminated in *reflective* telescopes by increasing the focal length thus resulting in very long telescopes which ultimately become somewhat impractical (Fig. 3.1).

Through solar studies, Fraunhofer was able to determine that these dark lines had fixed positions in the solar spectrum. In order to categorize these lines, he named the

⁷ Chromatic aberration develops when a lens is unable to focus all the wavelengths of the visible spectrum to a single convergence point. In a reflective telescope, this is reduced by increasing the focal point resulting in very long telescopes. The effect of chromatic aberration is a blurred image. Before Fraunhofer, precise measurements of refracting indices were unknown thus lens quality was poor. The dark Fraunhofer lines became *precise* refracting indices for specific wavelengths of visible light thereby eliminating chromatic aberration. The precision of refracting indices allowed for lenses of incredible quality.

Fig. 3.2 Fraunhofer lines

eight most prominent lines the capital letters A thru H. Mapping 700 of these lines of varying width, Fraunhofer used these lines as "landmarks" in producing accurate measurements of the refractive indices of glass samples, which in turn, allowed him to create lenses of incredible quality (see footnote 7). Due solely to Fraunhofer's discovery, "refractive" telescopes with advanced lenses quickly replaced the "reflective" telescopes, which were the most widely used astronomical devices up to that time. Beyond this remarkable accomplishment, however, Fraunhofer did not delve further into understanding the *nature* of these dark lines, which ultimately became known as "Fraunhofer Lines." Rather, he only used them as calibration lines for the glass to craft the highest-quality lenses at the time. Reverend Henry Coddington, an expert on optics in the early 1820s wrote of Fraunhofer's discovery (Fig. 3.2):

The [spectral] interruptions, first observed imperfectly by Dr. Wollaston, and afterward independently, and with great precision, by Professor Fraunhofer of Munich, and by him termed the *fixed lines* in the spectrum, are one of the most important discoveries in the whole range of Optical science.⁸

Reading the Lines

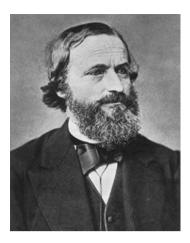
The year 1859 would mark the date when the mysterious Fraunhofer Lines would become fully understood, ushering in a new wave of scientific discovery. From 1810 until 1860, the discovery of new elements was at a virtual standstill. From 1830 until 1860, only two elements had been discovered, Lanthanum (La) and Erbium (Er), and none were discovered in the decade of 1850.⁹ Periodic law (the systematic grouping of elements), developed by Dimitri Ivanovich Mendeleev (1834–1907), had not been discovered until 1869.

The mystery of the Fraunhofer lines was finally solved by a German physicist named Gustav Robert Kirchhoff (1824–1887). Kirchhoff's work focused on the relationships between the various kinds of spectra (of which the dark Fraunhofer lines were one) by using a device he co-invented known as a spectrometer (the analysis of spectra is called spectrometry). Using the spectrometer, Kirchhoff experimented on common elements and the spectra derived from each under

⁸ Ibid., p. 40.

⁹ The Periodic Table: Its Story and Its Significance, Eric R. Scerri, 2007, p. 7.

Fig. 3.3 Gustav Robert Kirchoff (1824–1887) (public domain)



various conditions. For instance, when Kirchhoff would put sodium salts into a flame, he would use the spectrometer to analyze the resulting spectrum of heated sodium. Further, the hot gases which were analyzed were also passed through colder gases which would reveal a different spectra. In 1859, Kirchhoff developed three laws which would quickly usher in the discovery of new elements and also completely change astronomy forever. These laws state (Fig. 3.3):

- 1. Solid and liquid bodies (also gases under high pressure) yield, when incandescent, a *continuous* **spectrum**
- 2. Gases under low pressure give a discontinuous but characteristic bright-line spectrum (*emission* line spectrum)
- 3. When white light (i.e. sunlight) passes through a gas, this medium absorbs rays of identical wave-length with those composing its own bright-line spectrum¹⁰ (*absorption* line spectrum).

The development of these laws fully explained the dark Fraunhofer lines in the solar spectrum. As Fraunhofer noted, the dark lines were fixed in the solar spectrum which meant that *dark* lines were actual *bright* lines *absorbed* in white light (daylight). It had been known for over 100 years, for instance, that pouring sodium salts onto a flame would reveal a yellow "D" line in the spectrum but it was Kirchhoff and the discovery of his three laws that gave meaning to such phenomena. (Sodium actually produces a double yellow line which would be analyzed with more precision later). Kirchhoff was able to prove, that the dark "D" sodium line in the *absorption* line spectrum corresponded exactly with the "D" *emission* line. In other words, they were merely reversals of the same line. Therefore, each of the dark lines in the absorption line spectrum represented the characteristic signature of an element or combination of elements that were merely absorbed by the sunlight. Each element, then, had its own unique spectra, much like human finger-prints. No two are the same (Figs. 3.4 and 3.5).

¹⁰ The Sun, David P. Todd, Science, Vol. 2, No. 28, July 122, 1895, p. 34.



Fig. 3.4 Sodium spectrum (public domain)

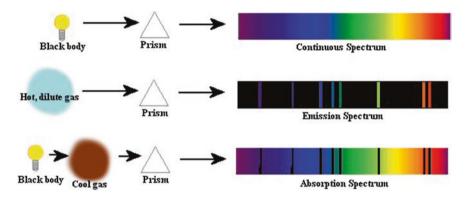


Fig. 3.5 Absorption-emission-continuous spectra (Dr. Siobahn Morgan-U. of Northern Iowa)

Armed with this new discovery, Kirchhoff (Kirchhoff and Robert Bunsen (1811–1899) of Bunsen burner fame) began examining emission spectra of various terrestrial elements in order to confirm or deny their presence in the Sun. Kirchhoff and Bunsen were quickly able to confirm the presence of sodium, iron, magnesium, barium, copper, zinc, calcium, chromium, nickel, and aluminum in the Sun's atmosphere.¹¹ All of these elements, of course, were in their gaseous state so when viewed through a spectroscope, the dark "reversal" Fraunhofer lines appeared, meaning that these elements' emission lines were absorbed. Through this work, Kirchhoff had been the first to form a theory of the constitution of the Sun and conceived the notion that the Sun is surrounded by vapors of many elements whose emission lines are absorbed by white light emitted by the Sun.¹²

¹¹ Contributions to Solar Physics, Norman Lockyer, 1874, pp. 116–128.

 $^{^{12}}$ Recall that the Sun is primarily hydrogen and helium. Hydrogen and helium together comprise roughly 99.9 % of all the atoms in the Sun. Everything else combined make up only 0.1 %. That is not to say that the amount of other elements are insignificant in the Sun, they are. The Sun was formed from a gas cloud that was rich in these other elements, like iron, for example which were available from a previous star that went supernova. Although these other elements are present in the Sun, they are not responsible for any nuclear reaction that powers the Sun. This is why it is possible to see these elements spectroscopically. The presence of these elements are also clues that our Sun was formed from a supernova of a first or second generation star.

Although Kirchhoff and Bunsen's work on solar and terrestrial spectra was extremely thorough, a problem arose when utilizing a proper method of measurement. All of their results were expressed on an arbitrary scale in that the entire spectrum was divided into equal portions, which were then numbered, and positions of various lines were noted on this scale. The units of measurement, therefore, were meaningless.¹³ Anders Jonas Ångström (1814–1874) in 1868, using a grating¹⁴ instead of a prism, measured the wavelengths of hundreds of lines and each was placed on a scale of their respective wavelengths. These units became known as Ångström Units (Å) which equals ten millionths of a millimeter $(1 \times 10^{-10} \text{ m})$.¹⁵ For instance, sodium has a wavelength of 5,889 Å, in the yellow region of the spectrum. This yellow emission line is the reason, for example, why sodium lamps produce such a bright yellow color.

The nature of these emission and absorption lines were not understood until the development of quantum theory by Neils Bohr many years later. Quantum leaps (electrons moving from one orbit to another) was the explanation for the bright lines. When an electron drops to a lower orbit it is moving from a higher energy orbit to a lower energy orbit. If you recall grade school chemistry, you know that energy can never be created or destroyed. Thus, in this case of dropping to a lower energy orbit, some energy has to be released and it is done so in the form of light. It is not just any light, however, but rather a precise wavelength of light that corresponds to the energy difference between the two orbits. As this process is occurring repeatedly with atoms of a single element, it produces a bright line(s) spectrum. Conversely, if an electron moves from a low energy orbit up to a high energy orbit, it absorbs energy and thus produces a dark line in the spectrum. Every element in the periodic table has its own specific electron energy levels and thus each element has a specific "fingerprint" of spectral lines.

Gustav Kirchhoff and Robert Bunsen were able to make the above mentioned achievements because of the spectroscope, which was invented by both Kirchhoff and Bunsen in 1859. Although spectral analysis had occurred long before Kirchhoff's time, it was these two scientists who created a devise which would later become a key component in terrestrial and astronomical observation. The spectroscope is a simple devise that consists of a small slit to allow the passage of light, a prism to refract the light, and an eyepiece or display to view the results (Fig. 3.6).

Shortly after Kirchhoff's introduction of the spectroscope and three new laws which bore his name, spectroscopic analysis took center stage where it was immediately used to map the emission lines of both terrestrial and astronomical

¹³ Spectroscopy, ECC Bally, Vol. 1, 3rd Ed., 1924, p. all.

¹⁴ A grating produces similar results as a prism. A grating is an optical device that separates visible light through evenly-spaced parallel slits in a material resulting in a higher resolution spectrum. A common example of a material that acts like a grating is a CD or DVD. The grooves on the data side are equidistant and very close together. When you move the CD in the light, a noticeable spectrum will appear.

¹⁵ Spectroscopy, ECC Bally, Vol. 1, 3rd Ed., 1924, p. all.

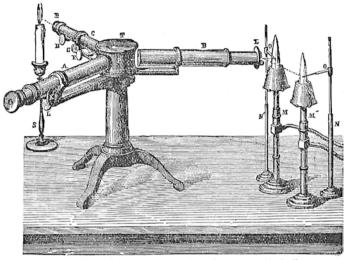


Fig. 15. - Spectroscope de MM. Bunsen et Kirchoff.

Fig. 3.6 Kirchoff spectroscope (public domain)

substances. Armed with this new ability to find what elements make up the solar atmosphere, Kirchhoff was also able to discover entirely new elements through laboratory work. In 1860, one year after delivering his three new laws, Kirchhoff and Bunsen discovered Caesium using the spectroscope which represented the first element to be discovered spectroscopically.

After Caesium, three more elements in 3 years were discovered spectroscopically: Thallium, discovered in 1861 by Sir William Crookes (1832–1919); Rubidium, discovered in 1862 by Kirchhoff and Bunsen; and Indium, discovered in 1863 by Ferdinand Reich (1799–1882) and Hieronymous Theodor Richter (1824–1898). The spectroscope was now able to detect elements which would have been impossible using general chemistry. Lithium, for example, was only known to exist in four minerals but after the advent of the spectroscope, it was found to exist nearly everywhere, mostly in the form of compounds.^{16,17}

When the spectroscope was used to analyze a substance via emission line spectra, the lines themselves represented a "fingerprint" of the specific substance being studied. Therefore, both single elements or compounds of different elements, could now be detected by the lines they emitted. The origin of the lines were not clearly understood at the time but its ability to identify a specific element was absolute. An atom or compound, then, could be predicted solely by the line that was emitted.

¹⁶ The Spectroscope, J. Norman Lockyer, 1873, pp. 52–53.

¹⁷ Chemical Analysis by Observation of Spectra, G. Kirchhoff, R. Bunsen, Annalen der Physik und der Chemie (Poggendorff), Vol. 110 (1860), pp. 161–189.

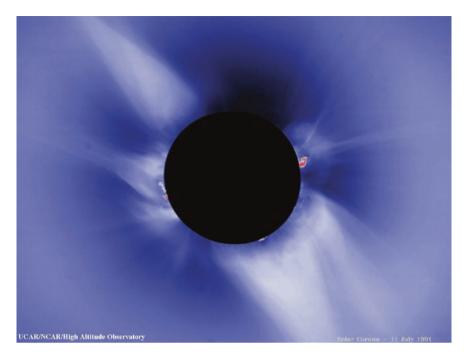


Fig. 3.7 Solar corona with prominences—NASA

With the success of the spectroscope, the rush was on to understand the nature of the Sun, especially the composition of the "protuberances" (later to be known as prominences) seen only during a total eclipse, which puzzled nearly every astronomer. It wasn't until 1860 when Father Pietro Angelo Secchi (1818–1878), a Jesuit priest, and Warren de la Rue (1815–1889) (in separate locations) took the first photographs of the corona during a total eclipse in Spain, which proved that the prominences were actually features that were attached to the Sun, rather than produced by the Earth's (or moon's) atmosphere as some had suspected.¹⁸ Armed with this knowledge of the prominences origin and the introduction of the spectroscope, scientists could now use the spectroscope to study these events further during a solar eclipse. Unfortunately, scientists would have to wait to use their spectroscopes until the next eclipse, which was due to arrive on August 18, 1868 in parts of India. During this next eclipse, astronomers and scientists viewing the prominences with a spectrometer should be able to learn if these prominences were solid, liquid, or gaseous in nature. If they were gaseous, as many had believed, then a bright emission line spectrum would be revealed (Fig. 3.7).

¹⁸ Total Eclipses of the Sun, J.B. Zirker, Science, Vol. 210, No. 4476, December 19, 1980, p. 1313.

Understanding the Sun

Until about the middle of the 19th century, very little was known about the Sun. The Sun was a difficult orb to study because of its brightness; very little was to be gleaned from visual inspection and eyesight could easily be damaged. Due to the general lack of knowledge, scientists could dream anything they wished as to its composition. Sir William Herschel (1738–1822), the discoverer of the planet Uranus and one of the most respected astronomers of his day, for instance, believed that the Sun's composition was Earth-like (i.e. rock) and the interior of the Sun was cool and that it could very well be inhabited in the cooler regions. He believed that low level clouds on the Sun protected its inhabitants from the heat above.

It should be noted that during this time, every astronomer believed the composition of the Sun was Earth-like. Nuclear fusion was an unknown phenomenon at this time and thus there was no reason to believe that the Sun was made of materials that differ from our own Earth. At the time, there was no method to determine that the Sun was made of gas and because the Earth was made of rock, so too must be the Sun.

Given the difficult task of studying the sun in broad daylight, the only time to perform solar observations among scientists, amateur and professional alike, was during a total solar eclipse when the moon passes directly in front of the Sun, which occur with little frequency. Eclipse observations had been noted since the early 1600s but very little could be learned from these events beyond thoughts created by the imagination. Observers were mystified by the spectacular halo or "corona" (the Sun's outer atmosphere) which would appear during the moment of totality raising the question of its origin. In addition to the corona, many had noticed "red flames" that would appear as gigantic fire flames protruding from the edges of Sun during totality.

In 1842, a stockbroker and amateur astronomer named Francis Bailey made observations during a total eclipse that were so descriptive that it almost certainly ushered in a new wave of eclipse observers. Bailey called these red flames "protuberances" because these flames appeared to protrude from the limb of the Sun. Bailey wrote:

I was astounded by a tremendous burst of applause from the streets below and at the same moment was electrified at the sight of one of the most brilliant and splendid phenomena that can be imagined. For at that instant the dark body of the moon was suddenly surrounded with a corona, a kind of bright glory. I had anticipated a luminous circle around the moon during the time of the total obscurity but I did not expect from any of the accounts of previous eclipses that I had read, to witness so magnificent an exhibition as that which took place. Splendid and astonishing, however, this remarkable phenomena really was, and though it could not fail to call forth the admiration and applause of every beholder, yet I must confess there was at the same time something in its singular and wonderful appearance that was appalling. But the most remarkable circumstance attending this phenomenon was the appearance of three large protuberances apparently emanating from the circumference of the moon but evidently forming a portion of the corona.¹⁹

¹⁹ Total Eclipses of the Sun, J.B. Zirker, Science, Vol. 210, No. 4476, December 19, 1980, p. 1313.

Soon the impetus was given to understand the nature, and composition, of these protuberances. Solar eclipses became the *only* way to study the otherwise very difficult to study Sun. As evidenced by Bailey's description above, the only evidence as to the composition of the Sun was what could be dreamed by the imagination. It was only through the use of a spectroscope where more definitive and concrete conclusions could be derived. The same general principals of spectroscopy are still used today to study other stars and galaxies albeit with much more advanced equipment.

Joseph Norman Lockyer

During the year 1866 a scientist and relatively novice astronomer, J. Norman Lockyer (1836–1920), became anxious like many other astronomers to learn the composition of the prominences found only during a total solar eclipse. If, when viewed for the first time by a spectroscope revealed a continuous spectrum, then the prominences would be liquid or solid. If, on the other hand, an emission line spectrum was revealed, they would prove to be of a gaseous nature (Fig. 3.8).

Lockyer had spent several years observing the Sun's sunspots with a spectroscope and quickly learned (with the spectroscope) that in certain parts of the Sun, more absorption occurred. Due to this observation, both Lockyer and his friend, Dr. Balfour Stewart (1828–1887), believed the prominences to be of *probable* gaseous nature. *If* they were made of gas, then emission lines should be present even without waiting for the occurrence of an eclipse. The primary problem was viewing the Sun during normal daylight hours. Lockyer wrote:

...the conclusion we arrived at was that the red flames were probably masses of incandescent gas. On this hypothesis it became at once obvious that their existence should be revealed by the spectroscope without the occurrence of a total eclipse, as they are not then rendered visible by any magical or mysterious process, but simply by the absence of the

Fig. 3.8 Joseph Norman Lockyer (public domain)



overpowering light of the sun: for although the red flames are only visible to the eye when the sun is eclipsed, it does not follow that their existence will not be detected by the spectroscope at other times; and for this reason, - the prominences are not visible to the eye and ordinary sunshine, because the regions near the sun are as bright or brighter than the prominences; they are, therefore, "put out", as the stars are in daytime.²⁰

In order to solve this problem of daylight, Lockyer believed if he could make the slit in the spectroscope even smaller and slimmer, then any light emitted would be displayed over a wide area thus becoming somewhat diluted as a consequence. Then as the diluted "background" of the spectrum was reduced in brightness, then it would be possible for the bright emission lines to appear brighter against this faded background.

Although Lockyer was confident that this idea would work as he had suggested in a publication in 1866, he lacked a spectroscope of significant dispersement powers to prove his hypothesis. Lockyer stated in 1866, "and may not the spectroscope afford us the evidence of the existence of the 'red flames' which total eclipses have revealed to us in the Sun's atmosphere; although they escape all other methods of observation at other times? And if so, may we not learn something from this of the recent outbursts of the star and Corona?"²¹ In order to prove this hypothesis, Lockyer needed a more powerful spectroscope.

Determined to prove that the prominences were gaseous, Lockyer quickly approached the Government Grant Committee (United Kingdom) which supplied him with funds for the construction of a more powerful spectroscope. Construction began in early 1867 and was delivered, incomplete, on October 16, 1868.²² Unfortunately for Lockyer, the total eclipse had already occurred nearly two months earlier.

The Solar Eclipse of August 18, 1868

Teams of scientists and astronomers sailed to India armed with spectroscopes in order to determine the composition of the "red flames" or prominences for the August eclipse, which was to be the first expedition where a spectroscope was used. Representatives from the Royal Society, Royal Astronomical Society, Academy of Sciences, and the Bureau des Longitudes, were just a few of the teams on attendance for this rare event. During the totality of the eclipse, all an observer had to do was aim their spectroscope directly at a part of a prominence and the composition should be revealed in a brief moment (Fig. 3.9).

²⁰ <u>Contributions to Solar Physics</u>, Norman Lockyer, 1874, pp. 116–128.

²¹ Spectroscopic Observations of the Sun, J. Norman Lockyer, Communicated by Dr. Sharpey, Received October 11, 1866, Proceedings of the Royal Society of London, Vol. 15, Nov. 15, 1866, pp. 256–258.

²² Spectroscopic Observations of the Sun, No. II, J. Norman Lockyer, Philosophical Transactions of the Royal Society of London, Vol. 159, November 19, 1868, p. 425.

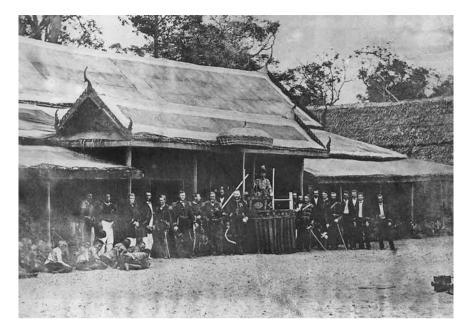


Fig. 3.9 August 18, 1868 (public domain). King Mongut of Siam and English party viewing a solar eclipse on August 18, 1868

As soon as the moment of full totality arrived, most, if not all, scientists saw the bright lines immediately. The red flames were made of gas.

Telegraphs began to arrive to the fact that these events were indeed made of gas because of the "bright lines" that were seen. Several astronomers made remarks of what they had observed but nearly every witness marked varied positions of each of the lines.²³ Regardless, all observers had learned that the principle component of the Sun's prominences was Hydrogen, as seen by the bright C (red) and F (light blue) lines which represent that element. Although additional lines were noticed by these observers, there was one particular bright line in the yellow region of the spectrum that was unusual. Some of the written accounts of the observers of the August 18 eclipse are as follows:

Georges Rayet (viewed eclipse at Malacca): "...je vis immédiatement une série de neuf lignes brillantes qui", ...me semblent devoir être assimilées aux lignes principales du spectre solaire, B, D, E, b, une ligne inconnue, F, et deux lignes du groupe G." Translated: I immediately saw a series of nine brilliant lines, ...seem to me to have to be comparable with the principal lines of the solar spectrum, B, D, E, b, an unknown line, F, and two lines of the group G.²⁴

²³ Spectroscopic Observations of the Sun, J. Norman Lockyer, Communicated by Dr. Sharpey, Received October 11, 1866, Proceedings of the Royal Society of London, Vol. 15, Nov. 15, 1866, pp. 256–258.

²⁴ Comptes Rendus, M.G. Rayet, Vol. 67, August 18, 1868, p. 758.

Captain C.T. Haig (viewed eclipse at Beejapoor, India): "I may state at once that I observed the spectra of two red flames close to each other, and in their spectra two broad bright bands quite sharply defined, one rose-madder and the other light golden".

Norman Robert Pogson (viewed at Masulipatam): yellow line was "at D, or near D".²⁵

Lieut. John Herschel (viewed at Jamkandi): "I recorded an increasing brilliancy in the spectrum in the neighborhood of D, so great in fact as to prevent any measurement of that line till an opportune cloud moderated the light. I am not prepared to offer any explanation of this." And, "I consider that there can be no question that the ORANGE LINE was identical with D, so far as the capacity of the instrument to establish any such identity is concerned".²⁶

Pierre Janssen (viewed at Guntur, India): "Immédiatement après la totalité, deux magnifiques protuberances ont apparu: l'une d'elles, de plus de 3 min de hauteur, brillait d'une splendeur qu'il est difficile d'imaginer. L'analyse de sa lumière m'a immédiatement montré qu'elle était formée par une immense colonne gazeuse incandescente, principalement compose de gaz hydrogéne." Translated: Immediately after totality, two splendid protuberances appeared; one of them, of more than 3 minute height, shone of a splendor which it is difficult to imagine. The analysis of its light showed me immediately that it was formed by an immense incandescent gas column, mainly made up of hydrogen gas. (Janssen fails to mention anything about the yellow line in this publication.)²⁷

The most obvious question when reading the reports of these various astronomers is: *who was the first to see the yellow "helium" line during the eclipse of August 18, 1868?* The answer would logically be that nearly all of the astronomers represented probably saw the yellow line and we know that many did. Because of the shear volumes of helium in the Sun, the yellow line would have certainly been one of the most prominent after the hydrogen lines.

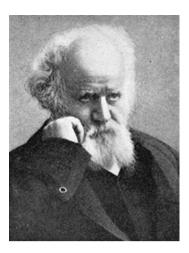
It should be noted that although Pierre Janssen (1824–1907) is frequently given credit for being the first to see the yellow helium line during this eclipse, he failed to make any mention of it in his September 1868 publication (Comptes Rendus) detailing his observations. The reason why Janssen is frequently given credit for its discovery is due to he being the first astronomer to view the Sun's promiences *without* an eclipse, as Lockyer had suggested could be done two years prior. Somehow history has linked this accomplishment with the discovery of the yellow line during the total eclipse of August 18, 1868. This will be discussed further in a moment (Fig. 3.10).

²⁵ The Story of Helium, Nature, J. Norman Lockyer, February 6, 1896, p. 320.

²⁶ Account of the Solar Eclipse of 1868, Lieut. J. Herschel, Proceedings of the Royal Society of London, November 19, 1868, p. 113 and 117.

²⁷ Comptes Rendus, M. Janssen, Vol. 67, September 19, 1868, p. 838.

Fig. 3.10 Pierre Janssen (public domain)



After the Eclipse

When J. Norman Lockyer's new, more powerful, spectroscope was finally delivered on October 16, 1868, it was still incomplete. Despite its deficiencies, it was still in a condition which allowed Lockyer to proceed with observations. After numerous adjustments, Lockyer was finally able to view the emission lines while scanning the limb of the Sun during normal daylight on October 20, 1868 with much excitement. His account of this observation was recorded on October 20, 1868 and was received the following day:

SIR, I beg to anticipate a more detailed communication by informing you that, after a number of failures, which made the attempt seem hopeless, I have this morning perfectly succeeded in obtaining and observing part of the spectrum of a solar prominence.

As a result I have established the existence of three bright lines and the following positions:-

- I. Absolutely coincident with C.
- II. Nearly coincident with F.
- III. Near D.

The third line (the one near D) is more refrangible than the more refrangible of the two darkest lines by eight or nine degrees of Kirchhoff's scale. I cannot speak with exactness, as this part of the spectrum requires mapping.

I have evidence that the prominence was a very fine one.

The instrument employed is the solar spectroscope, the funds for the construction of which were supplied by the Government-Grant Committee. It is to be regretted that its construction has been so long delayed.

I have &c.,

J. NORMAN LOCKYER²⁸

²⁸ Notice of an Observation of the Spectrum of a Solar Prominence, Proceedings of the Royal Society of London, J. Norman Lockyer, Vol. 17, October 1868, pp. 91–92.

This letter written by Lockyer was received by the Academy of Sciences (Paris) on October 21, 1868. Interestingly, the letter written by Pierre Janssen in India recording his observations of the prominences without an eclipse, also arrived in Paris on October 21 only a few minutes later than Lockyer's. Janssen had written his letter on September 19, 1868 but its travel time from India took over one month.

The emission line observations of the Sun's prominences without an eclipse, and *not* the actual eclipse of August 18, 1868, is what Janssen is given credit for discovering. In addition, Janssen might not have known to attempt the viewing of the Sun's prominences in broad daylight had it not been for Lockyer's published hypothesis in 1866. The question arose, then, who should receive the credit for this particular discovery? The answer was best addressed by M. Faye, a distinguished astronomical member of the Academie des Sciences:

Instead therefore of endeavoring to apportion, and therefore to weaken the merit of the discovery, is it not better to attribute the whole honor, without any reservation, to both of these men of science, who, separated by some thousands of miles, have each been fortunate enough to reach the intangible and the invisible by the method the most astonishing, probably, that the genius of observation has ever conceived?²⁹

This discovery made it possible to further de-mystify the riddle of the Sun's atmosphere. The French Academy thus awarded the discovery to both Lockyer and Janssen and a medal was cast bearing the images of both men commemorating the analysis of the Sun's prominences. This award had nothing to do with the discovery of the inexplicable yellow "helium" line. Rather, it was awarded because it proved that emission lines (many lines) could be seen at any time of the day, rather than waiting for the next solar eclipse. Both Janssen and Lockyer had now paved the way to analyzing the Sun on a daily basis.

The Meaning of the D Line

Shortly after the August 18 eclipse, observations in November of the same year by Father Angelo Secchi, provided the impetus to determine exactly what this D line represents. Secchi first noticed the yellow D line in his letter, *Red Protuberances* on November 4, 1868.³⁰ Secchi was skeptical and believed that this new D line probably represented hydrogen under intense pressures. Later, in a November 30 publication, it became apparent to Secchi that the line did not belong to hydrogen because the yellow line could not be reproduced in laboratory studies.

Lockyer also continued his spectroscopic work after the eclipse and had further defined a new layer on the Sun which he named the Chromosphere (the name was suggested by Dr. William Sharpey, Sec. of the Royal Society³¹) in early November

²⁹ Solar Physics, J. Norman Lockyer, 1874, p. 127.

³⁰ Protubérances rouges, Comptes Rendus, A. Secchi, Vol. 67, November 4, 1868, p. 937.

³¹ Spectroscopic Observations of the Sun.—No. II, J. Norman Lockyer, Philosophical Transactions of the Royal Society of London, Vol. 159, November 19, 1868, p. 430.

Fig. 3.11 Edward Frankland (public domain)



1868. Lockyer was still uncertain as to how to explain the yellow line and in an effort to confront this issue, recruited the help of Dr. Edward Franklin (1825–1899) of the Royal College of Chemistry in London to help with laboratory work of which Lockyer had little experience. It was hoped that with the combined efforts of Lockyer and Frankland, that they would be able to find the meaning behind the mysterious yellow line (Fig. 3.11).

Frankland became enamored with the yellow line as soon as it was introduced to him by Lockyer stating, "there was nothing about that splendid mountain of glowing hydrogen you [Lockyer] showed me last Sunday, that impressed me so deeply as the brilliancy of the yellow line and I think we ought not so easily to give up all efforts to get it from terrestrial hydrogen."³² By the time of this particular comment by Frankland, Lockyer had already begun to consider that the yellow line may represent a new element. The prospect of discovering a new element via a spectrometer was certainly an exciting possibility because of the four elements recently discovered through its use.

Determined to learn more about this new yellow line, Lockyer and Frankland poured themselves into the study of any terrestrial substance that might yield this same line when viewed through a spectroscope. Although Lockyer held some faith in that a new element may be present, Frankland was adamantly opposed to agreeing to such a statement until all studies had been exhausted. Still a curiosity, helium finally became known as the D₃ line in 1869 due to its proximity to the D₁ and D₂ lines of sodium. The new label, given by Father Secchi, first appeared in a sketch in his paper of May 21, 1869 in the Comptes Rendus.³³

Throughout the 1870s Lockyer appeared to be tormented that this line could not be reproduced, especially with hydrogen studies. At some point between January 19, 1871 and August 3, 1871, the name "helium" was finally introduced to

³² Science and Controversy, The MIT Press, A.J. Meadows, 1972, p. 59.

³³ Comptes Rendus, A. Secchi, Vol. 68, May 21, 1869, p. 1869.

the world although there is no written record of its naming. Lockyer had given the mysterious line the name helium, after the greek sun god, *helios*, only in order to differentiate it from hydrogen. Lockyer wrote:

I found that the yellow line behaved quite differently from either the red or the blue line; so then we knew that we were not dealing with hydrogen; hence we had to do with an element which we could not get in our laboratories, and therefore I took upon myself the responsibility of coining the word helium, in the first instance for laboratory use.³⁴

Although the above quote implies that Lockyer knew that the D_3 line was not a form of hydrogen, we know that from the time of its detection until its final discovery on Earth, Lockyer could never maintain his complete faith in its full discovery simply because it could not be reproduced anywhere on Earth.

The first public mentioning of the word helium occurred at Sir William Thomson's (1824–1907, later known as Lord Kelvin) presidential address to the British Association at Edinburg in 1871. Kelvin stated:

...it seems to have been proved that at least some sensible part of the light of the "corona" is a terrestrial atmospheric halo or dispersive reflection of the light of the glowing hydrogen and "helium" round the sun. (Frankland and Lockyer find the yellow prominences to give a very decided bright line not far from D, but hitherto not identified with any terrestrial flame. It seems to indicate a new substance, which they propose to call Helium.)³⁵

Although Kelvin had given credit to both Lockyer and Frankland, the credit for the name belongs solely to Lockyer. Shortly after Kelvin's address, Frankland, who was still not convinced of the idea of a new element, appeared to let the implication of the joint naming pass. One year later as the next president of the British Association, William Benjamin Carpenter (1813–1885), referred to helium in less than favorable terms, Frankland quickly distanced himself entirely from the matter. Frankland, seemingly fearing any damage to his reputation through a potentially bogus claim stated (as a result to Carpenter's statement):

Surely Dr. Carpenter is wrong and coupling my name with yours in connection with helium as I remember always protesting in our conversation about the yellow line, against making this assumption, until we had exhausted every effort to get the line out of hydrogen.³⁶

The next public mentioning of the word helium appeared to be by Professor Pietro Tacchini (1838–1905) at a Public Conference at the Royal University of Palermo on February 18, 1872. Tacchini stated:

In all therefore eighteen elements (in the protuberances), besides hydrogen and the element provisionally named Helium, which is never absent, and represents the constant material of the entire chromosphere.³⁷

³⁴ The Story of Helium, J. Norman Lockyer, Nature, February 6, 1896, p. 321.

³⁵ Inaugural Address of Sir William Thompson, Nature, August 3, 1871, p. 268.

³⁶ Science and Controversy, MIT Press, A.J. Meadows, 1972, p. 60.

³⁷ Forms of Solar Protuberances, Tacchini, August 8, 1872, p. 293.

After these two public events where the name helium was revealed, it was again mentioned by Dr. John W. Draper (1811–1882) in his Inaugural Address as the first President of the American Chemical Society in November 16, 1876.³⁸ Lockyer, on the other hand, made little mention of the name in the period until its terrestrial discovery, choosing rather to call it "D₃". Still extremely confused by the fact that he could not be certain of its existence, his mental gyrations are best explained in his writings over the period:

February 11, 1869: the bright line near D has apparently no representative among the Fraunhofer lines. This fact implies that, assuming the line to be a hydrogen line, the selective absorption of the chromosphere is insufficient to reverse the spectrum...We have altogether failed to detect any line in the hydrogen spectrum in the place indicated, i.e., near the line D, but we have not yet completed all the experiments we had proposed to ourselves.³⁹

March 18, 1869: With regard to the yellow line which Dr. Frankland and myself have stated may possibly be due to the radiation of a great thickness of hydrogen.⁴⁰

March 19, 1869: The D line of hydrogen (?) also bore a similar appearance.

January 19, 1871: X (new element).....near D.⁴¹

Book written in 1874: ...In the first place, we are perfectly certain now that the line D_3 has nothing in the world to do with hydrogen.⁴² (Lockyer makes no reference to "helium" in this book.)

November 17, 1887: if however, it should eventually be established that the line is really D_3 , which probably represents a fine form of hydrogen.⁴³

December 19, 1889: the evidence tends to show that D_3 and f are finer vapours than hydrogen. 44

Although helium was first *detected* in the summer of 1868, there was still no conclusive evidence that a new element was discovered until Sir William Ramsay found the yellow line in a uranium-based mineral in 1896. Even after its Earthly discovery its existence was still very much open for debate.

³⁸ Science in America, Inaugural Address of Dr. John W. Draper, as President of the American Chemical Society, Delivered on November 16, 1876.

³⁹ Contributions to Solar Physics, J. Norman Lockyer, 1874, pp. 526–527.

⁴⁰ Spectroscopic Observations of the Sun—No. III, J. Norman Lockyer, Proceedings of the Royal Society of London, Vol. 17, March 18, 1869, pp. 350 and 356.

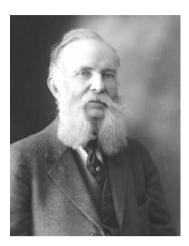
⁴¹ The Mediterranean Eclipse, 1870, Nature, J. Norman Lockyer, January 19, 1871, p. 223.

⁴² Contributions to Solar Physics, J. Norman Lockyer, 1874, p. 406.

⁴³ Researches on the Spectra of Meteorites, Proceedings of the Royal Society of London, November 17, 1887, Vol. 43, p. 139.

⁴⁴ Nebulae and Stars with those Comets and Aurorae, Proceedings of the Royal Society of London, December 19, 1889, Vol. 47, p. 31.

Fig. 3.12 Francis Hillebrand (American Chemical Society)



Terrestrial Discovery

Helium's discovery is most definitely a story of "almosts" in that had several scientists taken further steps, they might have hastened its ultimate discovery on Earth. For instance, had Lockyer and Frankland investigated more rock samples, as opposed to focusing on creating the yellow line from the manipulation of hydrogen samples, helium might have been discovered on Earth in the 1870s. Helium, like many other scientific discoveries, was only known to exist thanks to hundreds of years of scientific advancement that came before it. Unlike any other previously identified element, helium's long road to discovery was far from complete and many more years would pass until it was proven decisively.

The road to helium's terrestrial discovery began in 1887 when William Francis Hillebrand (1853–1925) of the United States Geological Survey investigated a uraninite crystal mined from a quarry in Connecticut. As was common in mineral investigation, Hillebrand crushed a portion of this rock into a powder and then treated the sample with sulfuric acid. This uraninite sample, upon treatment, slowly began to emit a gas which was at first blush believed to be carbon dioxide. However, any carbon dioxide emitted would occur rapidly during the reaction with sulfuric acid. This particular sample, rather, emitted a slow continuous stream of gas⁴⁵ (Fig. 3.12).

After Hillebrand collected and analyzed the gas sample with a spectrometer, he determined that it revealed the spectrum of nitrogen. Not exactly the results he anticipated, further experimentation continued on more uraninite samples collected from other areas in the United States. Nearly all of the samples he tested revealed a similar emission of gas. Hillebrand published his findings in 1890 in

⁴⁵ Biographical Memoir of William Francis Hillebrand, Frank Wigglesworth Clarke, National Academy of Sciences, 1928, pp. 54–55.

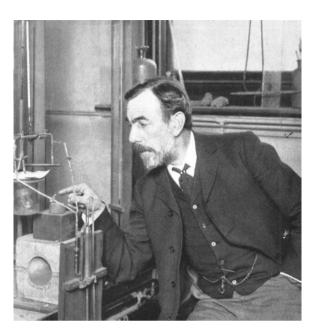


Fig. 3.13 William Ramsay (public domain)

the U.S. Geological Survey Bulletin titled, On the Occurrence of Nitrogen in Uraninite.

Ordinarily, a *geological* publication of this type would seldom find its way to a non-geologist but Hillebrand's paper was presented to Professor William Ramsay (1852–1916), an English chemist in 1895. Ramsay, who had just discovered argon through nitrogen experimentation, was introduced to this paper by his friend, Sir William Miers of the British Museum and at once became intrigued (Fig. 3.13).

Ramsay, the previous year (1894) had discovered the new element, argon, with Lord Rayleigh (a.k.a. John William Strutt, 1842–1919) which directly paved the way to helium's terrestrial discovery. In September 1892, Lord Rayleigh had written in *Nature* asking for suggestions from readers as to why the density of nitrogen isolated from air was slightly higher that laboratory nitrogen derived from ammonia.⁴⁶ Ramsay took up the cause and immediately sought, through experimentation, to either find a heavier gas in the atmosphere or a lighter gas in the nitrogen derived from ammonia. Ramsay believed that due to periodic law, there was room for a gaseous element (or elements) at the end of the first column of the periodic table. His calculations led him to believe that the density of this gas(es) should be 20 (or 1/120th of nitrogen).⁴⁷ On April 23, 1894, Ramsay revealed in a letter to his wife that through his work with nitrogen, "it is quite possible that there is some inert gas in nitrogen which as escaped notice. …We may discover a new

⁴⁶ Sir William Ramsay, Sir W.A. Tilden, 1919, p. 125.

⁴⁷ Sir William Ramsay, Sir W.A. Tilden, 1919, p. 130.

element."⁴⁸ In a May 24 letter to Lord Rayleigh, Ramsay revealed the possible locations of any new gases (as denoted by asterisks).

Ramsay's method of isolating atmospheric nitrogen was by first removing the oxygen, water vapor, and carbon dioxide thus leaving relatively pure nitrogen. By using heated magnesium to absorb the nitrogen, any remaining residual gas should be revealed spectroscopically.

One month later, Ramsay revealed in a private letter to Lord Rayleigh that he believed he may have isolated this residual gas and by early August, he stated firmly, "I have isolated the gas." Initially, he identified this gas as "Q"⁴⁹ but the name *Argon* (Greek origin meaning "inactive") was quickly established. It was so named because of its inertness (i.e. it would not react with any other known substance). The story of Argon was publicly revealed on January 31, 1895 to the Royal Society.

Fresh off this incredible discovery of the first noble gas in 1894, Ramsay began to focus on Hillebrand's results after being introduced to his paper. Ramsay was immediately suspicious that the gas observed by Hillebrand was nitrogen and stated, "I was skeptical enough to doubt that any compound of nitrogen, when boiled with acid, would yield free nitrogen."⁵⁰ Thus, Ramsay quickly acquired another uranium-based mineral, clèveite, and upon treating the mineral in much the same fashion as his argon experiments, a residual gas was collected in vacuum-tubes for analysis. On March 24, 1895, Ramsay wrote to his wife:

Let's take the biggest piece of news first. I bottled the new gas in a vacuum tube, and arranged so that I could see its spectrum and that of argon in the same spectroscope at the same time. There is argon in the gas; but there was a magnificent yellow line, brilliantly bright, not coincident with but very close to the sodium yellow line. I was puzzled, but began to smell a rat. I told Crookes, and on Saturday morning when Harley, Shields and I were looking at the spectrum in the dark room a telegram came from Crookes. He had sent a copy here and I enclose that copy. You may wonder what it means. Helium is the name given to a line in the solar spectrum, known to belong to an element, but that element has hitherto been unknown on earth. Krypton was what I called the gas I gave Crookes, knowing the spectrum to point to something new. 587.49 is the wave-length of the brilliant line. It is quite overwhelming and beats argon.⁵¹

Immediately after observation, Ramsay believed he had discovered a new element which he very briefly named, Krypton. Later that evening a telegraph from William Crookes arrived identifying the wavelength of the new line. Crookes determined that it was, in fact, the D_3 line which had tormented Lockyer for years. At that moment, helium was known to exist on Earth.

⁴⁸ Sir William Ramsay, Sir W.A. Tilden, 1919, p. 129.

⁴⁹ Sir William Ramsay, Sir W.A. Tilden, 1919, p. 131.

⁵⁰ On a Gas showing the Spectrum of Helium, William Ramsay, Proceedings of the Royal Society of London, Vol. 58, April 25, 1895, p. 65.

⁵¹ Sir William Ramsay, Sir W.A. Tilden, 1918, pp. 136–137.

Helium Revealed

The first public account of the discovery of helium occurred on March 27, 1895 at the Annual Meeting of the Chemical Society in which the Faraday medal was being awarded to Lord Rayleigh. During the course of the proceedings, Ramsay was allowed to interrupt and reveal his discovery. In Ramsay's words, the discovery was revealed as follows:

In seeking a clue to the compounds of argon I was led to repeat experiments of Hillebrand on cleveite, which, as is well known, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen; its spectrum in a Plücker tube showed all the prominent argon lines, and in addition a brilliant line close to, but not coinciding with, the D lines of sodium. There are, moreover, a number of other lines, of which one in the green blue is especially prominent. Atmospheric argon shows, besides, three lines in the violet which are not to be seen, or if present, are excessively feeble in the spectrum of the gas from cleveite. This suggests that atmospheric argon contains, besides argon, some other gas which has as yet not been separated and which may possibly account for the anomalous position of argon in its numerical relations with other elements.

Not having a spectroscope with which accurate measurements could be made, I sent a tube of the gas to Mr. Crookes, who has identified the yellow line with that of the solar element to which the name 'helium' has been given. He has kindly undertaken to make an exhaustive study of its spectrum.

I have obtained a considerable quantity of this mixture and hope soon to be able to report concerning its properties. A determination of its density promises to be of great interest.⁵²

High off this phenomenal discovery, Ramsay quickly went to work attempting to discover helium in other minerals. Two days before the public revelation of helium's terrestrial existence, Ramsay had written to Professor Frank Wigglesworth Clarke (1847–1931, a colleague of Francis Hillebrand) of the United States Geological Survey in order to obtain a sample of the American uraninite,⁵³ which was forwarded to Hillebrand. Ramsay suspected, of course, that helium should be found in any sample of uraninite as well. Hillebrand, upon reading Ramsay's letter, replied expressing his remorse that he had not paid closer attention to the spectrum during his work with uraninite. Hillebrand was a relative novice to spectroscopic analysis and therefore placed little importance in his spectral observations. Hillebrand's response to Ramsay's letter addressed to Prof. Clarke April 4, 1895 (to Ramsay):

...and I finally came to the conclusion that the bright lines – since to the best of my recollection they were not constant or always the same in two or three samples of gas examined – were probably not due to any original constituent of it. For this reason I most unfortunately made no reference in my published paper to an unusual appearance of the spectrum, which I so much the more regret because I have thereby laid myself open to criticism on the score of careless observation.⁵⁴

⁵² <u>Sir William Ramsay</u>, Sir W.A. Tilden, 1919, pp. 137–138.

⁵³ Biographical Memoir of William Francis Hillebrand, Frank Wigglesworth Clarke, National Academy of Sciences, 1928, p. 56.

⁵⁴ Biographical Memoir of William Francis Hillebrand, Frank Wigglesworth Clarke, National Academy of Sciences, 1928, p. 58.

In this letter, Hillebrand also agreed to provide Ramsay with a sample of the uraninite mineral so that he could perform his own analysis of the mineral which Ramsay later proved to reveal the helium spectrum. Ramsay wasted no time analyzing many more minerals and quickly realized that helium was found in nearly all minerals that contain uranium.⁵⁵

Over the course of another month and continued research, Ramsay became uncertain as to whether helium (and argon) was a single element or rather a combination of elements. Spectral analysis made it difficult to determine, in the case of helium (and argon), if other lines in a spectral sequence were a fingerprint of a specific element or a compound of multiple elements. That is, because it was possible that another element could be present, without being able to isolate that element, there would be no way to know if the emission lines represented one or more elements. Ramsay had noted, however, that if they were indeed two *unique* gases, both helium and argon possessed similar properties. They appeared to be completely inert despite repeated efforts to produce some sort of reaction. In part due to Mendeleev's periodic system, Ramsay was able to speculate that both elements, *if* they were both unique single elements, probably belonged to the same natural group. Ramsay wrote:

Only one remark may be permitted on a speculative nature: the general similarity of helium to argon, and not being affected either by red hot magnesium or by sparking with oxygen in presence of potash, makes the inference probable that they belong to the same natural group. If the atomic weight of argon be 20, then, on subtracting 16, which is the average difference between the atomic weights of members of the first line, beginning with lithium and continued to fluorine, and the second line, beginning with sodium and ending with chlorine, the number four is obtained; and this closely approximates to the found density of helium, if that number is not too high.⁵⁶

More studies by many other scientists attempted to understand the properties of this newly discovered terrestrial element. By the autumn of 1895, many of these scientists believed that helium was not a single element but rather a mixture of two or more unknown gases. The reason for this belief was due to the current arrangements of some elements in the periodic system. Under this 1895 periodic arrangement, it was inferred that *several* elements existed between hydrogen (atomic weight of 1) and lithium (atomic weight of 7) of which helium (atomic weight of 4) was only one. Therefore, according to H.N. Stokes in his paper titled, *Helium and Argon*, published in Science magazine in October 1895, "...careful spectroscopic studies by Crookes, Lockyer, Runge, and Paschen, and others, have shown, however, that what we now call helium is not a single substance, but a mixture of two or more hitherto unknown gases."⁵⁷

⁵⁵ Biographical Memoir of William Francis Hillebrand, Frank Wigglesworth Clarke, National Academy of Sciences, 1928, p. 61.

⁵⁶ Helium, a Gaseous Constituent of certain Minerals, Part I, William Ramsay, Proceedings of the Royal Society of London, May 2, 1985, p. 88.

⁵⁷ Helium and Argon, H.N. Stokes, Science, Vol. 2, No. 43, October 25, 1895, p. 534.

Undeterred by the fact that helium may represent two or more elements, Ramsay, now joined by English Chemist, Morris William Travers (1872–1961), continued to pour himself into his studies where most focus turned to placing helium and argon on Mendeleev's periodic system. *If* Mendeleev's system was correct and *if* helium and argon were to be identified as individual elements, then Ramsay believed that another inert gas ought to be present between helium and argon. After repeated unsuccessful efforts to find this *predicted* element from any mineral or meteoric source, Ramsay returned his focus to argon. Ramsay soon discovered that argon, through diffusion, could be separated into a lighter and heavier portion, thus representing an impurity in argon.⁵⁸ In the early summer of 1898, two new *atmospheric* elements were discovered by William Ramsay and Morris Travers. A gas lighter than argon, named Neon (meaning "new") and one heavier gas named Krypton (meaning "hidden"). Shortly after this discovery, another element, Xenon (meaning "stranger"), was discovered by Ramsay and Travers, thus nearly completing the noble gas column in the current periodic table.⁵⁹

X-rays and Radioactivity

As the 19th century was drawing to a close, the pace of scientific progress was increasing dramatically. After helium's first detection in 1868 until the close of the century, eighteen new elements had been discovered including five out of the six noble gases. Just before the turn of the century, X-rays (discovered in 1895 by Wilhelm Conrad Röntgen), Radioactivity (1896 by Henri Becquerel), and the electron (1897 by J.J. Thomson) had been discovered. Each of these discoveries, building on the advancements of the previous discovery, would ultimately help demystify the strange new element called helium.

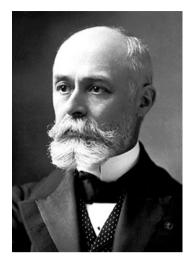
In early 1896, a French physicist had just learned of the newly discovered X-rays (a.k.a. Röntgen rays) being emitted from phosphorescent cathode tubes. Henri Becquerel (1852–1908) had for several years been attempting to understand the phenomenon of luminescence (phosphorescence⁶⁰) but was unable to form any conclusion until learning of the German physicist Wilhelm Röntgen's (1845–1923)

⁵⁸ William Ramsay, Benjamin Harrow, The Scientific Monthly, Vol. 9, No. 2, August 1919, p. 174.

⁵⁹ These three new gases were found through studies of normal ambient air while helium had not yet been found to exist in the atmosphere. C. Friedländer of Berlin and Professor H. Kayser of Bonn, were given credit for finally discovering helium's existence in the atmosphere in the Fall of 1898. Kayser was also given credit for discovering helium gas emitted from a spring in Wildbad in the Black Forest prior to his detection of helium in the atmosphere.

⁶⁰ A "phosphorescent" material is one that will immediately absorb light and will then *gradually* emit visible light. As the phosphorescent material absorbs light, the atoms within the material become excited, release this excited state of energy as visible light, and remain in this state until all of the atoms fall back into their normal state. An example of a phosphorescent material is a wristwatch with hour/minute hands that glow in the dark after being exposed to normal light.

Fig. 3.14 Henri Becquerel



discovery. Becquerel began to speculate that there could possibly be a relationship between phosphorescent minerals and the production of X-rays. That is, he believed that after a phosphorescent mineral when exposed to sunlight might release X-rays in its excited state of phosphorescence (Fig. 3.14).

Becquerel's method of experimentation was to place uranium salts on a photographic plate covered completely by black paper and then a thin sheet of copper placed in between the uranium and black paper. Although various minerals were tested, Becquerel had reported in late February 1896 to the French Academy that uranium salts, after exposure to sunlight, had emitted rays that had penetrated the copper and the black paper that enveloped the photographic plate. Unfortunately, this effect in itself was not terribly insightful because two scientists had already revealed, earlier that month, a similar experiment revealing the photographic effect of a phosphorescent material penetrating black paper.⁶¹

The real breakthrough for Becquerel would occur, oddly enough, because of his inability to work. During a day of overcast skies, Becquerel had placed the experiment inside a desk drawer and waited for a clear day to resume his studies. After four days Becquerel removed the plates that had been in complete darkness and developed one of them. To his complete surprise, the plate was completely black where the uranium and copper sheet had been placed. After several more experiments all showing the same result, Becquerel had shown that invisible rays were present in the uranium while not in a state of phosphorescence. Numerous experiments on these invisible rays would reveal that they were not X-rays as Becquerel had initially believed. Rather they were a new form of invisible radiation which became known as Becquerel rays.

Becquerel was able to conclude that phosphorescence had no bearing on the production of these new rays. Many of the uranium samples he studied had no phosphorescent properties, thus the effect noted must be due solely to the presence

⁶¹ The Early Years of Radioactivity, G.E.M. Jauncey, 1946, p. 227.

Fig. 3.15 Marie and Pierre Curie (creative commons)



of uranium; the uranium itself must be emitting this new radiation. Becquerel had discovered spontaneous radioactivity.

As soon as Becquerel had revealed these monumental discoveries, he appeared to have left the scene immediately after his last publication in May of 1896. It would not be until early 1898, when Marie and Pierre Curie, studying the ray emitting effects of various uranium compounds, would further explain the phenomena of *radioactivity*.⁶²

Before 1898, the element with the highest atomic weight known, uranium, was the only identified substance that possessed radioactive properties. Interestingly, from the time of Becquerel's discovery until early 1898, no one had bothered to test the element with the next highest atomic weight, thorium.⁶³ By mid April 1898, it was revealed by German chemist Gerhard Carl Schmidt (1865–1949) and Polish-French physicist and chemist Marie Skłodowska-Curie (1867–1934), independently, that thorium possessed radioactive properties as well. Repeating similar experiments with photographic plates, both thorium and uranium revealed the same results (Fig. 3.15).

⁶² The word radioactivity was coined by the Curies.

⁶³ The element between thorium and uranium, protactinium, wasn't discovered until 1910. It was predicted to exist much sooner by Mendeleev.

Marie Curie, along with her husband, French physicist Pierre Curie (1859– 1906) were quickly able to discover that the radioactivity of uranium and thorium was directly proportional to the amount of uranium and/or thorium in a compound. Through this observation, Marie and Pierre Curie were ultimately able to form the conclusion that their radioactivity was an atomic *property* of uranium and thorium. If this conclusion was correct, then they should be able to understand why other uranium-based minerals such as pitchblende were far more radioactive than what their uranium concentrations normally reveal. The Curies believed that another far more radioactive, and unknown, element must be present in pitchblende.

As predicted, the Curies had found a new radioactive element which they named Polonium on behalf of Marie's homeland of Poland; the results being revealed to the French Academy of July 18, 1898.⁶⁴ While still working with pitchblende, they were again able to discover another new element that was even more radioactive than polonium. Radium, which was discovered to be 900 times more radioactive than uranium, was revealed to the French Academy on December 26, 1898. The spectrum of radium introduced a new emission line in the ultraviolet whose wavelength was calculated to be 3,814.8 Å,⁶⁵ leaving little doubt of a newly discovered element.

The Curies, then, were able to conclude that radioactivity originates from the atom, and not activity between molecules. That is, radioactivity was an *atomic property* of the radioactive substance being studied. For their contributions of the phenomenon of radioactivity, Becquerel and the Curies were awarded the Nobel Prize in 1903.

Ernest Rutherford

The discovery of radioactivity proved to be the most significant contribution in unlocking the mysteries of helium. Although the origin of helium was unknown before the turn of the century, it was the advent of radioactivity and subsequent studies that led to its rapid explanation. Perhaps one of the most important discoveries of a property of helium was discovered by a New Zealand physicist, Ernest Rutherford (1871–1937), considered by many to be the father of quantum physics (Fig. 3.16).

In January 1899, while other scientists were trying to find more radioactive substances, Ernest Rutherford had turned his attention to the actual radiations of radioactive substances. By studying the radiations after layering successive sheets of aluminum over a uranium compound, he quickly discovered that the Becquerel

⁶⁴ Although the results of Polonium's discovery were revealed at the French Academy in July 1898, there was still some doubt as to its existence. The amount of Polonium collected was so minute that it could not reveal a unique emission line spectrum. In addition, radioactivity was still a very new and unknown phenomenon.

⁶⁵ The Early Years of Radioactivity, G.E.M. Jauncey, 1946, p. 231.

Fig. 3.16 Ernest Rutherford (U.S. Library of Congress)



rays were actually composed of two differing rays. Addressing this discovery during his acceptance of the Nobel Prize in Chemistry (1908), Rutherford stated:

These experiments show that uranium, radiation is complex and that there are present at least two distinct types of radiation – one that is very readily absorbed, which will be termed for convenience the α -radiation, and the other of a more penetrative character, which will be termed the β -radiation. When other radioactive substances were discovered, it was seen that the types of radiation present were analogous to the β - and α -rays of uranium and when a still more penetrating type of radiation from radium was discovered by Villard, the term γ -rays applied to them.

 $(\alpha = alpha, \beta = beta, and \gamma = gamma)$

Rutherford was quickly able to determine that Becquerel rays emitted from uranium consisted of two forms of radiation, with the main difference being in their penetrating powers. In order to differentiate between the two, he named them α -radiation (alpha) and β -radiation (beta). Rutherford was awarded the Nobel Prize in chemistry (despite the fact that Rutherford was a physicist) in 1908 for his extensive work ushering in the new scientific field of radiochemistry.

After this discovery, many scientists had begun to focus on the beta particle (beta particles are electrons) because of its penetrating power. A biographer of Rutherford in 1940⁶⁶ noted that popular interest in particle radiation was directly proportional to its penetrating powers thus little attention was placed on the lowly alpha particle. The alpha particle, once expelled from a radioactive nucleus could only travel 2 or 3 cm in air before it would come to a stop. As the particle was ejected from the nucleus of the radioactive atom (uranium in this case), it ionized everything in its path stripping electrons from other matter until it finally came to a halt. A piece of paper would be perfectly adequate in stopping an alpha particle. Nevertheless, Rutherford chose to focus on this particle not because of any

⁶⁶ Lord Rutherford, Norman Feather, 1940.

particular property of the particle but rather to understand the nature of the atom from which it was expelled. His devotion to the alpha particle would later change the way we would view the atom forever.

Between the years 1900 and 1903, Rutherford and English chemist, Frederick Soddy (1877–1956) had discovered that radioactivity was the result of the spontaneous disintegration of a radioactive, unstable atom. That is, the atom of a radioactive element would literally transform itself into another lighter element while emitting a particle and giving off energy (heat) in the process. In other words, alchemy was finally a reality.

Rutherford had noticed that helium was always present when working with emanations from uranium or thorium. At first, he believed that helium was the ultimate product of the elements transformation because of its continued presence. After extensive research, Rutherford began to believe that the alpha particle, which was positively charged, was actually the nucleus of the helium atom. The mere weight of the alpha particle was essentially the same as helium.

Further studies involving collection of alpha particles in glass emanated from radon showed that the spectrum of helium would eventually appear as alpha particles were accumulating. In his Nobel Prize acceptance speech in 1908 titled, *The Chemical Nature of the Alpha Particles from Radioactive Substances*, the 37 year old Rutherford ended his speech by saying:

Considering the evidence together, we conclude that the α - particle is a projected atom of helium, which has, or in some way during its flight acquires, two unit charges of positive electricity. It is somewhat unexpected that the atom of a monatomic gas like helium should carry a double charge. It must not however be forgotten that the α -particle is released at a high speed as a result of an intense atomic explosion, and plunges through the molecules of matter in its path. Such conditions are exceptionably favourable to the release of loosely attached electrons from the atomic system. If the α -particle can lose two electrons in this way, the double positive charge is explained.

The next year (1909), German physicist Hans Geiger (1882–1945) and English-New Zealand physicist Ernest Marsden (1889–1970), under the tutelage of Rutherford, had discovered using the famous "gold-foil experiment"⁶⁷ that alpha particles could be deflected back in the same direction from which they were emitted. Although this may appear to be an unusual and meaningless discovery to the non-scientist, it was a discovery of monumental proportions. Prior to this discovery, the common model of the atom was then known as the Plum Pudding model (coined by English physicist Joseph John "J.J." Thomson (1856–1940), where the entire atom consisted of a positive charge which housed the negatively charged electrons, much like plumbs in a pie. Under this model of the atom, any alpha particles focused on the atoms should easily pass through with little or no deflection. This is precisely what Rutherford had expected.

The mere fact that a large alpha particle could be "deflected" back was best explained by Geiger who said, "it was quite the most incredible event that has

⁶⁷ Also, known as the Geiger-Marsden experiments. For an active demonstration of this gold-foil experiment, see: http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/ruther14.swf.

ever happened to me. It was almost as incredible as if you fired a 15-in. shell at a piece of tissue paper and it came back and hit you."⁶⁸ This phenomenon meant that as an alpha particle was shot through matter (gold foil in this case), some particles scored a direct hit on the "nucleus" of a gold atom and by repulsion was expelled back in the direction from whence it came. Those particles that were deflected marginally came close enough to the nucleus that repulsion skewed its trajectory.

These findings led Rutherford to propose a new model of the atom in 1911 which came to be known as the Rutherford Atom. Because some alpha particles (about 1 in 8,000) would be completely deflected back towards the source, there must be a compact mass of positive charge in the center of the atom. In other words, a "nucleus" of positive charge which was so tightly packed that it could send an alpha particle backwards. In the plumb pudding model, the positive charge was supposed to be so spread out that alpha particles should easily pass through unaffected. Rutherford became convinced that the atom consisted of a tiny nucleus that contained most of the mass surrounded by a "cloud" of negatively charged orbiting electrons. In order to put things into perspective, the radius of an atom is about 20,000 times greater than the radius of the nucleus. On March 7, 1911 Rutherford reported his experimentation titled, *The Scattering of the Alpha and Beta Rays and the Structure of the Atom.* Rutherford wrote:

It is well known that the alpha and beta particles are deflected from their rectilinear path by encounters with the atoms of matter...There seems to be no doubt that these swiftly moving particles actually pass through the atomic system, and the deflexions observed should throw light on the electrical structure of the atom...Geiger and Marsden found that a small fraction of α particles incident on a thin foil of gold suffers a deflexion of more than 90-degrees...It seems certain that these large deviations of the α particle are produced by a single atomic encounter...A simple calculation shows that the atom must be the seat of an intense electric field in order to produce such a large deflexion at a single encounter. Considering the evidence as a whole, it seems simplest to suppose that the atom contains a central charge distributed through a very small volume...In comparing the theory outlined in this paper with the experimental results, it has been supposed that the atom consists of a central charge concentrated on a point.⁶⁹

Thus, todays understanding of atomic structures were only understood because of experiments with helium nuclei. Further, it became clear that helium was "produced" here on Earth due to the radioactive decay of the heavy natural elements, uranium and thorium. These heavy elements, although somewhat rare, are the only source for the helium that we see today in all of its various applications. Chapter 4 will talk about how and why helium is produced here on Earth and how it can accumulate in commercial reservoirs for extraction.

⁶⁸ <u>Radioactivity: Introduction and History</u>, Michael F. L'Annunziata, Elsevier, 2007, p. 61.

⁶⁹ The scattering of the alpha and beta rays and the structure of the atom. *Manchester Lit. and Phil. Soc., Mem.*, IV:**55**: March 1911, pp. 18–20.

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Chapter 4 Helium on Earth

Back to the Stars

We just learned in Chap. 3 that terrestrial helium (rather, the nucleus of the helium atom, or alpha particle) is derived from the radioactive decay of uranium and thorium and can be found in minerals which house these heavy elements. Where did this uranium and thorium come from? Where can we find it in the Earth? The answer to these questions takes us back to the cosmos and a continuing discussion about stars and later to the formation of the Earth.

We learned in Chap. 2 the fate of most stars in the Universe. That is, although our Sun is considered very average with regards to its mass (size), most stars simply fade away into existence after their long stellar lives. Only in very rare events in massive stars do they undergo what is known as a supernova which was touched on very briefly at the end of Chap. 2. In most stars, elemental production via fusion stops after the production of iron in the core. There are many types of stars varying in size and mass which are discussed in volumes of books but for our purposes, we will focus on the very rare event of a supernova which is the mechanism by which all of the natural elements beyond iron are formed. Uranium and thorium, which we discussed in the last chapter were created from supernovas, or the phenomenal explosion of a massive star.

What is a supernova and how is uranium and thorium created? The lifetimes of super-massive stars are, relatively speaking, much shorter than our own Sun. This tends to make logical sense because larger stars need to burn more fuel in order to support its massive size. An industrial blast furnace, for example, must burn far more fuel than a household oven to keep it in operation. Due to their larger sizes, however, they have more mass to compress the core in order to burn each sequential element produced from the previous fusion process. For instance, in a massive star, after the hydrogen in the core has fused into helium, there is still plenty of mass to compress the core to escalate the temperatures in order to begin the fusion

of helium. After the helium fuel is spent, the extra mass allows the core to contract thereby starting the fusion of carbon, and so on and so forth. In very large stars, this process can continue all the way up to iron as mentioned in Chap. 2.

When massive stars have burned each sequential product after hydrogen, the core of a star is filled with the last remaining product, iron (and unstable nickel). Iron is the most stable element in the periodic table; its nucleus is extremely compact. Because of this, there is not enough energy available, no matter how large the star, to begin the fusion of iron into heavier elements. Thus, when iron fills the core of a massive star, the furnace effectively stops.

This is not the end of the line, however, for massive stars. When the nuclear reactions cease due to inability of iron to fuse, its primary foundation of energy production from fusion is eliminated making the inward pull of gravity very strong. Let us use our Sun as an example to demonstrate the inward pull of gravity. Our Sun is considered to be in hydrostatic equilibrium. That is, the inward pull of gravity is precisely the same as the pressure created from the energy created in the core. This is the reason why the Sun can neither explode nor collapse. So, when a massive star loses the furnace in the core, there is nothing to stop the inward gravitational pull so the star literally implodes.

As gravity pulls the massive star inward, the core temperature rises to around 10 billion Kelvin (still not high enough to fuse iron) and the iron in the core begins to break up into lighter nuclei (and the lighter nuclei break up to even smaller nuclei) because they are bombarded with high energy photons. After which, all that is left are the elementary products of protons and neutrons. This process is known as Photodisintegration and it absorbs much of the energy from the core making it cooler. At this point, the core becomes even more unstable due to its lower temperatures and the implosion process accelerates dramatically.

Although there are other steps in the implosion process which are beyond the scope of this book, the end result is a rapidly imploding star whose core is filled with only neutrons which are extremely compacted and under a great deal of pressure. The density of these neutrons halts the implosion process because of the pressure they exert on the inward collapse. This rapid halt of the collapse is still not the end, however. At the halting stage, the core is far beyond the point of equilibrium, causing the core to bounce back, creating massive shock waves, in enormous fashion. The shock waves move completely through the outer layers of the star at very high speeds blowing apart the star in an event unparalleled in the cosmic realm. The explosion of a supernova produces as much light as an entire galaxy which itself contains hundreds of billions of stars.

It is in the moment immediately after a supernova where the heaviest of elements are produced. You may recall at the end of Chap. 2 the discussion about neutron capture which is a *fission* process, specifically the s-process that created all the elements up to Bismuth (specifically the isotope, Bismuth-209). Due to the lower speed of the s-process, many isotopes decay prior to the entry of another available neutron. This process stops with Bismuth because the rate of neutron bombardment is too slow to keep up with faster decaying isotopes after Bismuth.

The heavier elements beyond Bismuth are also created by neutron capture but this time they are created by the r-process (r means rapid). In the unfathomable severe conditions after a supernova explosion, neutrons are everywhere plugging themselves into the nuclei of atoms at very high rates of speed. They are bombarding these nuclei so fast that the affected isotope doesn't have time to decay before it absorbs another neutron. Ultimately, these very heavy isotopes decay and this is the origin of all of the elements after Bismuth. It should be noted that because a supernova is an extremely rare event, the elements (isotopes) produced in this r-process are rare as well.

If we look at the composition of our Earth, the most common elements in our planet are (in order) iron, oxygen, silicon, magnesium, sulfur, nickel, calcium, and aluminum. Together these elements constitute nearly 99 % of our planet. Interestingly, these elements are very common in the cosmos because they are created with great regularity in the fusion process in stars. Each of these elements come *before* and up to iron in the periodic table. The elements *after* Iron and up to Bismuth are much rarer because they are only synthesized in massive stars which are less abundant. Lastly, the elements after Bismuth and up to Uranium are rarer still because of the rare event of a supernova. A supernova spreads all of these new elements into space where they can ultimately be picked up, for instance, in solar systems much like our own.

To recap, all of the elements, besides hydrogen, up to iron are created by *fusion*. All of the elements after iron are created via *fission*. Recall that fusion is the combination of two nuclei while fission is the breaking apart of nuclei into smaller components. It should be noted here that our own Sun, which is a very average-sized star, will cease to exist after the production of oxygen. It will never go supernova and will not reach the iron burning phase found in larger stars. Afterwards, the nuclear furnace will shut down where it will ultimately fade away as will all the light in our solar system.

Back to the Earth

Now that we know where all of the elements are created and how, we can now begin our topic of helium generation in the Earth. First, however, it is important to learn a few things about how and why uranium and thorium are present and why helium is able to be harnessed at all.

Our solar system is about 4.6 billion years old, and as you recall is about the age of our Sun. Our Earth was formed from the debris and dust called the primitive solar nebula that revolved around the young Sun. The *Terrestrial* (or, Earthlike) planets are the four planets closest to the Sun (Mercury, Venus, Earth, and Mars). The larger *Jovian* planets (Jupiter, Saturn, Uranus, and Neptune) have no hard surface and are made exclusively of gas. All of the planets in our solar system (and other planets revolving around other stars) formed from gas and dust debris which consist, of course of principally hydrogen and helium but also smaller amounts of the heavier elements. Over time, the gas and dust debris gravitationally clump into clusters as they are spinning and orbiting around the Sun. These clusters go on to form smaller planetesimals which ultimately merge creating larger planets over time. Our Earth was no different, as it was formed from cosmic dust, meteorites, etc. that just happened to be close enough to find its way to the Earth's surface. Heavier materials found their way closer to the center of the solar system while the lighter gases were pulled further out, hence the reason why the "rocky" planets are near the Sun and the gaseous planets are beyond the rocky planets.

Without delving too deeply into accretionary processes, the end result of accretion in our planet resulted in the formation of a layered Earth. That is, if we were to slice the Earth in half, in the center would reside a solid inner core which is comprised primarily of heavy iron and nickel, which are relatively abundant in the Universe. This inner core is surrounded by a liquid outer core which also contains iron and nickel but also has a component of a lighter element(s) such as oxygen and/or sulfur which readily react with both iron and nickel. As the Earth rotates in its orbit, the liquid outer core also rotates and is responsible for forming Earth's magnetic field via a dynamo effect.¹ This magnetic field is extremely important on our planet as it prohibits stellar particles from entering our atmosphere which would be fatal for animal life on Earth if exposed. Surrounding the liquid outer core is the mantle which can be further divided into an upper and lower mantle. Mantle composition will be discussed in a moment but it exists as a ductile solid and is the driving force behind plate tectonics. Finally, surrounding the mantle is a very small fragile shell called the Crust which is where life takes place. In the very hot and magmatic early period of our Earth, the heavier and dense metals sunk to the bottom (center) of the Earth while the lighter elements floated to the surface.

The mantle is roughly 3,000 km thick and represents about 80 % of the planets bulk volume. The composition of the mantle is much different from the underlying core in that it is composed primarily of extremely dense "rock" consisting primarily of oxygen (~45 %), magnesium (~23 %), and silicon (21.5 %)-based minerals. After the Earth's accretion and prior to crustal formation, the Earth was a very hot and inhospitable place represented by magma oceans. The heat generated for this condition was primarily derived from two main factors such as heat formed during accretion (impacting of materials on the Earth results in enormous heat and this heat remains trapped in the core and mantle) and the presence of radioactive elements like uranium, thorium, and potassium.

In the early Earth the radioactive elements, although present in smaller quantities compared to lighter elements, were plentiful enough to create enormous heat. In addition, 4.6 billion years ago, there was twice as much heavy radioactive element inventory available than today. For example, uranium-238 (the most abundant uranium isotope) has a half-life of 4.5 billion years (roughly the same age as the earth itself). This means that after 4.5 billion years, half of that uranium that existed since the beginning of Earth has decayed into lighter elements while producing heat as a by-product. More will be discussed about radioactive heat later.

¹ The core of the Earth is too hot to be magnetic. All magnetic materials lose magnetism with the presence of heat. Our Earths magnetism is created as a result of this liquid metal movement which creates a dynamo.

Nevertheless, as the Earth began to cool, a crust formed from mantle material. This crust is far less dense than the underlying mantle thus allowing it to essentially "float". The primary composition of the crust is silicon, aluminum, and oxygen-based minerals which make up a quite loosely named, granite. Of course, granite can be composed of a variety of minerals but for the purposes of naming a basement rock (basement rock inferring rock below sedimentary rock) that is composed primarily of silicon dioxide, SiO₂ (~66 % composition in upper continental crust) and aluminum oxide, AlO₂ (~15 % in upper crust) will be referred to as "granite." This granite makes up a very thin veneer of the Earth's radius (much like the top thin and dry layer of an onion) and constitutes only 0.6 % of the Earths total mass. It is this rock which all of the sediments lie upon across the planet. In geological terms, this can be referred to as "basement" rock.

With regards to helium *production*, the primary source of helium in the Earth is the crust. The Earth's crust can be further divided into upper and lower and even further by oceanic and continental crust. The oceanic crust is newly formed mantlederived crust as is evidenced by mid-ocean ridge spreading where molten material derived from the mantle creates new crust. The oceanic crust and mid-ocean ridges are extremely important when studying helium's other isotope, helium-3, but for normal helium production, it is not a commercial source for helium-4. The continental crust, on the other hand, is much older material which and is responsible for housing the elements and minerals which we use on a daily basis. More importantly, for helium production, the crust (in particular the upper crust) is enriched with the radioactive elements uranium, thorium, and potassium which are responsible for much of the heat produced on the planet outside of that generated from the core.

Helium Generation

Uranium, thorium, and potassium, like many other heavier elements, are highly incompatible and thus are very mobile. That is, they prefer to form chemical compounds in environments where they have more stability. Uranium and thorium, in particular, are classified as "lithophile"² elements meaning they have an affinity for silicates and oxygen more commonly found in the crust and will actually remain mobile until it finds these companion elements located primarily in the crust. Because the crust is enriched in both silicon and oxygen, uranium and thorium "want" to fractionate out of the mantle and attach to crustal material as they are being recycled upwards in the mantle during convection or via volcanic activity. After uranium and thorium fractionated out of the mantle and into the crust, chemistry took over where these elements would remain mobile enough until they could

 $^{^2}$ The name "lithophile" was coined in the 1930s by Victor Goldschmidt (1888–1947). The term lithophile literally means "rock-loving". Thus, the lithophile elements are generally found in the rocky crustal rock rather than the iron-rich mantle and core.

find silicon and oxygen atoms to bond with. As uranium and thorium made their way into the crust, some areas would have the opportunity to become more enriched than others due to ease of transportation of uranium and thorium atoms. For instance, deep ground waters could provide one source of mobility and allow enrichment in specific areas over others. Over the history of the Earth, the mantle became largely depleted of volatile elements such as uranium and thorium and subsequent geological processes concentrated these elements (in compounds) in the upper crust.

The importance of uranium, thorium, and also potassium in the crust cannot be overstated. As each of these elements (in particular the isotopes: uranium-238, uranium-235, thorium-232, and potassium-40) are responsible for the majority of the Earth's crustal heat. Of these isotopes, uranium-238 is the primary heat engine due to its relative abundance while thorium-232 comes in a close second. The uranium-235 isotope is rare but is the isotope used for fission in nuclear warheads and reactors. Both uranium and thorium isotopes decay through a process known as alpha decay and each isotope eventually becomes a stable lead isotope at the end of its decay chain. It is this alpha decay process which is responsible for all helium generation and accumulation on Earth. The potassium-40 decay cycle, which is also a large contributor of crustal heat, decays through a process known as beta decay which is far less heat generative than alpha decay. However, potassium is concentrated in the percentage range representing the seventh most abundant element in the crust and due to this abundance it is a significant contributor of heat. Uranium and thorium, on the other hand, are only concentrated in the *parts per million* (ppm) range. Thorium is ranked 39th in elemental abundance in the Earth's crust while uranium is 51st (Fig. 4.1).

As a general rule of thumb, the concentration of the radioactive isotopes listed above (uranium, thorium, and potassium) decrease exponentially with depth. That is, they are much more abundant in the upper crust than the lower. As stated before, their abundance in the upper crust is primarily caused by their affinities to

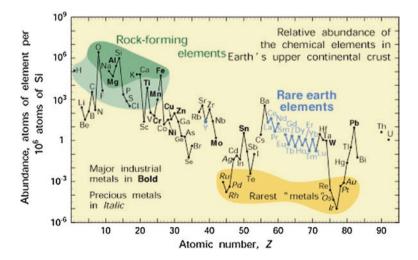


Fig. 4.1 Elemental abundances in upper crust (USGS)

the presence of silica and oxygen-rich minerals in which these isotopes are chemically attracted. Its concentration in the upper crust is very important otherwise we would have far fewer known helium reserves.

The presence of these radioactive isotopes, as mentioned, is responsible for producing a large portion of the heat generated from the Earth. In the case of the uranium and thorium isotopes, as these isotopes decay, an alpha particle (two protons and two neutrons) is ejected from the nucleus of the parent. The alpha particle, which is nothing more than the nucleus of a helium atom, is a very large particle as atomic particles are concerned. Most subatomic particles are very small (i.e. beta particles which are high-energy electrons) in size yet some produce much more energy in the form of electromagnetic radiation (such as gamma ray radiation). There are, of course, many more particles but the alpha particle derived from the uranium and thorium isotopes is by far the largest in size. As a particle this size is ejected from the parent nucleus, heat is generated both by the kinetic energy of the projected large alpha particle and the recoil of the parent nucleus. It is this heat, coupled with the heat generation from the fission reaction itself,³ which is responsible for a large portion of Earth-generated heat.

During the uranium and thorium decay cycles which produce heat, many alpha particles (helium nuclei) are expelled over the long half-life of the parent nucleus *and* the shorter half-lives of its daughter isotopes. When an alpha particle is ejected from the nucleus of its parent, it travels quickly and ionizes everything in its path until it slows to the point where it picks up two free electrons to form a helium atom. The distance traveled by an alpha particle is only 1–2 cms in air which is why they are relatively harmless to life on earth. Other particles such as beta and gamma radiation can pose health problems because of their penetration rates. An alpha particle, on the other hand, can be stopped by a thin sheet of paper.

Over the course of the Earth's 4.6 billion year history, helium has been produced by this radioactive decay cycle. Prior to crustal formation, much of this helium produced would have been able to escape into the early atmosphere and ultimately into space (helium is light enough to escape the Earth's gravitational pull). When the crust began to form from mantle material, however, some helium produced was able to remain entombed in granitic crystal lattices and unable to escape. Although much helium has been able to escape through fractures and find its way into the atmosphere, more has been produced and remained in the crust than has been expelled. It is interesting to note that the helium present in our atmosphere is solely a result of helium allowed to escape up through the sedimentary column, through the soil, and into the air. The air in which we breathe, although containing a very small 0.0006 % helium, is an enormous helium reserve but the concentration is too small to warrant economic extraction (the power required to extract this helium would be extreme).

All of the helium which we use today from MRI machines all the way down to toy balloons is derived from the radioactive decay of the uranium and thorium

³ Recall that when mass is lost, energy is released.

isotopes mentioned above. Each isotopes decay cycle has been producing helium since the formation of our planet and will continue to produce until it runs out. When this uranium and thorium runs out as stipulated by the length of their halflives, an important heat engine of the Earth will cease to exist resulting in a vastly different Earth. Fortunately for life on Earth, the half-lives of these isotopes are so long that we have a few billion more years to work with.

The helium produced from these decay cycles are highlighted below. Although their production rates are rather small from a single thorium or uranium isotope, over the course of several billion years and due to the relative abundance of these isotopes in the crust, the helium produced became significant. Uranium and thorium are both "not highly" radioactive by themselves, relatively speaking. That is, although they are radioactive and unstable, their extremely long half-lives make them much less radioactive than say, radium which has a far shorter half-life making it extremely dangerous to health. For instance, it was Marie Curies work with and exposure to radium that ultimately caused leukemia which took her life in 1920. The most common radium isotope, radium-226 has a half-life of 1,601 years. The half-lives of uranium and thorium are shown on page....

It is this lengthy half-life of uranium and thorium which has led to the accumulation of helium in specific reservoirs allowing for sequestration. A good example of helium production from these isotopes is best described by Dr. Mike Reimer (formerly of the USGS):

Several helium-4 atoms are produced from each decay series of U-238, U-235, and Th-232. One gram of uranium will produce $\sim 10^5$ atoms of helium-4 per second, and one gram of thorium produces $\sim 2.5 \times 104$ atoms of helium per second. Calculations of the helium produced from the crust and mantle reveal that $1,125 \times 10^{30}$ atoms per year are produced, but only 7×10^{30} atoms per year escape from the earth (Damon and Kulp 1958). More is being produced than is being lost; in fact, the total atmospheric content of helium could be produced in only 2 million years (MacDonald 1963). However, all the crustal and mantle helium-4 does not degas into the atmosphere as it is formed. It is trapped in crystal lattices and in pore spaces within the earth. What this means is that there is excess helium-4 in the earth—excess, that is, compared to the atmospheric concentration in equilibrium with the helium-4 escape rate into space and the helium-4 flux from the crust and mantle (Nicolet 1957). Near-surface pockets of high helium-4 concentrations are known, and some natural gas fields are so enriched that they are the source for commercial production of helium.⁴

The point that needs to be made is that plenty of helium is being produced in the Earth and some has been accumulating in certain reservoirs since the crust formed.

Helium Migration and Accumulation

As previously noted, helium generation has been going on for billions of years in the Earth's continental crust and still continues today. The upper continental crust is enriched in many incompatible elements such as uranium and thorium where

⁴ Helium detection as a guide for uranium exploration, open-file report 76–240, G.M Reimer, 1976.

chemistry ultimately paves the way for these minerals' ultimate resting place in the upper crust. Both uranium and thorium exist in basement rock (and sedimentary rock) on each continent on the globe and have been producing helium since the continental plates were formed. A legitimate question arises then: because helium is produced in crustal material across the planet, why are there only a few places on Earth where helium exists in relative abundance to warrant extraction?

Helium generation occurs everywhere in crustal rock but commercial sources of helium are found in areas where uranium or thorium are somewhat enriched in the crust or where it has a greater chance of emitting alpha particles that have the ability to enter sedimentary rock. The next steps involved for the accumulation of any helium, however, require two more geological steps. If just one of these next steps does not take place, then no helium will accumulate in a natural gas reservoir where it can ultimately be extracted.

Much of the helium that has been produced has been stored in the granites from which it was born. The crystal lattices in many granites are so tight that not even a helium atom can escape⁵ thus resulting in a massive inventory of helium left deep within the Earth. Most of this helium, however, resides in the upper continental crust where the uranium and thorium are located. In order for any significant quantities of helium to escape, it must be expelled from the granites from which it forms. A fracture or fault can cause helium atoms to be released from where they are trapped. A great example of this occurred in 2014 in Yellowstone National Park (Wyoming, U.S.A.) when massive quantities of helium, enough to fill a Goodyear Blimp every week, were found seeping out of geysers in the park. The reason for this phenomenon was due to a crustal disturbance which allowed for the release of enormous amounts of previously trapped helium.

When helium is produced, the alpha particle, as it is ejected, can create a micro fissure (crack) both through the kinetic energy produced by the ejected particle and from recoil of the parent nucleus. This, in effect, can begin to produce an area for more helium atoms to reside and become trapped. The major event, however, that causes the helium to be released into the sedimentary rock above is due to deep, basement faults where the brittle, granitic rock can become so fractured as to cause enormous quantities of helium atoms to escape and to create a new path for commercial deposits of helium to form.

Many geological events can be responsible for creating such a deep-seated fault but the root cause is plate-tectonics. Plate movements are responsible for contorting basement and sedimentary rock through compression and contraction. These geological events cause both stratigraphic and structural traps in sedimentary rock where hydrocarbon exploration can occur. Many of these geological events manifest themselves into only sedimentary features which are more easily malleable than the underlying, brittle basement rock. However, some of these sedimentary features are indicative of a deep-seated fault or uplift which has created very deep and extensive faults into the basement rock.

⁵ The use of helium in mineral exploration, Willy Dyck, Geological Survey of Canada, Ottowa, Ont., Journal of Geochemical Exploration, 5 (1976), p. 4.

In the United States, the areas which are high in helium are very close in proximity to areas of deep basement activity. For instance, in Kansas, the highest helium concentrations in the State occur on a geological event known as the Central Kansas Uplift which is a deep-seated basement uplift which has created enough fracturing to the point where enormous amounts of helium have been able to become expelled from the deep, granitic rock. The highest helium concentrations in this area occur nearest the fault plane and decrease in composition as the distance from the fault increases.

One of the best examples of high helium percentages associated with deep faults was provided by A.P. Pierce, G.B. Scott, and J.W. Mytton in their publication titled, *Uranium and Helium in the Panhandle Gas Field Texas, and Adjacent Areas*, published in 1964 (see diagram below⁶). In this publication, the authors created a cross section of helium percentages in a gas stream starting from the Amarillo-Wichita Uplift (a deep tectonic event located near the U.S. Government's Cliffside Field Helium Storage Facility north of Amarillo, Texas) and traversing away from this fault in a WSW-ENE-direction (Fig. 4.2a, b). The helium concentrations are clearly higher on top of the deep fault and become progressively smaller as you move away from this fault. This provides the most compelling evidence that helium concentrations are related to deep basement faulting where helium is able to escape and become trapped. Interestingly, and as will be explained later, the correlation between nitrogen and high helium concentrations reveal a clear trend in this study.

Another example is the Four Corners region of New Mexico, Arizona, Utah, and Colorado where very large helium concentrations are known to exist. This area was once a very active volcanic region resulting in communication from the mantle to the crust. The volcanic activity in this area has created dikes and sills deep within the basement rock creating both tensional and thermal fractures which provided another conduit for helium's passage into the overlying sediments. The presence of excessive mantle-derived heat into the crust could allow for significant expulsion of helium gas into the overlying sediments.⁷ In addition to volcanic activity, the highest helium concentrations take place nearest the regional geological event known as the Defiance Uplift. M. Dane Picard highlighted this highhelium percentage nearest the uplift in a 1964 study. It is possible that this uplift coupled with volcanic activity allowed for the passage of much more helium out of the basement resulting in much higher helium concentrations.

Of course, these are only a few examples of geological events causing helium migration but the key concept is deep faulting either caused by deep uplifting and/ or volcanic activity is the primary cause for helium to become liberated from its deep trap. Geological events like this occur all over the world and it is likely that large amounts of helium have been expelled from the upper crust and into the

⁶ *Source* Uranium and helium in the Panhandle Gas Field Texas, and adjacent areas, by A.P. Pierce, G.B. Gott, and J.W. Mytton, Geological Survey Professional Paper 454-G, United States Government Printing Office, Washington, 1964, pp. G51–G52.

⁷ Elements of Petroleum Geology, R.C. Selley, 1998, p. 18.

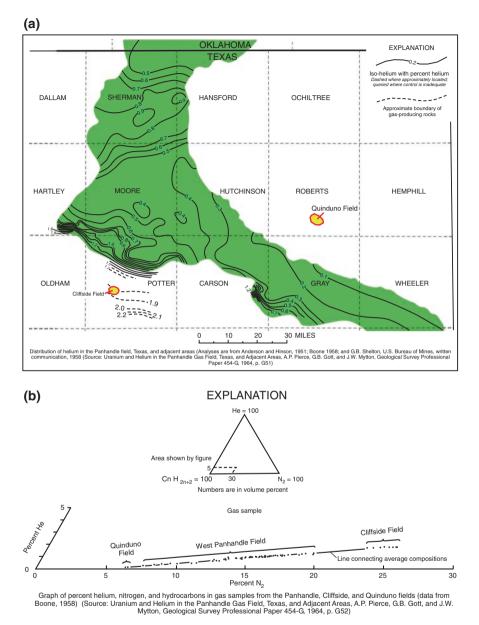


Fig. 4.2 A distribution of helium in the panhandle field

sediments in significant quantities. However, one more geological event must transpire before any helium can accumulate: a trap.

A geological trap or seal strong enough to hold a helium atom is a relatively rare occurrence and is the primary reason why there are only certain parts of the world where helium is able to accumulate. The helium atom is very small (0.02 nm in diameter) and is very capable of escaping the smallest of pore spaces which makes it the ideal gas for leak detection. Due to its extreme mobility and small size, helium is not easily trapped in the sedimentary rock because all rock has some pore space. Some rocks, however, like anhydrite and/or salt and tight shales are sometimes so tightly packed and non-permeable that helium can accumulate in the underlying strata with other gases. It is only due to this type of trap why helium does not exist in larger concentrations (i.e. high percentages of helium in the overall gas composition) in other parts of the world. This is not to say that there are no more large helium reservoirs, there most certainly are. The reason why they have not been found yet, however, is because they have not been drilled. Indeed, virtually all of the helium-rich resources in the United States (the primary country for helium-rich reservoirs) were found rather serendipitously in the search for hydrocarbons (oil and/or natural gas).

Helium generation, migration, and entrapment must all be present for any helium deposit worthy of economic significance to be extracted. Another question arises, however, when considering differing percentage concentrations of helium in various parts of the world. For instance, why is there roughly 8 % helium in natural gases in the Four Corners region of the United States while only 0.6 % helium in natural gas reservoirs in Wyoming? Or for that matter, why is there less than 0.2 % helium in natural gases produced in Qatar and 0.04 % in Algeria?

These questions, although not simple to answer, are due to the relative absence of one or more of the geological events mentioned above. That is, in a gas stream with only 0.6 % helium, there might be less uranium and thorium in the basement rock, the seal might allow more seepage, or fewer conduits may exist for helium to migrate out of the upper continental crust. It is quite possible for helium to accumulate in smaller percentages if only a portion of the stringent requirements of helium generation, migration, and accumulation occur.

In the case of some of the highest helium concentrations in the world such as the Four Corners region of New Mexico and Arizona, nearly all of the requirements for helium accumulation to occur exist. Anywhere where the gas stream contains higher than $\sim 2\%$ helium, nearly all conditions mentioned above are met because helium is able to accumulate enough to displace some of the host gas and remained trapped.

Helium Association with Nitrogen

Since helium was first discovered in natural gas in Kansas, it was quickly observed through the analysis of subsequent gases that helium was always found with nitrogen. The early studies revealed that as helium concentrations in a gas reservoir rose, so too did their nitrogen composition, thus lowering the heating value British Thermal Units (Btu) of the natural gas. However, it also became evident that high nitrogen gas wells did not always imply a high helium percentage. Through a broad early investigation of many gases across the United States, it was realized that there was a correlation between helium and nitrogen.

Helium is always found with nitrogen. Although the correlation between helium and nitrogen is stronger is areas like Texas, Oklahoma, Colorado, and Kansas, it still exists in the helium-rich gases (albeit in small volumes) of the Four Corners region of the United States where carbon dioxide is the primary host gas. More will be discussed about the carbon dioxide in this gas later.

The reason for helium's association with nitrogen is not known with absolute certainty but we can speculate that helium was degassed with nitrogen at about the same time. When investigations began in the early helium industry to explain the correlation between helium and nitrogen, many theories were proposed but no single theory took hold. As stated in the history portion of this book, Ramsay found both helium *and* nitrogen in Hillebrand's uraninite rock sample in 1895 but it was unclear how the nitrogen got there. The most logical conclusion at the time was the proximity to organic shales which were known to contain nitrogenous matter. Sherburne Rogers had theorized (incorrectly) that alpha particles ejected from uranium or thorium would react with these nitrogenous shales and effectively decompose them to create both free nitrogen and hydrocarbons.⁸ The alpha particles, of course, would be responsible for the presence of helium.

Our atmosphere is 78 % nitrogen which is present as the strongly bonded N₂ molecule. During the Earth's accretion, it is possible that this nitrogen existed and accreted as a solid due to the cold temperatures of space (-270 °C) thus trapping higher volumes of nitrogen. As previously stated, nitrogen was a very common element created during stellar nucleosynthesis. As the Earth began to warm, the solid nitrogen would have been converted into a gas where it would become mobile in both the mantle and crust. Prior to crustal formation, it is likely that most of this nitrogen was degassed to form near the composition which we see today. It would not be until the advent of photosynthesis when we would begin to see any accumulation of the diatomic oxygen molecule (O₂). Before oxygen was introduced into the atmosphere, CO₂ was a major constituent in the early atmosphere before it was consumed through photosynthesis.

Nitrogen played an important part in the early Earth and had degassed relatively early helping to create the foundation for our atmosphere. One can speculate that during this early degassing, helium was able to escape via the same process as nitrogen out of the crust. In this instance, nitrogen is helium's carrier gas out of the crust following the path of least resistance. Since the formation of earth, helium has been produced through the radioactive decay of both uranium and thorium so it would appear plausible that both helium and nitrogen would have been released at roughly the same time (from the crust) despite differing origins.⁹ If helium did

⁸ The origin of terrestrial helium and its association with other gases, S.C. Lind, <u>Chemistry: S.C.</u> <u>Lind</u>, April 27, 1925, p. 776.

⁹ Molecular nitrogen in natural gas accumulations: generation from sedimentary organic matter at high temperatures, R. Littke, E. Idiz, J. Frielingsdorf, AAPG Bulletin, V. 79, No. 3, March 1995, p. 412.

not have a carrier gas, then we would likely see nearly pure helium reservoirs which we know do not exist, at least in the upper crust. Thus, due to the presence of nitrogen with nearly all helium reservoirs, nitrogen is the likely carrier gas that carried it to its final destination.

As the Earth aged and sedimentary rock was formed via the weathering of granitic basement rock and the manufacturing of limestones and shales, both helium and nitrogen would have to travel along similar paths within the sedimentary column to find their way to the surface and ultimately into the atmosphere. In some cases, these gases would become trapped along with hydrocarbons which were formed and migrated within the sedimentary rock. Although both helium and nitrogen could become trapped in sedimentary rock, the ability to hold helium in place is much more difficult than nitrogen, which can easily become trapped with hydrocarbons.¹⁰ This is one reason why nitrogen (and CO_2) exists without helium in some low-btu gas fields across the world.

Another interesting host gas for some helium reservoirs is carbon dioxide, which is found most commonly in the Four Corners region of the United States. The reason for the presence of this gas is due primarily to volcanic processes from where it was degassed from the Earth's interior. Although it is possible that some of this CO₂ could be derived from biogenetic processes, the majority is sourced by volcanic activity as confirmed by isotopic analysis. The other helium-rich areas like Kansas, Texas, and Oklahoma do not have any large concentrations of carbon dioxide because of the lack of volcanic activity in the area. That is, the helium derived from these areas are only due to deep tectonic movement (such as the Mid-Continental Rift) where nitrogen and helium could be degassed from crustal material. In the Four Corners region (and in other parts of New Mexico) there is much ancient volcanic activity as can be evidenced by the Rio Grande rift, remaining (extinct) volcanic cones, and extensive dikes and sills which litter the landscape. Volcanic activity in New Mexico can be explained by both the thinning of the lithosphere as evidenced by the Rio Grande Rift where continental separation took place. The Rio Grande river follows this ancient rift.

As stated before, although carbon dioxide is the primary host gas in this area, all of this gas contains at least some percentage of nitrogen, albeit at much lower concentrations than you would expect from other helium-rich areas. The Four Corners gas represents some of the highest helium percentages in the world reaching upwards of nearly 10 % helium. These helium-rich gases are found at shallow depths and most have been depleted since their discovery in the 1930s through 1960s.

Although the origin of the other gases (nitrogen and carbon dioxide) in helium-rich reservoirs can be debated, helium's presence in a gas stream will nearly always imply a low heating value to a gas (principally methane, CH₄). High helium percentages will nearly always mean a reduction in its heating value

 $^{^{10}}$ The helium atom has a diameter of 0.2 nm, or 10^{-9} m. CO₂, N₂, and CH₄ have molecular diameters of 0.33 nm, 0.34 nm, and 0.38 nm, respectively. (*Source* Petroleum geochemistry and geology, 2nd Ed., J.M. Hunt, 1996.)

(assuming part of the host gas contains hydrocarbons). Of course, many of the helium-rich gases in New Mexico contain carbon dioxide and only negligible hydrocarbons thus will not burn at all. Any gas that contains over 1 % helium, however, needs to be closely investigated for its economic recovery because even a seemingly low 1 % helium is actually quite high and could be of significant value if enough reserves can be quantified.

Rate of Helium Production

Uranium and thorium is most concentrated in the Earth's crust where they exist in concentrations of 4 and 16 ppm, respectively. The mantle is largely deprived of uranium and thorium where concentrations are only 0.02 and 0.06 ppm, respectively. During the early, hotter Earth, most of the uranium and thorium that existed since its accretion had fractionated out of the mantle and now resides primarily in the crust (both in basement rock and sedimentary rock). These two elements (three isotopes) and potassium-40 represent an enormous heat engine in the crust which helps prevent the earth from cooling too quickly. Were it not for the elements uranium, thorium, and potassium, the primordial heat of the Earth would have rapidly dissipated leaving the Earth much cooler and unable to maintain plate tectonics. Without plate tectonics, it is likely that there would be no life on earth. As a matter of fact, we could owe part of our very existence to the presence of these three elements.

The helium-producing isotopes of uranium and thorium have very long halflives which mean that their heat production will continue for billions of years more. A single atom of uranium or thorium will decay spontaneously at very slow varying rates. However, with greater concentrations, we can estimate with great precision what the half-life is for all of the uranium and thorium inventory in the Earth.

The production of helium from these isotopes and their decay cycles are as follows (Figs. 4.3, 4.4 and 4.5).

As can be seen from the information above, uranium-238 produces the most helium with 8 helium atoms produced through the entire decay chain. The far less abundant uranium-235 produces 7 helium atoms and thorium-232 produces 6 atoms. Uranium-235 actually generates the most heat per unit but it only represents 0.71 % of the total uranium inventory on Earth.¹¹ Uranium-232 and thorium-232 represents 43 and 42 %, respectfully, of total uranium and thorium abundances. Total helium production from uranium and thorium is as follows:

 1.03×10^5 He atom/s⁻¹ = 1gU 2.46 × 10⁴ He atom/s⁻¹ = 1gTh

¹¹ Radioactivity in geology, principals and applications, Durrance (1986).

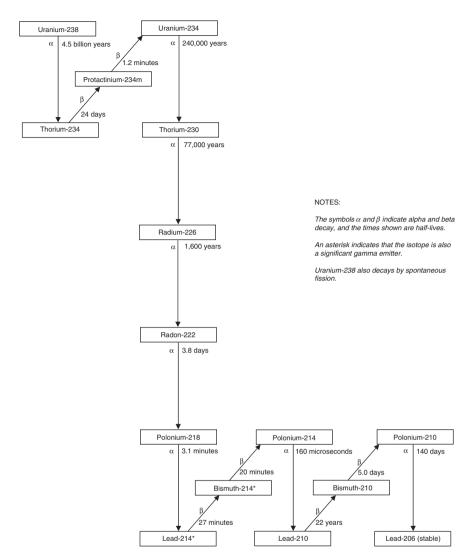


Fig. 4.3 Natural decay series: Uranium-238. Source Argonne National Laboratory

The annual crust and mantle production of helium is as follows:

$$1.125 \times 10^{30}$$
 He atoms/year⁻¹

In order to put these production rates into perspective, the number of helium atoms required to fill a 22.4 l mylar balloon is roughly 4 g of helium or 6×10^{23} atoms. At the full production rate of the mantle and crust (assuming that all which is produced is degassed out of the crust and mantle), enough helium is produced to fill over 5 million balloons per day. However, only 7×10^{30} helium atoms escape the

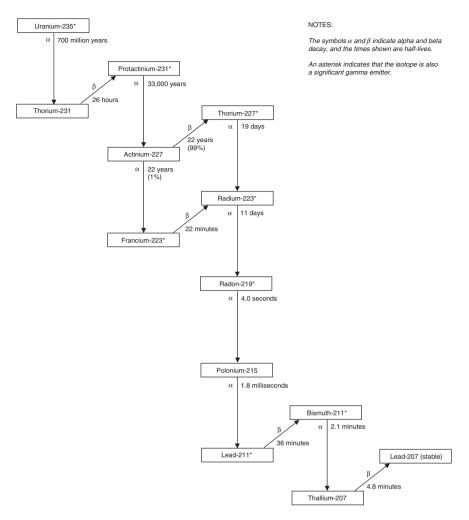


Fig. 4.4 Natural decay series: Uranium-235. Source Argonne National Laboratory

crust and mantle per year, meaning that the remaining helium inventory is still locked away in the deep Earth.¹² This is good news for those involved in helium exploration.

¹² These production rates and balloon comparison information were provided to the author by Dr. Mike Reimer.

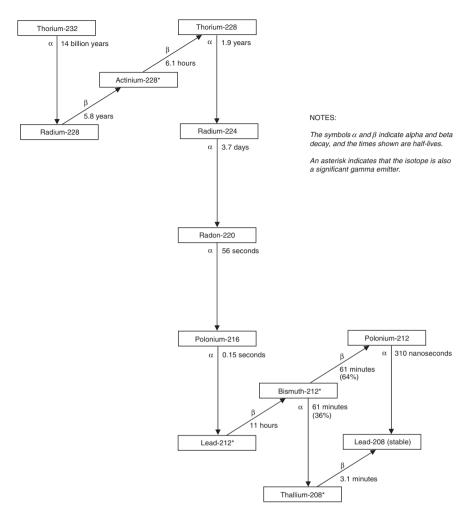


Fig. 4.5 Natural decay series: Thorium-232. Source Argonne National Laboratory

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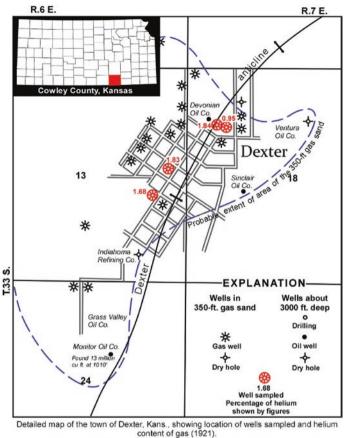
Chapter 5 The Helium Industry

The Dexter, Kansas Well

In the first decade of the 1900s, the pursuit of oil and natural gas was growing exponentially due to the country's ever increasing power requirements. Both oil and natural gas (methane and heavier components) were used to provide power to factories and other facets of the expanding industrial age. J.D. Rockefeller, by this time, had firmly gained control of the majority of the production and sale of oil in the United States. One by-product of oil refining, gasoline, was at this time primarily a waste product as the automobile was not yet available to the masses. Rockefeller's stranglehold of U.S. production, however, did nothing to dissuade smaller oil and gas companies from pursuing these commodities of ever increasing value. Small oil and gas companies were still responsible for the discovery of new reserves and were willing to take on increasing amounts of risk in order to find the next new Spindletop, the East Texas gusher that produced 100,000 barrels of oil per day in 1901.

In the Spring of 1903, a small company called the Gas, Oil and Development Company, drilled a well just off main street in the town of Dexter, Kansas in pursuit of oil and/or natural gas. Very quickly, a large gas reservoir estimated at 9 million cubic feet of gas per day was found at a shallow depth of 400 feet. Celebrations were planned and the excitement was rampant throughout the small Kansas town. Crowds gathered to witness (and hear) the huge gas flow and they anxiously awaited to see the gas ignited, thus putting Dexter, Kansas on the map as a major resource. As the flame was placed in front of the gas stream, it was quickly *extinguished* (Fig. 5.1).

Despite shutting the well in and attempting to ignite the gas again, it would simply not burn. News of this inflammable gas traveled quickly within the State where it ultimately became known as "wind gas." Despite the fact that the dreams of a new Dexter were crushed, the news sparked the curiosity of the Kansas State geologist, Erasmus Haworth (1855–1932), who requested a gas sample. The sample was sent to the



SOURCE: Helium-Bearing Natural Gas, Professional Paper No. 121, U.S. Geol. Sur., 1921, p. 76

Fig. 5.1 Detailed map of the town of Dexter, Kans., showing location of wells sampled and helium content of gas (1921). *Source* Helium-bearing natural gas, Professional Paper No. 121, U.S. Geol. Sur., 1921, p. 76

University of Kansas during the summer where David Ford McFarland (1878–1955), a University of Kansas chemistry professor, performed a careful analysis, which were as follows (Source: The Dexter, Kansas, Nitrogen Well, Erasmus Haworth, D.F. McFarland, H.L. Fairchild, Science, New Series, Vol. 21, No. 527. February 3, 1905, p. 192):

Oxygen	0.20
Carbon dioxide	0.00
Carbon monoxide	0.00
Methane, CH ₄	15.02
Hydrogen	0.80
Nitrogen	71.89
Inert residue	12.09

These results were published in Science magazine in 1905. The authors, Erasmus Haworth, David F. McFarland, and H.L. Fairchild, noted:

No examination into the constitution of this residue has yet been made, because of lack of time, and until this is done nothing can be said concerning its composition, save that there is a possibility of its containing argon or other inert gaseous elements which have been found in atmospheric air. The investigation of the inert gases will be carried out as soon as time will permit.¹

The results of this mysterious "inert residue" were finally revealed by Dr. Edgar Henry Summerfield "E.M.S." Bailey (1848–1933), head of the chemistry department at the University of Kansas, at the annual meeting of the American Chemical Society in New Orleans in 1906. Bailey revealed a helium composition of 1.84 %.²

Despite the fact that this well had a very large concentration of helium, the enormity of the situation would not be revealed until several years later. The helium present in this natural gas well, rather, was more of a laboratory curiosity. Immediately after receiving the results of the Dexter well, forty-four gas wells in Kansas and Missouri were sampled and analyzed by the end of 1906, each of which contained helium albeit in smaller concentrations than the Dexter well.³ The results of this sampling also revealed a "remarkable regularity in the distribution of helium" showing that elevated helium concentrations appeared to be related to linear geological structures. The most important observation in this first natural gas sample survey was helium's relationship to nitrogen.

It is further to be noted that the quantity of nitrogen in the gases rises or falls generally with the quantity of helium, although a strict proportionality has not been found; also, in general, the quantity of combustible constituents in the gas varies inversely with the quantity of helium and of nitrogen. A gas high in helium is low in methane and other combustibles, and high in nitrogen, while the gas low in helium is high in combustibles and low in nitrogen – a much better gas for heat production.

Kansas is to be congratulated on the possession of an unlimited and easily available supply of what has been considered a very rare element, a supply which has never been suspected before. It assures the fact that helium is no longer a rare element, but a very common element, existing in goodly quantity for the uses which are yet to be found for it.⁴

Hamilton Perkins Cady (1874–1943) and David Ford McFarland (1878–1955), both of the University of Kansas, were the two chemists responsible for the analysis of these initial Kansas and Missouri natural gas wells, while members of the University Geological Society were responsible for the majority of the collection

¹ The Dexter, Kansas, Nitrogen Gas Well, Erasmus Haworth, D.F. McFarland, and H.L. Fairchild, Science, Vol. 21, No. 527, February 3, 1905, pp. 191–192.

² Helium in Natural Gas, Hamilton P. Cady and David F. McFarland, Science, New Series, Vol. 24, No. 611, September 14, 1906, p. 344.

³ Helium in Kansas Natural Gas, H.P. Cady and D.F. McFarland, Transactions of the Kansas Academy of Science (1903–), Vol. 20, December 1906, p. 80.

⁴ Helium in Kansas Natural Gas, H.P. Cady and D.F. McFarland, Transactions of the Kansas Academy of Science (1903–), Vol. 20, December 1906, pp. 80–81.

of samples.⁵ Cady and McFarland's observations in 1905 through 1907 would reveal some of the most important ideas on the relationship between helium accumulation and geological events. The results of their labors showed that helium was available in ample supplies, and in the summer of 1906 stated, "we feel that we have here a very unusual opportunity for obtaining helium in practically unlimited quantities."⁶

The method by which Cady and McFarland were able to determine the concentrations of helium was gaseous absorption via cocoanut charcoal at liquid air (nitrogen) temperatures. Discovered by James Dewar in 1904, activated charcoal would absorb all gases under liquid air temperatures except (in varying degrees) helium, neon, and hydrogen. Of these three remaining gases, helium is the least absorbed thus easily able to become sequestered for analysis. A brief sequence for helium separation and analysis is as follows (simplified explanation of the apparatus used by Cady and McFarland in 1906–1907. Source: The Journal of the American Chemical Society, Vol. XXIX, November 1907):

- 1. A water-filled glass bulb is filled with 100 % of the sample gas. As the gas fills the bulb, all of the water becomes displaced. Once completely filled with gas, the bulb is cooled to liquid air temperatures where a large majority of the methane and other hydrocarbons liquefy.
- 2. The next bulb contains activated charcoal which receives the residual gas from the first bulb where it is held for several minutes. This bulb with charcoal is submerged in a bath of liquid air. After this step, nearly everything but helium has been absorbed by the charcoal.
- 3. Step 2 is repeated with another bulb of activated charcoal thus achieving an even greater purity of helium.
- 4. The gas from step 3 is then passed into two U-shaped glass tubes which are also immersed in liquid air. This step removes any possible water or mercury vapor that might exist in the helium sample.
- 5. After step 4, this gas is collected in Plucker tubes, the helium is examined with a spectroscope, and then removed by a pump.
- 6. Steps 1 through 6 are repeated until no detection of helium can be found spectroscopically.

As can be seen, the spectroscope was still a very important instrument in elemental identification where no other method existed.

Both Cady and McFarland were also cognizant of Rutherford and Soddy's earlier proof of helium generation through the decay of radioactive elements (principally radium as per their studies). At this embryonic stage of helium gas sampling, it was too early to know exactly why helium was present in natural gas. In addition

⁵ The Occurrence of Helium in Natural Gas and the Composition of Natural Gas, Hamilton P. Cady and David F. McFarland, The Journal of the American Chemical Society, Vol. XXIX, No. II, November 1907, p. 1524.

⁶ See Footnote 2.

to helium found in these natural gases, Cady and McFarland in 1907 found that the Dexter gas well contained both argon and neon, which represented a new discovery in natural gas.⁷

After Cady and McFarland made these significant discoveries of helium in natural gas, further helium work was curtailed in the coming years because there was no commercial need for the gas. After their unsuccessful attempts to liquefy helium,⁸ they went on to pursue their other duties as chemistry professors at the University of Kansas. All that was left of the helium gas collected was placed in three small bottles submerged in mercury, to prevent leakage, and placed on the top shelf of a laboratory at the University. Collecting dust, these bottles were simply labeled, "He 1905."⁹

The Helium Idea

As the Great War was firmly established by mid-summer of 1914, one particular event and one publication in this year would provide the catalyst for a new helium "industry" to be born. Prior to 1914, helium was of little use beyond applications of experimental nature. Despite the fact that helium could now be found in rather unlimited quantities, it was simply not required for any commercial application.

All of this changed in 1914, when a German book titled, <u>Die angewandte</u> <u>Chemie in der Luftfahrt</u> (translated: Applied Chemistry in Aviation) by Dr. Géza Austerweil was published. A section in chapter one of this text titled, *Helium als Ballonfüllgas* (Helium as a Balloon-filling gas), specifically mentions the advantages of using non-inflammable helium as a replacement to hydrogen for filling military balloons. Austerweil went on to mention, however, that the probability of obtaining enough helium to fill a balloon was unlikely because all of the world's known helium was held in extremely small quantities in the laboratory of Professor Kammerlingh Onnes, who had been the first to liquefy helium six year prior.¹⁰ Austerweil clearly had no knowledge of the helium discovered in United States natural gases in 1906.

Another event in 1914 had a much more profound effect on the history of helium industry. During that year, a German zeppelin was attacked and pierced by many incendiary bullets but would not catch fire, leading many to believe that Germany had found a non-inflammable gas.¹¹ If, as it was suspected, that

⁷ Neon and Argon in Natural Gas, Transactions of the Kansas Academy of Science, Hamilton P. Cady and David F. McFarland, Vol. 21, December 1907.

⁸ The Dutch physicist, Heike Kamerlingh Onnes, was the first to liquefy helium in 1908 in his laboratory at the University of Leiden.

⁹ Helium, Child of the Sun, Clifford Seibel, 1964, p. 1.

¹⁰ <u>Die angewandte Chemie in der Luftfahrt</u>, Dr. Géza Austerweil, 1914, pp. 8–9.

¹¹ Commercial Production of Radium, Mesothorium, and Helium, R.B. Moore, Industrial and Engineering Chemistry, Vol. 18, No. 2, 1926, p. 203.

Germany had somehow been able to obtain helium for military use, they would have a supreme advantage in the air over the allies. (It would later become obvious that Germany did not possess any helium and in fact this particular dirigible was filled with hydrogen.)

Germany was already firmly established and had pioneered lighter-than-air zeppelins. Prior to the war, the German company Deutsche Luftschiffart A.G. (DELAG) had proven that airship travel was a reality; roughly 34,000 people had been flown commercially without injury.¹² Germany's successful record of zeppelin manufacturing and transport created great discomfort among the allies because of the obvious military advantages they possessed.

English physicist and chemical engineer, Sir Richard Threlfall (1861–1932) caught wind of the German airship that could not be brought down (and possibly Austerweil's book) and fearing that helium had somehow been obtained by the Germans, immediately wrote to the British Admiralty voicing his concerns. Upon receipt of this letter, the British Admiralty authorized Threlfall (who would later be joined by Sir William Ramsay) to report on possible locations where helium could possibly be extracted. Having not yet learned of the Dexter well and subsequent publications in the United States, Threlfall and Ramsay analyzed the gases emitted from coal mines and firedamps. They were able to locate two sources of helium in coal mines in Anzin, France and Frankenolz, Germany (bordering Brussells). The amounts expelled from these two locations, unfortunately, were not voluminous enough to adequately fill military balloons. The amount of helium liberated from the Anzin mine, for example, amounted to just over 141,000 cubic feet of helium *per year.*¹³

By December 1914, Threlfall finally became knowledgeable of Cady and McFarland's work in the United States and by February 1915 had reported these American discoveries to the British Admiralty's Air Department. Learning for the first time that helium could potentially be extracted from natural gas in unlimited quantities, the British Admiralty quickly appropriated a small sum of money to investigate helium from natural gas within the British Empire, principally Canada.

The United States, not yet a participant in the War, would learn about the British attempts to find helium for use in military airships in February 1915 in a letter from Sir William Ramsay addressed to Richard Bishop Moore (1871–1931). (R.B. Moore had formerly worked with Ramsay in the United Kingdom when studying the rare gases of the atmosphere) In this letter Ramsay writes:

I have investigated blowers – that is, coal-damp rush of gas – for helium for our Government. There does not appear to be anything in the English blowers, but I am getting samples from Canada and the United States. The idea is to use helium for airships.¹⁴

¹² USS Los Angeles: The Navy's Venerable Airship and Aviation Technology, William F. Althoff, p. xv.

¹³ Commercial Production of Radium, Mesothorium, and Helium, R.B. Moore, Industrial and Engineering Chemistry, Vol. 18, No. 2, 1926, p. 204.

¹⁴ Helium, Child of the Sun, Clifford Seibel, 1964, p. 23.

After receipt of this letter, R.B. Moore had put it aside because the U.S. was not yet involved in the War. In addition, President Woodrow Wilson forbade any war preparations as a part of his strict policy of neutrality.

Nevertheless, the British moved forward with haste on their Canadian project and appropriated a sum of money in 1915 to Canadian scientist, Professor John C. McLennan of the University of Toronto to experiment on the possibility of using helium for use in airships. McLennan was asked to determine the helium content of natural gases within the British Empire and to conceive a way to process helium from this gas. In relative short order, McLennan had discovered several areas within eastern Canada which possessed helium concentrations ranging from 0.1 to 0.33 % and had negotiated a contract with Air Liquide Company (France) to manufacture an experimental helium plant to process this natural gas. Air Liquide was formed in 1902 by Georges Claude and Paul Delorme as an air liquefaction company. The site chosen for this plant was in the town of Hamilton, Ontario and the gas supply was to come from Western Ontario gases via pipeline.¹⁵

The Air Liquid plant in Hamilton, Ontario was a modified air separation unit which utilized cold temperatures in order to separate oxygen from the air (air is ~21 % Oxygen). This plant represented the first functional helium plant in the world but it did not operate without problems. During the early years of its useful life, the problem of removing the heavier hydrocarbons found in the western Ontario gas proved to be quite difficult.¹⁶ Through trial and error and numerous modifications, the primary purpose of separating helium from natural gas was finally achieved in by mid year 1918. Towards the end of its operation in Hamilton it was able to achieve a helium purity of 87 %, with the residual gas primarily composed of nitrogen. However, just as progress on purification was being made, the volume of gas from the Western Ontario fields began to decline substantially and the plant was subsequently moved to Calgary to process gas from the Bow Island Field.¹⁷

Meanwhile in the United States, while still not in the War although the likelihood of its entry appearing eminent, a young chemistry student named Clifford Winslow Seibel (1890–1984) at the University of Kansas was seeking an advanced degree and sought the help of Professor Cady for an idea on his thesis. Cady had suggested that Seibel re-examine the previous work done on helium and the other rare gases of the Dexter, Kansas natural gases. Seibel had no interest in undertaking this study but as this advice had come from such a distinguished chemist, Seibel reluctantly agreed and began his studies.

¹⁵ Report on Some Sources of Helium in the British Empire, Bulletin No. 31, Canada Department of Mines, J.C. McLennan, 1920.

¹⁶ See Footnote 15.

 $^{^{17}}$ By the time the Calgary gas was processed for helium, the War had ended. During its time in Calgary, the plant had produced nearly 60,000 cubic feet of gas ranging from 60 to 90 % pure helium.

Seibel had finished this thesis in early 1917 and was scheduled to present his work at the 54th annual meeting of the American Chemical Society held in Kansas City in April 1917, only days after the United States entered the War. Seibel's paper, *The Rare Gases of Natural Gas* was read, reluctantly, by Seibel and when finished expressed regret and stated, "I'm sorry, gentlemen, but there is no practical application for this information."¹⁸ Seibel's statement was referring to the point that as most Americans were focused on the war, his paper posed no practical benefit to the war effort.

American chemist, Dr. Richard Bishop Moore (1871–1931), who was keenly interested in Seibel's thesis, was present at this meeting and immediately responded to Seibel's last statement by producing the February 28, 1915 letter that Sir William Ramsay had written to Moore and stated, "there is your practical application."¹⁹ Moore highlighted the British interest in helium for use in airships for wartime and reasoned that it would be possible to extract and process helium for American military use at a reasonable cost.

As the dialogue progressed, the mere idea of sequestering enough helium to fill an airship seemed incomprehensible to Seibel as he held in his hand nearly the entire United States supply of the gas which amounted to less than one cubic foot.²⁰ The most obvious problems as perceived by Seibel were:

- 1. The United States only possessed at the time less than one cubic foot of helium
- 2. A small blimp would require roughly 100,000 cubic feet of helium
- 3. The current cost of extraction was astonishingly high. Seibel had recently sold one cubic foot of the gas for \$2,500
- 4. At this price, it would cost more than \$200 million to fill one dirigible.

Completely unfazed by Seibel's points, Moore began a dialogue with Dr. Charles Lathrop Parsons, chief chemist of the Bureau of Mines who was also in attendance at the meeting. Commenting on the superior benefits of using helium instead of hydrogen for airships, Moore asked Parsons, who was traveling back to Washington D.C. after the meeting, to pass on this information to his superiors at the Bureau of Mines and also the War Department (Fig. 5.2).

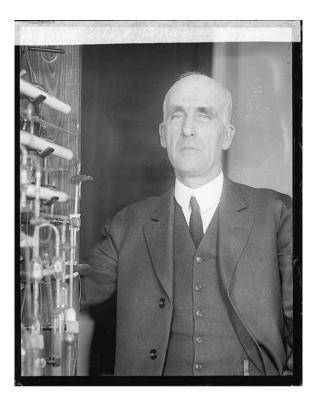
The ensuing discussions held in April and May at the Bureau of Mines in Washington were very well received, especially by the Bureau's head of War Gas Investigations, George Arthur Burrell (1882–1957). Before the war, Burrell had examined numerous samples of natural gas wells in Texas, particularly the fully developed Petrolia Gas Field near the town of Wichita Falls. The gas from Petrolia had contained 20–30 % nitrogen but was good enough to be used as fuel and was pipelined down to Dallas and Fort Worth, Texas in large volumes. Having learned of helium's association with nitrogen, Burrell speculated that it was possible

¹⁸ American Chemical Society, http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_page Label=PP_ARTICLEMAIN&node_id=928&content_id=CTP_006343&use_sec=true&sec_url _var=region1.

¹⁹ See Footnote 14.

²⁰ See Footnote 14.

Fig. 5.2 Richard Bishop Moore (library of congressnational photo company collection)



that gas from the Petrolia field might contain helium due to its nitrogen content. Burrell sent a gas sample to Dr. Cady at the University of Kansas where it was revealed to contain roughly 1 % helium. Burrell immediately informed his colleague, and chief metallurgist of the Bureau of Mines, Frederick Gardner Cottrell (1877–1948) to join he and R.B. Moore to discuss using this Petrolia gas for helium recovery. The Petrolia field, thus, became the likely place to begin should the project proceed.

Progress on the helium question had gained steam on May 12, 1917 when Burrell wrote a letter to Major Charles deForest Chandler (1878–1939), who was in charge of the Balloon Division of the Aviation Section of the Signal Corps (United States Army).²¹ In this letter, Burrell had asked an opinion of Chandler on whether helium would prove to be advantageous enough to warrant production of the gas if it could be recovered inexpensively. Intrigued with the idea, Chandler would meet both Moore and Burrell in June to discuss the feasibility of the idea.

Before the start of the war in 1914, the U.S. Army had already appropriated \$250,000 for army aviation purposes but the majority of these funds were for airplanes. After the war had begun, the threat of airships was a growing problem for

²¹ See Footnote 13.

the United States. In addition, because of President Woodrow Wilson's policy of neutrality, little focus was placed on developing American airships, creating a tremendous disadvantage. By March 1915, an appropriation of \$1 million was awarded to the Navy, part of which was for its first airship (designed for hydrogen). Leading up to the United States entry into the war, Jerome Clarke Hunsaker²² (1886–1984) of the U.S. Navy stated, "it seemed evident that a new weapon had appeared and that the U.S. should consider its possibilities carefully."²³

Now that the United States was in the war, interest in airships, especially those which could be filled with helium, was a high priority. The meeting in June 1917 between Moore, Burrell, and Chandler would constitute the beginning of the helium industry.

An Industry Born

The meeting between Moore, Cottrell, and Chandler was designed to further gauge the potential interest of the Army and to determine if the Army would be willing to contribute monies for a pilot helium project. Chandler became interested at once. Recalling the event several years after the end of the war (December 19, 1923), Chandler wrote:

It was one day in June of 1917 that you and Dr. Burrell called at my office, presumably because I was at that time in charge of the Balloon Division of the Aviation Section of the Signal Corps. You told me of helium being one of the constituents of natural gas in the central part of the United States, adding remarks about its characteristics that would make it superior to hydrogen for military balloons provided suitable extraction processes could be developed. I was then asked whether the Signal Corps desired helium sufficiently to encourage development of the extraction processes by allotment of funds for the purpose.

My personal opinion was that it should be done, even though the cost would be considerably more than hydrogen, for the reason that anything that would give us an advantage over an enemy in time of war ought not to be overlooked simply on account of greater cost. This matter involved new policy and would surely require a greater expenditure of funds than amounts subject to my approval, therefore, I agreed to confer promptly with the Chief Signal Officer of the Army, which was done within a few hours. General Squier [Major General George Owen Squier, 1865-1934] was much interested in the proposal and instructed me to present the matter to the Aircraft Production Board at its next meeting a day or two later; that board was responsible for decisions regarding aircraft policy affecting both the Army and Navy. The questions asked by members of the board indicated a favorable interest and I was directed to secure approximate estimates from the Bureau of Mines of the funds required for developing a practicable extraction process.²⁴

²² J.C. Hunsaker would later become President of the Goodyear Zeppelin Company.

²³ USS Los Angeles.

²⁴ See Footnote 13.

Interest in helium continued to expand as Chandler informed G.O. Carter of the Navy's Bureau of Steam Engineering who immediately became interested on behalf of the Navy. Both Carter and Chandler agreed to move forward with a helium program as quickly as possible. Enthusiasm for helium would also reach the Assistant Secretary of the Navy, Franklin D. Roosevelt, who would later say, "with the fire risk eliminated the rigid airship or Zeppelin will hence be one of the most powerful weapons known."²⁵

Immediately as a result of these communications with Moore, Burrell, Chandler, and Carter, a recommendation was made by Frederick Cottrell to contact Fred H. Norton of the Jeffries-Norton Corporation to begin discussions on the processing of helium. Norton, a Massachusetts Institute of Technology graduate and a very well respected engineer of international reputation, was called to Washington on June 4, 1917 to discuss an experimental process where helium could be extracted from natural gas, which had never before been achieved in the United States. Cottrell, who was introduced to the Norton process by the Bureau of Mines director, Van H. Manning in 1916, was of the opinion that Norton might be the engineer who could tackle this issue with relative low cost. Norton had developed the drawings for a "new process for air separation that embodied some novel and striking features"²⁶ to produce oxygen inexpensively for use in blast furnaces, of which the Bureau of Mines had an interest. The oxygen, in Norton's process, was extracted using low-temperatures like other air separation units, but his design was supposed to achieve the results with reduced compression costs, which was the primary cost of extraction.

Norton estimated that it would cost \$28,000 to build a plant that could process 5,000 cubic feet of helium per day (because this plant was experimental in nature, only very small volumes of gas were required to test the process). The request for \$28,000 was granted and soon Norton was making designs to build the first experimental helium plant and negotiating a contract with the Lone Star Gas Company to withdrawal a small portion of the Petrolia gas from the pipeline in Fort Worth, Texas.

In the meantime, conferences were held in Washington D.C. in July 1917, to hold open discussions on all matters pertaining to the production of helium but also addressing many scientific questions concerning helium permeability through balloon fabric, solubility of helium in liquid methane and nitrogen, and combustibility studies on mixtures of helium and hydrogen (it was learned that a 10 % component of hydrogen in helium would not ignite). More importantly, a relationship between the United States and Great Britain was recommended in order to aid the allied forces resulting in the dispatch of Captain R.B. Owens of the U.S. Army's Signal Corp to the United Kingdom to discuss cooperation between the two countries. All attendees of these conferences were in agreement to move forward on all fronts.

²⁵ Helium-Bearing Natural Gas, G. Sherburne Rogers, 1920, p. 6.

²⁶ Petroleum Investigations and Production of Helium, by Van. H. Manning, Bureau of Mines Bulletin 178c, (1919) pp. 77–78.

Not willing to risk the future of the entire United States industry on the experiment of one processing company, R.B. Moore recommended that two other wellestablished companies in air separation be considered as well. Moore had recommended to Frederick Cottrell that both Linde Air Products Company²⁷ and the Air Reduction Company,²⁸ two well respected air separation companies, be given a chance to compete for processing rights, to which he readily agreed.²⁹ By late July 1917, a recommendation was made by the joint Army and Navy Airship Boards for an increased appropriation of \$100,000 (to be split evenly between Army and Navy) to be divvied between these two companies and one other that withdrew shortly afterwards.³⁰ It was also recommended at this time that helium operations be consolidated and run by the U.S. Bureau of Mines, with George Burrell leading operations. Dr. Hamilton Cady and his assistant, Dr. Clifford Seibel, would become the Bureau of Mines' consulting chemists in charge of the majority of helium analytical and research work.

As negotiations were proceeding with the well known Linde Air Products Company and the Air Reduction Company, representatives from the Jeffries-Norton Company had already negotiated a verbal contract with the Lone Star Gas Company for processing rights and had chosen a location for their experimental helium processing plant in Fort Worth. The Norton representatives were quickly moving forward until all momentum would come to a screeching halt in October 1917 when G.O. Carter prohibited any Navy funds to be diverted to the Jeffries-Norton Company. G.O. Carter, the Navy representative in Washington, was also a former Linde Air Products employee who had some knowledge in low-temperature processing. The Norton process, according to Carter, was an unsound technology that was not deserving of any Navy appropriation. The Army would ultimately side with Carter and leave Norton out of any Army appropriation as well.³¹

Less than one week before the Norton process was excluded from any funds, the British Admiralty had informed the United States of their helium requirements for the war. The amount requested was enormous, 100 million cubic feet at once and 1 million cubic feet per week thereafter.³² The British believed this amount

²⁷ Linde Air Products Company was formed in 1907 by German Linde. After the United States joined World War I, German Linde had to divest their shares in the American Linde Air Products Company. Union Carbide and Carbon Corporation (UCC) took over the American subsidiary. UCC would later become Praxair. (*Source* Mergers & Acquisitions in the U.S. Industrial Gas Business, Part II—The Major Industry Shapers, Peter V. Anania, November 2006, Cryogas International.)

²⁸ Air Reduction Company, later to be known as Airco, is no longer an entity. It was formed in 1916 by American Oxygen Company and Air Liquide. (*Source* IBID).

²⁹ See Footnote 13.

 $^{^{30}}$ A process known as the "Lacy Process" was also intended for a portion of this appropriation but they were quickly withdrawn from consideration.

³¹ Helium, Child of the Sun, Clifford Seibel, 1964, pp. 32–33.

³² See Footnote 26.

was entirely feasible primarily because of their belief in the Norton process. Through the convincing of Captain R.B. Owens on his mission to the United Kingdom after the helium conferences, he assured the British authorities that the Norton process would prove to be theoretically sound, thus assuring the allies a low-cost method of helium extraction. Now that the Norton process was excluded from any Army or Navy appropriation, this left the British Admiralty and the U.S. Bureau of Mines somewhat embarrassed because of their unwavering belief in the Norton process.

Despite the stalling of the Norton fiasco, progress by the Bureau of Mines remained swift and an increased appropriation of \$500,000³³ (a portion of which was supposed to be allocated to the Norton process) was approved for the two remaining processing companies. Both the Linde Air Products and Air Reduction contracts were signed in November 1917 and construction on both facilities began immediately. During construction and as a precautionary war measure, both plants became known as "argon" plants for added secrecy.

Luckily for the Jeffries-Norton Company, they would get a new life in January 1918 when, as a result of their process being re-investigated by the National Research Council, were again deemed worthy of a chance to compete. On Jan 14, 1918, the National Research Council stated, "...the committee is unanimously of the opinion that the Norton process... is scientifically sound, that it should accomplish the desired result, and that every part of it seems to have been conceived in the light of a clear understanding of the problem and of the means which good engineering would suggest as conducive to economy..."³⁴ During the time it took to have the Norton process re-instated, the original plant site negotiated by Norton was assigned to both Linde Air Products and Air Reduction Company. Having no plant site at the end of the pipeline in Fort Worth, Norton decided to install his plant at the Petrolia field.

The three experimental helium plants were placed under the control of R.B. Moore in June, 1918. A brief description of these plants are as follows:

1. The Linde Air Products plant (Argon Plant No. 1) in Fort Worth, which had a capacity of 5,000 cubic feet of gas per day, was completed in March 1918 at a cost of \$245,000. This plant utilized the Joule-Thomson effect, which is brought about by the rapid expansion of compressed gas through a small orifice (which is why an aerosol can becomes cold during spraying). As the incoming gas is compressed to 2,000 pounds per square inch (psi) and subsequently cooled by water, carbon dioxide, and previously processed liquid gases, it is then expanded and thus cooled as it returns to normal pressure. This process is then repeated several times until the gases fall below their boiling points. The main drawback to this process was the enormous gas compression requirements which necessitated large amounts of energy, thus increasing processing costs.

³³ <u>Helium, Child of the Sun</u>, Clifford Seibel, 1964, p. 34.

³⁴ See Footnote 33.

Although this plant was the most expensive to operate, the plant was able to produce 70 % pure helium initially, then 92 % purity after reprocessing.³⁵

- 2. The Air Reduction plant (Argon Plant No. 2), with nearly identical capacity as the Linde began operations on May 1, 1918 and cost \$135,000 to manufacture. Air Reduction used a "Claude" cycle (a process designed by Georges Claude of L'Air Liquide) which also utilized the Joule-Thomson effect. This system had much less compression requirements resulting in lower operating costs. The main difference between the this plant and the Linde was the use of an expansion "engine" that utilized the expanded gas to enhance further cooling effects, thus lowering compression requirements. Despite lower operating costs, the Air Products plant was only able to produce a maximum of 70 % helium purity. In order to achieve higher purity helium to send overseas, this 70 % helium gas stream was reprocessed in the Linde Plant where 92 % purity could be attained.³⁶
- 3. Construction on the Norton plant (Argon Plant No. 3) didn't begin until early April 1918 and was not completed until October 1, 1918. Manufacturing costs were just over \$148,000 with a capacity of 30,000 cubic feet per day.³⁷ This process, which was the most heavily touted due to perceived low operating costs, was designed to operate with very low compression requirements. This process utilized three expansion engines instead of one, that that of the Claude process. It was believed that the use of three expansion engines that would negate heavy compression requirements would be much more efficient. Despite repeated failures over the course of just under three years, the Norton process continued to draw support from Bureau officials. By April 3, 1919, the Norton process was only able to produce 20 % helium and was finally sold as scrap two months later. The Norton process would ultimately cost more than the Linde and Air Reduction plants combined.

By June 1918 it was clear that Linde Air Products had the superior process and by August it was determined by the Army and Navy that a large, full-scale production plant was going to be required to meet the escalating demand for helium. In addition to new plant requirements, it was also deemed necessary to find new helium-bearing gas fields because the mature Petrolia field was rapidly declining. The Bureau of Mines then began an exhaustive search for helium reserves beginning in June under the leadership of Gaillard Sherburne Rogers (1889–1919) of the United States Geological Survey.

The work carried out by G. Sherburne Rogers was to initially identify, as quickly as possible, new helium reserves to aid the war effort. Natural gas wells from across the country were analyzed only for their helium content (and no other gas) due to

³⁵ Petroleum Investigations and Production of Helium, by Van H. Manning, Bureau of Mines Bulletin 178c, (1919) pp.

³⁶ See Footnote 35.

³⁷ See Footnote 35.

the rush on the war. Throughout this initial research, the maximum helium content discovered was that of Petrolia field in Clay County, Texas. In Rogers' extensive publication, he would write:

As the Survey's (U.S. Geological Survey) investigation was made strictly for military purposes it was necessarily directed toward locating an adequate supply of helium-bearing gas as speedily as possible, and practically no attention was given to the broader scientific problems involved in the origin or ultimate source of the helium. Considerable research will evidently be necessary before this problem can be successfully attacked, and in view of the probable development of commercial aircraft during the coming decade, and the probability that the cost of extracting helium from natural gas will be reduced sufficiently to permit its use in commercial balloons, it has been deemed desirable to present immediately a brief description of the chief sources of helium in the United States. At the same time the writer (Rogers) has endeavored to describe the broader geologic relations of the helium-bearing gas, to discuss various theories of its origin, and to review the reported occurrences of helium in minerals and in other gases, in the hope that such a value to others who may later attempt to solve it.³⁸

Rogers' publication would become the primary resource of helium resources for the government in the years after its release. An extremely proficient geologist, Rogers delicately analyzed the geology of particular areas in order to hypothesize helium's probable origin. Although Rogers' work had been underway since the start of the experimental plants, it would not be released until 1920. It was also Rogers that predicted that the Petrolia field was never going to last at the rate in which it was currently being produced, thus alerting Government officials to negotiate with Lone Star Gas Company to reduce its production rate.

Operations on both experimental plants (Linde Air Products and Air Reduction) would continue throughout the duration of the First World War and by July of 1918 it was well established that large-scale helium processing was going to be a reality. Fair quantities of gas had been produced by both experimental plants. Two small shipments of helium for experimental use were sent to France and Britain early in the year and just prior to the signing of the November 1918 armistice ending the war, a much larger shipment of 145,000 cubic feet³⁹ of 92 % helium, shipped in 750 cylinders, was shipped to the New Orleans docks destined for France. The armistice was signed before this helium ever had a chance to aid the war effort and was shipped back to Fort Worth where it would be stored and later used to fill the first U.S. helium-filled dirigible, the Navy's C-7.

Linde Air Products was awarded the contract for the first full-scale production plant in the United States on October 22, 1918 which was designed to produce 30,000 cubic feet of helium per day from the Petrolia field. Negotiations had already been under way to lease the Petrolia gas from the Lone Star Gas Company and construction of a new pipeline from the gas field to the new Linde facility was quickly under construction in Fort Worth. The armistice ending the First World

³⁸ Helium-Bearing Natural Gas, G. Sherburne Rogers, 1920, p. 5.

³⁹ Helium Gas, Committee on Public Lands, House of Representatives, Washington, Tuesday December 5, 1922, p. 13.

War would be signed on November 11, 1918, just twenty days after the contract with Linde was signed.

Although the war was now over and there was no longer a need for large volumes of helium gas, the Aircraft Board of the U.S. Army made a review of the helium situation and determined that continuing the helium program was in the country's best interest. Four different scenarios were submitted of which "Plan C", with amendments, was adopted. The original "Plan C" which was submitted on December 8, 1918 was as follows:

Operation of plant no. 3 (Norton) for three months	\$36,000
Construction of production plant no. 1 (Linde)	\$1,700,000
Operation of production plant no. 1 for 8 Months, producing 7.2 mmcf helium	\$750,000
Pipeline construction	\$1,800,000
Petrolia gas lease	\$1,500,000
Total expenditures	\$5,786,000
Salvage	\$500,000
Net cost	\$5,286,000
Helium production (cubic ft.)	7,200,000

Although the Norton process had been in operation since October, it had still not been able to produce any helium of significant quality. Regardless, Bureau of Mines engineers firmly believed that helium processing costs could be reduced substantially, and adamantly lobbied for Norton's continued attempts. In addition to this Norton lifeline, it was later recommended by Dr. Van H. Manning (1861–1932), Director of the Bureau of Mines, to continue operations of all three experimental plants so that possible cost-reduction refinements could be explored.

Two days after Christmas 1918, the Secretary of the Navy, Josephus Daniels⁴⁰ (1862–1948), wrote to Van Manning of the Bureau of Mines expressing his intent to discontinue all Government helium experimental work except for the Norton process (apparently the notion of producing ultra-inexpensive helium was too tempting, even for upper Government officials). Daniels plan was adopted and both experimental plants were ordered to be shut down on January 23, 1919. Manning persuaded Daniels to keep the Air Reduction Plant in operation a bit longer, at the company's expense, to test a potential improvement. Despite this extension the Air Reduction plant was never able to make any sort of meaningful improvements and was finally released on April 1, 1919 to the Bureau of Yards and Docks (Navy). Parts of this plant would be used in the first Bureau of Mines purification plant in Langley Field, Virginia.⁴¹

⁴⁰ Josephus Daniels was a newspaper editor and publisher who was appointed Secretary of the Navy by President Woodrow Wilson in 1913.

⁴¹ Helium, Child of the Sun, Clifford Seibel, 1964, p. 48.

Post World War I

Before World War I, helium was selling for \$1,700 per cubic foot (\$1,700,000 per thousand cubic feet) simply because so little of the product existed. No more than 100 cubic feet had ever been sequestered.⁴² The two experimental plants in Fort Worth had been able to produce an amount of helium unimaginable just three years before and at a cost of roughly \$100 per thousand cubic feet.

Despite the end of the war in late 1918, the United States moved forward on the helium program so as not to be caught short again should another conflict arise. Plans on the Linde Air Products production plant would continue without interruption until it finally came on stream in April 1921, under the U.S. Navy's authority. The first four months of operations produced just over 260,000 cubic feet of helium at a cost of \$480 per thousand cubic feet but would later drop to \$174 per thousand cubic feet.⁴³ During the fabrication of the first production plant, it was recommended by the Army, Navy, and the Interior Department to develop a Cryogenic Research Laboratory in Washington D.C. in order to gain a firmer understanding of low temperature natural gas processing to extract helium. On May 21, 1921, just one month after the Production plant began operations, the Cryogenic Research Laboratory was dedicated by Madame Marie Curie, who happened to be in Washington D.C. during a six month visit.

The Cryogenic Research Laboratory would prove to be a very successful program for the advancement of helium research, under the leadership of R.B. Moore and Clifford Seibel. The primary purpose of this research was to scientifically understand the nature of helium during the processing of natural gas in order to achieve cost reductions. The success of lower cost separation depended upon various factors of helium experimentation. According to Clifford Seibel, "it was anticipated that with data obtainable by means of such a laboratory, more efficient plants could be designed for the future. In due course, workers in that research laboratory, established in Washington, D.C., supplied the answers to many questions dealing with such factors as specific heats, phase equilibria, solubility of helium in the liquid components of natural gas, behavior of metals at low temperatures, heat exchange, insulating materials, removal of carbon dioxide from the natural gas, special valves, analytical recorders, and methods of obtaining the necessary refrigeration."44 In addition to this research, it was also recommended by R.B. Moore that underground storage for helium should be tested as well. Between the years 1918–1920, one company had proved the success of underground natural gas

⁴² Hearing: Exportation of Helium Gas, before the Committee on Interstate and Foreign Commerce of the House of Representatives, Sixty-Sixth Congress, Second Session on H.R. 12376, May 21, 1970, p. 28.

⁴³ Helium, Child of the Sun, Clifford Seibel, 1964, p. 50.

⁴⁴ Production of Helium at Amarillo, C.W. Seibel, Industrial and Engineering Chemistry, Vol. 30, No. 8, p. 849.

storage in order to maintain a reserve for high-demand, winter months.⁴⁵ It would be R.B. Moore's incredible insight which would ultimately lead to the usage of Cliffside Field for helium storage decades later.

Another result of the Cryogenic Research Laboratory was the creation of railroad helium purification cars which would enable balloons and dirigibles to remove contaminated air from their gas envelopes. It had been learned through extensive study at this point that while helium would permeate balloon fabric into the atmosphere, atmospheric air would also seep into the balloon envelope. Thus, re-purification of air-contaminated balloon envelopes was a problem that needed prompt attention. In total, three purification railroad cars were built by 1925 which proved to be successful and inexpensive to operate.

The only known use for helium after the War was for balloons and dirigibles so it was still a very high priority for the United States Government, especially as they were to receive three new dirigibles: one to be manufactured in the United States (ZR-1; USS Shenandoah), one from the United Kingdom (ZR-2), and one from Germany (ZR-3; USS Los Angeles) as a result of war reparations. Each of these vessels would require between 1–2 million cubic feet of helium. With height-ened helium activity, it was recommended in a U.S. House of Representatives Hearing on January 22, 1920 to prohibit the export of any helium gas. Secretary of the Navy, Josephus Daniels would write:

Inclosed herewith I have the honor to transmit a draft of a proposed bill to prevent the exportation of helium, the noninflammable gas for inflatable aircraft. The sources of supply of helium in the United States are not numerous and the quantity obtainable is very much limited. This gas is noninflammable and is consequently of inestimable value for balloons of all kinds and especially for those of the dirigible types that the Navy Department is endeavoring under authorization by the Congress to develop and bring to a state of greatest efficiency.

It is manifest therefore that the public interests imperatively require conservation of the supply of this gas, as the demand for it abroad is insistent and great enough to consume, in all probability, within a short time, the available supply in this country.

The accompanying draft of the bill would admit of the control of the supply of this gas so that the interests of the Government would be given maximum of protection so far as affected by this matter.⁴⁶

A large, \$3 million hanger at the Navy Base in Lakehurst, New Jersey was already under construction in 1920 in order to facilitate the manufacturing of the ZR-1 (later USS Shenandoah) and house all three airships.

In 1923, the Bureau of Mines would lose the head of the Cryogenic Research Laboratory, Richard Bishop Moore, who accepted a private industry position at the Dorr Company in New York. Moore would be replaced by Dr. Samuel Colville

⁴⁵ Storage of Natural Gas in the Gas Sand, Handbook of Natural Gas, Henry P. Westcott, 3rd Ed., 1920, pp. 240–250.

⁴⁶ Hearing: Exportation of Helium Gas, before the Committee on Interstate and Foreign Commerce of the House of Representatives, Sixty-Sixth Congress, Second Session on H.R. 12376, May 21, 1970, p.

Lind (1879–1965), a former student of Marie Curie in the Sorbonne, France, who was the leading U.S. authority on radioactivity. During both Moore and Lind's leadership at the Research Laboratory, experimentation for new uses for helium had been actively pursued. Trials such as the treatment of tuberculosis and use in electric lightbulbs had been tested but with no success.

The Age of the U.S. Dirigibles

Prior to any helium activity in the United States, the only gas capable of creating lift for observation balloons, non-rigids, or dirigibles, was hydrogen. Hydrogen was very inexpensive to acquire and its primary method of extraction was the separation of hydrogen from water. As had been proven on countless occasions, the use of hydrogen posed a tremendous risk to anyone involved. Beyond the obvious incendiary bullet, any other possible accidents could cause disaster such as a spark from the engine or a wayward cigarette. In addition, when hydrogen was mixed with air, a violent explosion would ensue.

The United States had been actively involved in the production of balloons for military use but all were designed for hydrogen. This would all change on Monday, December 5, 1920, when the flight of the first helium-filled U.S. Navy semi-dirigible, the C-7, took off from its base and flew over Washington D.C. at 400 feet and returned back home in its maiden voyage. The helium gas used for this flight had come from the 92 % pure gas recovered from the two experimental helium plants in Fort Worth, including the 145,000 cubic feet that had been destined for France prior to the armistice. The flight of the C-7, which required about 197,000 cubic feet of helium,⁴⁷ represented an overwhelming accomplishment by the Army, Navy, and Bureau of Mines as the mere thought of such an undertaking was entirely inconceivable three years prior. The helium in the C-7 was ultimately saved, recompressed, and hauled back to Langley Field for further use.⁴⁸

Between the years 1922 and 1923, the first American-built dirigible, the ZR-1 was under construction at the nearly completed hanger at the Naval airbase in Lakehurst, New Jersey. On October 10, 1923, the ZR-1 was officially christened as a Navy airship, the U.S.S. Shenandoah (Daughter of the Stars). The helium required to fill this ship was roughly 2 million cubic feet, which would be supplied by the new Fort Worth *production* plant which began operations in April 1921. The first flight of a helium-filled rigid airship occurred on September 4, 1923 as the Shenandoah left the hanger at Lakehurst. The Shenandoah would later tragically be torn apart in the air on September 3, 1925. Fourteen out of the total of 43 crew

⁴⁷ Helium Gas, Committee on Public Lands, House of Representatives, Washington, Tuesday December 5, 1922, p. 9.

⁴⁸ USS Los Angeles: The Navy's Venerable Airship and Aviation Technology, William F. Althoff, p. 5.



Photo # NH 98227 USS Shenandoah moored at NAS Lakehurst, N.J., circa 1924-1925

Fig. 5.3 ZR1 USS Shenandoah at NAS Lalehurst, N.J., circa 1924–1925. Source U.S. Navy

members were killed in the incident. Had hydrogen been used, there might have been no survivors (Fig. 5.3).

Richard Bishop Moore would recall a conversation with Colonel E.C. Hall of the Army Air Service, one of the fourteen survivors of the U.S.S. Shenandoah disaster:

Col. Hall:	"If the control car had been attached in a different way to the framework
	and had not broken away, only three or four men out of the total crew
	would have been lost."
R.B. Moore:	"What did you say when you and the other survivors got on terra firma?"
Col. Hall:	"What did we say? Why we turned to each other and said 'thank God for
	helium." ⁴⁹

Shortly before the U.S.S. Shenandoah was completed, construction in Germany began on the third United States dirigible, the ZR-3. Built and paid for by Germany as a result of war reparations from World War I, it was later commissioned by the U.S. Navy, the U.S.S. Los Angeles on November 15, 1924 in Lakehurst, New Jersey. The Los Angeles was flown from Germany to the United States using hydrogen where it was replaced with helium from the Shenandoah. Prior to the Los Angeles maiden U.S. voyage, helium from the Shenandoah had to be removed in order to fill the newer ship. Despite its efforts, the Fort Worth plant (and Petrolia) could not produce enough helium to fill both vessels at the same

⁴⁹ Commercial Production of Radium, Mesothorium, and Helium, R.B. Moore, Industrial and Engineering Chemistry, Vol. 18, No. 2, 1926, p. 211.



Photo # NH 73285 USS Los Angeles moored to USS Patoka during the winter of 1931

Fig. 5.4 USS Los Angeles moored to USS Patoka during the winter of 1931. Source U.S. Navy

time.⁵⁰ A trade-off of helium occurred between ships as one would come in for repairs and vice versa. The Los Angeles would enjoy a long, eight year career in the United States Navy without incident before being decommissioned in 1932. After a very brief return to the skies in 1933, it was ultimately dismantled in 1939 (Fig. 5.4).

The ZR-2, which was the first authorized U.S. expenditure for a purchased dirigible, was destroyed due to a structural failure on August 24, 1921 before it was ever delivered to the United States. The ship, originally called the R-38 and manufactured by the Royal Airship Works in the United Kingdom, used hydrogen when it crashed and caught fire in England, killing 44 out of a crew of 49 (Fig. 5.5).

By October 1924, when the U.S. Army's helium-filled blimp, the TC-2 on its way to Newport News, Virginia, crashed due to the premature explosion of a bomb,⁵¹ the importance of helium as a replacement for hydrogen was confirmed.

⁵⁰ <u>USS Los Angeles: The Navy's Venerable Airship and Aviation Technology</u>, William F. Althoff, p. 47.

⁵¹ Helium Saves Lives, Industrial and Engineering Chemistry, Vol. 16, No. 11, (1924), p. 1200.



Fig. 5.5 Airship R-38 (U.S. Navy ZR-2) on its first trial flight, 23 June 1921. Source U.S. Navy

Four out of a five man crew survived the crash as their helium envelope was severely punctured as a result of the accident. It would be this particular event which would add fuel to the fire for the passing of a proposed Helium Conservation Act which would ultimately streamline Government helium operations.

The Helium Act of 1925

The Helium Conservation Act of March 3, 1925 would represent the first United States law involving helium production since the Government became interested in the product in 1917. The purpose of this Act was to establish a helium production and sales program under the direction of one entity, the Bureau of Mines. The need for a law requiring conservation was a foremost concern because it was estimated that 500 million cubic feet of helium was being wasted annually as a result of non-extraction of particular helium-rich natural gases.⁵² The Bureau of Mines

⁵² Conservation of Helium Gas: Hearings Before Committee on Military Affairs House of Representatives, 68th congress, 1st session. H.R. 5722, 1924.

would now be responsible for all government helium production, including "the purchase, lease, or condemnation of land, conservation of helium gas, construction and operation of helium plants, conducting experimental work, and the leasing of helium under certain conditions."⁵³ The Fort Worth production plant, which had previously been under the Navy's control, would be transferred to the Bureau of Mines under the guidance of Clifford W. Seibel. After this first Helium Act of 1925, the Bureau of Mines (and later the Bureau of Land Management) would continue to manage the Federal Helium program until 1996.

1925 would also represent the year when the first "other" use of helium would be discovered. Helium was found to be beneficial as a replacement to nitrogen in deep sea diving as a way to prevent caisson's disease (the bends) among Navy divers. Using helium enabled divers to stay under water longer and ascend to the surface in shorter periods.

With the Bureau of Mines under full control of the U.S. helium industry, no time was wasted in continuing their search for new reserves and improving laboratory work to facilitate processing. As a result of the second helium survey (1919–1933), three new helium-rich areas were discovered, one of which would become the most important reserve in United States helium history, the Cliffside Field near Amarillo, Texas. The two others would be the only helium-rich areas located on Government lands; all other helium-rich areas would come from private sources. The first, located in Emery County, Utah would become Helium Reserve Number One by executive order on March 21, 1924 and the second, located in Grand County, Utah would become Helium Reserve Number Two by executive order on June 26, 1933.⁵⁴

The U.S. Bureau of Mines would finally meet competition from private industry in 1927 when two plants were erected by the Girdler Corporation of Louisville, Kentucky at Dexter, Kansas and Thatcher, Colorado. Shallow helium-bearing gas at Model Dome in northern Las Animas County, Colorado (Thatcher) was discovered in March 1927 to contain more than 7 % helium and 81 % nitrogen.⁵⁵ Due to the passing of the Helium Act of 1927, very little helium could be used outside of Government entities, which posed a problem for privately funded scientists experimenting with new uses for helium such as asthma treatment, discovered in 1926. These two private plants would go on to produce about 8 million cubic feet of helium from October 1927 until February 1930.⁵⁶ Later, as a result of the Helium Act of 1937, the Government would negotiate to purchase both plants which would later be dismantled by 1944.

⁵³ Helium, Child of the Sun, Clifford Seibel, 1964, p. 73.

⁵⁴ Helium, Minerals Yearbook, C.W. Seibel and H.S. Kennedy, 1934, p. 759.

⁵⁵ Geology of Natural Gases Rich in Helium, Nitrogen, Carbon Dioxide, and Hydrogen Sulphide, C.E. Dobbin, U.S. Geological Survey, 1933, p. 1057.

⁵⁶ Helium, Minerals Yearbook 1934, C.W. Seibel and H.S. Kennedy.

A New Era in Amarillo

By the time the Cliffside field near Amarillo, Texas was discovered in 1924, the gas field at Petrolia was nearing the end of its useful life and by 1927 it became clear that the United States could no longer count on Petrolia to meet any future helium requirements. The fact that helium supplies were believed to be scarce, the Helium Act of March 3, 1927 was established to prohibit the sale of helium to foreign countries and non-governmental domestic use. Until the Bureau of Mines could find another helium producing field that would satisfactorily meet all government requirements, the Helium Act of 1927 would stay in effect for ten more years until the Hindenburg disaster at Lakehurst would help provide a catalyst for change in policy towards foreign helium distribution.

Although the nearby Nocona field in Montague County, Texas was given some consideration to supply the Fort Worth plant in order to continue operations, the Fort Worth plant was ultimately shut down and dismantled in early 1929 when the Amarillo plant became operational (discussed later). During its life of eight years, the plant produced about 480 million cubic feet of helium and towards the end of its life could produce this gas for only \$34 per thousand cubic feet.

The Cliffside field, located in Potter County, Texas was situated on a structure that covered roughly 50,000 acres and contained, on average, 1.75 % helium. This newly discovered field was producing gas at 700 psi (pounds per square inch) and very little gas had been produced since its discovery. After careful geological review, it was estimated that the Cliffside field contained enough helium to last the U.S. Government 100 years. Negotiations by the Bureau of Mines to purchase this field from its owners (and the two companies who leased these properties) began in 1926 and by 1927 and an operating contract was reached covering 20,000 acres, with an option to acquire the remaining 30,000 acres. The drilling for helium gas began in February 1928 followed by the construction of a pipeline from the new plant site to the new wells in July 1928. Construction on the Amarillo Helium Plant, located 7.5 miles west of town, began August 1928 and the first shipment of 200,000 cubic feet of helium was hauled to Langley, Virginia on May 6, 1929. The helium was transported in one of two railroad helium tank cars which were designed by the Bureau of Mines.⁵⁷

Now that the U.S. Navy only had one dirigible in operation (U.S.S. Los Angeles) and the Amarillo Helium Plant was in full operation, helium was no longer a scarce commodity as it was during the passage of the Helium Act of 1927. By December 1929, construction would begin on the largest U.S. dirigible in Akron, Ohio by the Goodyear Zeppelin Corporation. The ZRS-4, later to be christened the U.S.S. Akron, would require 6,500,000 cubic feet of helium. The fact that an airship this large was ever commissioned confirmed the United States'

⁵⁷ Helium Plant Makes Initial Shipment, Industrial and Engineering Chemistry, Vol. 21, No. 6, 1929, p. 524.

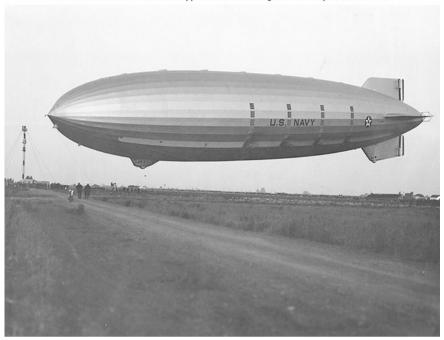


Photo # NH 42156 USS Akron approaches the mooring mast at Sunnyvale, California

Fig. 5.6 USS Akron approaches the mooring mast at Sunnyvale, California. Source U.S. Navy

belief that the helium supply was here to stay. Cliffside field and the Amarillo Plant could produce more than enough helium (Figs. 5.6 and 5.7).

The early 1930s would be a bittersweet period for the U.S. Bureau of Mines. The Amarillo Helium Plant was able to produce an amount of helium inconceivable only years earlier. The four wells which were supplying the Amarillo Plant were flowing at a volume of 30 million cubic feet of gas per day, resulting in over 450,000 cubic feet of helium per day.⁵⁸

While operating seamlessly, the Amarillo plant and their staff would be dealt one blow after another with the loss of the U.S.S. Akron on April 4, 1933 which killed 73 men, and later her sister ship, the U.S.S. Macon, which killed two men, on February 26, 1935, Government demand for helium ended abruptly after these two tragic losses. The loss of life on the Akron dealt a critical blow to the continuation of the dirigible program but after the Macon tragedy, there was little room in the Navy for dirigibles despite efforts by the Navy's Captain Charles E. Rosendahl's (1879–1965) push to continue their service. Therefore, the largest user of helium in the world would only require small volumes to fill smaller, nonrigid blimps and observation balloons. After the loss of the Macon in early 1935,

⁵⁸ Helium, Minerals Yearbook 1934, C.W. Seibel and H.S. Kennedy, p. 759.

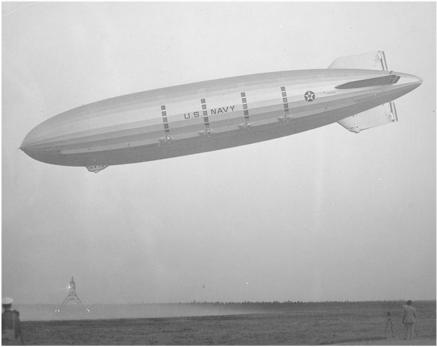


Photo # NH 669 USS Macon arriving at Lakehurst, N.J., June 1933

Fig. 5.7 USS Macon arriving at Lalehurst, N.J., June 1933. Source U.S. Navy

the Amarillo Helium Plant had reduced personnel and operated only intermittently for the rest of the year.

The Government had more helium supply than Government demand after the loss of the Macon and it was decided to "lease" helium gas to private companies in order to keep the Amarillo Plant functioning. Although the idea of a helium lease appears unreasonable due to the easily mobile helium atom, as per the Helium Act of 1927, no government helium could be sold to non-government entities. Therefore a leasing agreement was reached and in 1936, President Franklin D. Roosevelt, approved a lease to the Goodyear Zeppelin Corporation for commercial airship use. According to the Minerals Yearbook of 1937, "the purpose of leasing the government helium was to foster the development of commercial lighter than aircraft and to encourage the training of airship pilots."⁵⁹ In addition to airship use, helium was supplied to the U.S. public health service for use in the treatment of asthma and other respiratory ailments which were aided by the use of helium. The success of helium used in respiratory illnesses soon represented a heavily growing demand.

⁵⁹ Helium, Minerals Yearbook, 1937, C.W. Seibel and H.S. Kennedy.

By early 1937, it was clear that a change needed to be made to the Helium Act of 1927. New uses for helium were appearing quickly and the U.S. Army and Navy did not require anywhere near the output capacity of the Amarillo Helium Plant. Although met with criticism by Government officials who still believed that U.S. Government helium should remain a military asset, the tension became unbearable after the Hindenburg disaster at Lakehurst, New Jersey on May 6, 1937. Had the Germans had access to helium, the ship might have been filled with the non-flammable gas thus saving many more lives. Nevertheless, the incident provided the impetus to amend the Helium Act of March 3, 1927.

The Helium Act of September 1, 1937 was approved four months after the Hindenburg disaster, authorizing the sale of helium gas not needed by the Government. The bill which led to this Act was altered extensively during its time in the House of Representatives and Senate but its passing would ultimately lead to an explosion in helium usage across many scientific and commercial industries. The passage of this Act would also allow non-hostile foreign governments to purchase helium for their own commercial use. Section "Post World War I" of the Act read:

No helium shall be exported from the United States, or from its Territories and possessions, until after application has been made to the Secretary of State and a license authorizing said exportation has been obtained from him on the joint recommendation of all the members of the National Munitions Control Board and the Secretary of the Interior: Provided, That under regulations governing exportation of helium approved by the National Munitions Control Board and the Secretary of the Interior, export shipments of quantities of helium that are not of military importance as defined in said regulations, and which do not exceed a maximum to be specified therein, may be made under license granted by the Secretary of State without such specific recommendation. Such regulations shall not permit accumulations of helium in quantities of military importance in any foreign country,...⁶⁰

The first government to apply for nearly 18 million cubic feet of helium was Nazi Germany which needed helium more than ever if they were to ever reassure the German public that airship travel was safe. Germany's helium requirements were designed to fill the commercial airship, the LZ-130 which was then under construction.

Permission to export this helium to Germany was granted in November 1937 and the German freighter, the Dessau, was sent to the port of Houston, Texas to collect the gas in mid January 1938. The helium, however, would never make it on the German vessel because of only one man in President Roosevelt's Cabinet, Harold LeClair Ickes (1874–1952), the U.S. Secretary of the Interior. Although President Roosevelt felt an obligation to sell this helium to Germany due to the previous authorization, Ickes, who was deeply suspicious of Germany, held firm and refused any helium to leave American shores. Ickes would meet aggressive

⁶⁰ Helium Act of 1937, Public-No. 411–75th Congress, Chapter 895—1st Session, S. 1567, Sect. "Post World War I"

opposition in his pursuit to prohibit the sale. The U.S. Secretary of War, Harry Hines Woodring⁶¹ (1890–1967), would write to Ickes on April 27, 1938:

It is the opinion of this Department that the intent of the Congress by its passage of the Helium Act was that helium, a natural commodity of which the United States has known resources greatly in excess of its own domestic needs, should, for humanitarian reasons, be made available to other nations for commercial uses... Helium in itself is not a weapon but is merely a commodity that possesses certain value when used in connection with certain types of aircraft. In this respect, it is comparable to other commodities such as gasoline when used in connection with bombardment airplanes or tanks. The only known military use for helium is for the inflation of lighter-than-air craft. The military value of such craft, other than possibly that of captive observation balloons, has never been established either in this country or abroad. On the other hand, the military value of heavierthan-air craft has been definitely established. The ever-increasing efficiency and wide ranges of use of the latter are causing them to supplant all other means for aerial operations. The War Department has definitely abandoned the idea of employing airships in military operations... The diminishing military value of helium is evident... While hydrogen is highly inflammable...its greater buoyancy gives a craft added lifting power and greater maneuverability. Even though helium is non-inflammable, it is still debatable as to which of the two gases possesses the greater value for military operations. Regardless of the inflating agent, however, lighter-than-air craft are highly vulnerable to gunfire and their destruction is a comparatively easy accomplishment.⁶²

Despite numerous hard fought attempts by members of the U.S. Government to allow the sale, including a push by President Roosevelt who lacked the legal authority to bypass the Secretary's verdict, Ickes would simply not budge, saying "if helium has no military importance, why is a Zeppelin authorized for our own Navy?"⁶³ The allotment of 18 million cubic feet to Germany then expired on November 1, 1938. The Dessau, which had been docked in Houston since the beginning of the year would be sent back to Germany empty-handed in mid December. Harold Ickes would later feel vindicated after Germany invaded Poland in September 1939.

During the helium controversy of 1938, Bureau of Mines operations continued to supply helium to U.S. private parties selling more than 800,000 cubic feet through 20 private party contracts. In order to promote the private use of helium, the Bureau sold helium to pre paying customers at slightly higher than production cost. Slightly lower prices would be given to medical and scientific users. By the end of the year, the Bureau would once again control a complete monopoly of the helium industry when they acquired the Dexter, Kansas and Thatcher, Colorado properties from the Girdler Corporation on November 3, 1938.

During the year 1938, most of the mere 117,000 cubic feet destined for public use was to be used in medical facilities for the treatment of asthma. The method of using helium mixed with oxygen for asthma (and other respiratory

⁶¹ Harry Hines Woodring was the Governor of Kansas from 1931 to 1933 and the U.S. Secretary of War from 1936 to 1940 under President Franklin D. Roosevelt.

⁶² The Helium Controversy, American Civil-Military Decisions, 1963, p. 50.

⁶³ The Helium Controversy, American Civil-Military Decisions, 1963, p. 53.

ailments) was developed by American physician Dr. Alvan L. Barach (1895–1977) who had achieved great success with its use. The 1938 Minerals Yearbook best describes helium's usage as (derived from Dr. Barach's statement to the House of Representatives):

Helium is useful in the treatment of sufferers from asthma and for infants and children suffering from laryngitis, croup, or diphtheria, where the windpipe is constricted. The travel of gases through narrow orifices requires a pressure for a certain velocity of the gas that is inversely proportional to the square root of the weight of the gas. Therefore, breathing air requires approximately twice as much effort as breathing a helium-oxygen mixture. Owing to the high cost of helium in the past, some patients with asthma have died because of lack of helium for treatment. Where helium has been available, not a single patient has been lost, and five cases usually classified as "fatal" have been restored by the use of helium. This work has been confirmed by the Mayo Clinic and the Lahey Clinic.⁶⁴

World War II

During the U.S. fiscal year 1939 (July 1, 1938–June 30, 1939⁶⁵), the private sector demand for helium would increase to over 1 million cubic feet representing nearly 30 contracts, all of which would be supplied by the Amarillo helium plant. Although the majority of this private helium would go to the Goodyear Tire & Rubber Co. for the inflation of blimps, over a quarter of this supply went to medical and scientific purposes. In this year, the Federal Government would be supplied with over 5.2 million cubic feet of helium gas.⁶⁶

The use of helium for use in deep-sea diving would receive accolades when its importance in diving was revealed during the salvage of the Navy submarine, the Squalus (SS-192), in late fall 1939.⁶⁷ During a test dive on May 23, 1939, the Squalus suffered a valve failure, partially filled with water, and sank 240 feet to the ocean floor. Mounting a large rescue effort, the Navy replaced nitrogen with helium in breathing mixtures to allow for the extended diving required for the deep waters. Four divers would earn the Medal of Honor for the rescue of 32 Navy sailors and 1 civilian. The officer in charge of this operation was Charles Bowers "Swede" Momsen who led the Navy's experimental diving unit. It was Momsen's new decompression tables substituting nitrogen with helium which made this mission successful.⁶⁸ Helium was the only gas that allowed these divers to stay at these depths for extended periods of time without the occurrence of nitrogen narcosis (the bends) (Fig. 5.8).

⁶⁴ Helium, Minerals Yearbook, C.W. Seibel and H.S. Kennedy, 1938, pp. 974–975.

⁶⁵ Before 1976, the United States fiscal year was July 1 to June 30.

⁶⁶ Helium, Minerals Yearbook, C.W. Seibel and H.S. Kennedy, 1940, p. 1104.

⁶⁷ See Footnote 66.

⁶⁸ In 2000, the Secretary of the Navy announced the naming of the 42nd ship of the Arleigh Burke class of guided missile destroyers after Navy Vice Admiral Charles Bowers Momsen. The ship "Momsen" was commissioned on August 28, 2004 in Panama City, Florida.

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Photo # NH 57510 "USS Squalus (SS-192)"
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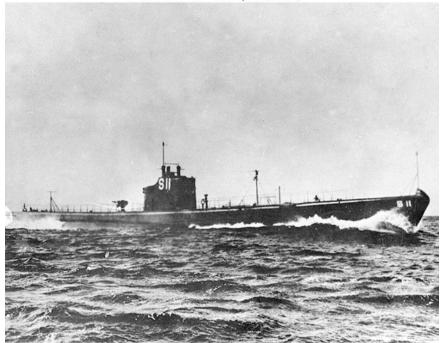


Fig. 5.8 USS squalus (SS-192). Source U.S. Navy

After Germany invaded Poland in September 1939 but before the U.S. involvement in the war, U.S. military requirements for helium would finally begin to see an increase surpassing the capacity of the Amarillo helium plant. Helium's importance to the national defense program was noted in mid-1941, leading to an appropriation for the expansion of the Amarillo helium plant and finding additional helium resources. The Navy (and other government agencies) had estimated that helium requirements might reach 50 million cubic feet per year thus requiring a rapid expansion of current helium operations. The expansion of the Amarillo helium plant would provide a maximum of 36 million cubic feet of helium per year, far less than the estimated requirements. Another plant was needed to makeup for this pending shortage.

It did not take long for the Bureau of Mines to identify the next Government helium source. Congress had appropriated an additional \$1.25 million in 1941 for the construction of a new Government plant to be located near the small town of Masterson, Texas (Exell Plant) which would process gas from the southwestern portion of the Panhandle field which contained, on average, 1 % helium. The capacity of this plant, which was to be completed by 1943 would be able to supply an additional 24 million cubic feet of helium per year. Throughout 1941, private demand for helium had exceeded 2.7 million cubic feet of helium and perhaps its greatest "new" need was for magnesium welding which provided far superior welds in airplane manufacturing. The use of helium for welding provided an "inert atmosphere" which prohibited the possible contamination of atmospheric air within the weld.

When the United States entered the war in December 1941, the Government had determined four months later that their helium requirements would reach upwards of 130 million cubic feet per year, a 160 % increase over the course of a year. By June of next year, they increased their estimated requirements to 230 million cubic feet per year. The combined output of both the Amarillo and Exell plants would only be 60 million cubic feet per year, and the Exell plant would not even finish construction until 1943. Clearly, more helium resources and plants were needed.

A break would occur in the early part of the war when the Rattlesnake field near Shiprock, New Mexico (Navajo Reservation) was discovered to contain an enormous non-combustible, high-pressure gas containing over 7.5 % helium. The highest concentration of helium ever found until this time was only approaching 2 % helium. The Continental Oil Company had drilled this well to 6,950 feet when the non-combustible gas was found and the decision was made to plug the well. After the gas analysis was received on July 1, 1942, a contract was made with the Bureau of Mines to take financial responsibility over the field and associated leases. Despite the fact that Continental had spent over \$100,000 in drilling the well, the Bureau of Mines obtained the well and ownership of 7,800 leased acres for only \$1.⁶⁹ The Rattlesnake field was considered a tremendous discovery considering the enormous demand for wartime helium.

Less than ten months after breaking ground on the new plant site, the Exell plant began operations on March 13, 1943, barely in time to meet the growing military demand. The gas supplying this plant was gathered from the Channing area (Moore, Potter, Oldham, and Hartley Counties, Texas) of the Panhandle field, which contained an average 1 % helium concentration. The month of July 1943 would see production from both plants reaching 12 million cubic feet which was beyond their rated capacities of 8 million cubic feet per month. Although still not enough to meet military demand, appropriations for three more plants were authorized for Otis and Cunningham, Kansas and Shiprock, New Mexico to process helium-rich gas from these areas. Construction would begin immediately in early 1943.

The addition of these three additional plants would provide a boost to United States helium production immediately after their successive launches. The first of the three plants to be put on production was the Otis, Kansas plant which was brought online in October 1943. The Cunningham plant would go on production in

⁶⁹ Helium-Bearing Gas Lands in the Navajo Indian Reservation, N. Mex, 80th Congress, 1st Session, Document No. 212, U.S. House of Representatives, 1947, pp. 7–8.

January 1944 and the Shiprock plant in March 1944. With each of these new plants on production, over 137 million cubic feet was produced in the fiscal year 1944 (July 1, 1944–June 30, 1944⁷⁰) which amounted to a 220 % increase from 1939.

When World War II came to an end in 1945, the U.S. military had been furnished with enough helium to meet all wartime demand thanks to the rushed work of the U.S. Bureau of Mines. Helium's role in World War II proved to be an extremely important resource. In its lighter-than-air properties, helium's use was best stated by Rear Admiral Charles E. Rosendahl, "In all, blimps escorted 89,000 surface craft in World War II without a single loss to enemy submarines. Of these, 50,000 were in areas where U-boats were known to be present at the time."⁷¹ The other uses during the war, as previously mentioned, would far exceed helium's use as a lifting medium in the years to come. In a letter from the Secretary of the Interior to Joseph W. Martin, Jr., the Speaker of the House of Representatives, the following text highlights helium's importance:

Helium played a very important, although little known, role in the winning of the war just ended. Helium-filled blimps were extremely effective weapons in the subjugation of the enemy submarines that menaced the Atlantic shipping lanes. Helium likewise facilitated the fabrication of magnesium and other metals by making possible the use of welding processes. Finally, helium was used in the production of atomic energy. The nature of that use is, of course, secret.⁷²

It was little known during the Manhattan project in Los Alamos, New Mexico that helium would play such a vital role in the creation of the atom bomb. Without helium, there would have been no atom bomb.

Production Explosion

By the end of the war, demand for helium had dropped precipitously thus leading to the operation of only the Exell plant. After only 18 days of operation beginning in March 1944, the Shiprock plant was placed on standby status pending further notice due to the slackened demand. The Cunningham, Kansas plant would be dismantled in July 1945 because the gas field supplying this plant was inadequate to justify further operation. Lastly, the Otis plant in Kansas was placed on standby the following month.

As all plants had been operating towards the end of the war when helium demand was slackening, the Bureau of Mines began a helium conservation program in January 1945 by injecting surplus helium into the Cliffside field. Immediately

⁷⁰ July 1 to June 30 was the United States fiscal year prior to 1976.

⁷¹ Personal Files of Captain Charles E. Rosendahl, University of Texas at Dallas.

⁷² Letter from the Secretary of the Interior, House of Representatives, 80th Congress, 1st Session, Document No. 212, April 21, 1947.

before the Cunningham and Otis plants had been removed from production, over 20 million cubic feet had been injected in Cliffside from January to June 30, 1945. Just as Richard B. Moore had envisioned years earlier, a one-of-a-kind underground storage facility was created.

Although only the Exell plant remained in operation throughout the end of the 1940s, helium had continued to be conserved in the Cliffside structure. By the end of calendar year 1947, over 69 million cubic feet had been injected underground. More helium was available to supply non-Government users of which 16 million cubic feet was supplied in 1948.

A technological breakthrough would occur in 1949 with the usage of activated charcoal at liquid nitrogen temperatures to achieve 99.95 % (Grade-A) pure helium, which was the highest grade of helium ever produced. Prior to 1949, only purities of 98.3 % could be achieved. Nearly half of the Exell plants production in 1949 was Grade-A helium. Helium of this purity was extremely effective in creating a pure atmosphere in electric arc welding, where minute impurities could damage the integrity of a weld.

Demand for helium began to increase during the close of 1949 and early 1950 which was adequately met by the operation of the single Exell plant. By the middle of 1950, however, demand for helium soared nearly 50 % primarily because of the production of Grade-A helium and its desirability for welding. The supply shock prompted the re-activation of the Amarillo plant by August of 1950 to bridge the gap before the Otis, Kansas plant could be ready for re-activation. The Otis plant would begin operation again in March 1951 while the Shiprock (Rattlesnake field), New Mexico plant would remain in standby condition despite Government increases due to the Korean War conflict (1950–1953).

The Exell, Otis, and Amarillo plants continued to operate until further escalation in demand required the re-activation of the Shiprock (Rattlesnake field) plant in 1953. With all four plants in operation in 1954, over 190 million cubic feet of helium was produced during the calendar year while also beginning a withdrawal of some conservation helium from Cliffside field. During this year another important source of helium-bearing gas containing nearly 2 % helium would be noticed by the Bureau of Mines.

The Keyes field of Cimarron County, Oklahoma, which was mostly controlled by the Colorado Interstate Gas Company of Colorado Springs, contained an enormous supply of gas and a feasibility study was quickly authorized in August 1954 to determine its potential. The primary problem with the Keyes field was its high nitrogen content which required removal if the natural gas was to be supplied to consumers. Therefore, a joint venture would be required to clean up two valuable products in the Keyes gas stream, methane and helium.

During the summer of 1955, the Rattlesnake field would ultimately fail due to the encroachment of water during gas production⁷³ and would represent one of the largest disappointments in the United States helium program. In its initial discovery,

⁷³ Helium, Minerals Yearbook, Mark K. Royston and Henry P. Wheeler, Jr., 1956, p. 444.

Bureau of Mines engineers believed that the Rattlesnake field contained roughly 800 million cubic feet of helium. After only 18 days of operation, it was placed on standby status in March 1944. The placement of the plant in standby condition meant that the Navajo Reservation would not be receiving royalty payments from the production of helium on their lands. After continued negotiations, a settlement was reached by the Navajo Reservation and the Department of the Interior where the Government would prepay a royalty based on total calculated reserves so that the plant and wells could be placed in standby until needed. Thus, the Rattlesnake field which had been placed on full production in 1953 until its end in mid 1955,⁷⁴ produced a mere 42 million cubic feet of helium, far below the calculated reserve of 800 million cubic feet. The Government helium plant at Shiprock would briefly begin operations again in July 1955 with the addition of a privately-owned gas well in the nearby Hogback field (New Mexico).

Helium demand in 1955, although met by the four producing Government helium plants, escalated dramatically. It was recognized by the Bureau of Mines that massive volumes of helium were being wasted through the production of gas that was not connected to any Government plant. The demand for Grade-A helium would soon reach a critical stage resulting in the appropriation of \$6 million for the expansion of the Exell plant, increasing its capacity by another 150 million cubic feet of helium per year which was expected to come on stream by April 1957.

Continued escalating demand for the next few years required Cliffside storage withdrawals in order to cushion the inadequate production. In 1957, 291 million cubic feet had been produced while another 22 million cubic feet had been withdrawn from Cliffside, leaving only 24 million cubic feet left in the storage field. Exell's expansion would come on line two months later than planned on June 2, 1957. In addition, a new source of helium-bearing gas was found near Otis, Kansas which helped to alleviate some of the supply issues. Despite the increased production, demand far outweighed supply leaving the Bureau of Mines to institute an "informal" allocation system allowing only "essential purpose" users get first call on the product. A helium triage unit was thus established. By 1958, the Macy's Thanksgiving parade in New York had no helium to inflate their balloons and were filled with air.

As negotiations with the Colorado Interstate Gas Company became tenable by both parties, a contract was signed in April 1958 for the exclusive rights to process helium out of the natural gas which was owned by the Company. An appropriation of \$18 million was delivered in August 1958 for the construction of a new plant to be located at Keyes, Oklahoma. The Fluor Company of Los Angeles was awarded the contract and construction on the \$12 million plant began by the end of the year.

⁷⁴ Numerous engineering studies were made on keeping the Rattlesnake field alive after being shut-in in the summer of 1955. It was even considered a "conservation" field in 1956. By September 1957, through the re-working of wells, it was deemed likely that no recoverable gas from Rattlesnake would be recovered.

One month after the contract with the Colorado Interstate Gas Company for the Keyes Gas field helium was signed (April 1958), a conservation policy was proposed in order to manage the current supply issues that the Bureau of Mines was facing. An estimated 4 billion cubic feet of helium was being lost annually,⁷⁵ especially from the giant Hugoton gas field which spanned from the Texas panhandle all the way into southwestern Kansas. Although the helium content in this gas field was 1 % or lower, the gas was marketable enough to burn thus wasting precious helium every time, for example, when a stove was turned on to boil water. The conservation policy was designed to encourage the participation of private industry to construct and manage new helium plants to process helium that would normally be wasted. By August, the conservation bill was introduced to Congress to amend the Helium Act of 1937. It was hoped that such an Act would conserve over 50 billion cubic feet of the precious commodity.

The severe helium shortage came to an abrupt end when the Keyes plant became operational in August 1959, only nine months after breaking ground. Supply became so abundant, in fact, that the Bureau was able to store 108 million cubic feet at Cliffside by the end of the 1959 fiscal year (June 30, 1960). In addition, the Shiprock, New Mexico plant resumed operations in July and a new large field at Pinta, Arizona was discovered to contain 8 % helium (and 90 % nitrogen) from a shallow formation (780–1,200 ft). The operator of this Pinta Dome field, Kerr-McGee Oil Industries, Inc. began construction on the first private plant since the Girdler plants were acquired in 1937. The additional Arizona plant and reserves, however, were not considered to have a sufficient impact on forecasted helium demands.

The Helium Act of 1960

The helium conservation bill, despite two years in Congress, was approved on September 12, 1960 by Congress and President Dwight D. Eisenhower and became effective on March 1, 1961. Private participation in the new conservation program was requested in October 1960 resulting in proposals from 14 different companies. The terms of the new Act would enable the U.S. Government to purchase helium (under contract) from private crude helium plants and store it for future use in the U.S. Governments Cliffside Field. Further helium refinements to Grade-A purity would be processed in the Government's Exell or Keyes plant.

The 1960 Act allowed the Department of the Interior to borrow (from the U.S. Treasury) up to \$47.5 million per year to purchase helium from private sources based on 22 year take-or-pay contracts.⁷⁶ Using a fixed price, the conservation

⁷⁵ Helium, Minerals Yearbook, Harold W. Lipper, 1959, p. 474.

⁷⁶ A take-or-pay contract is formed between a supplier and a purchaser. In this contract, a purchaser can either "take" the product from the supplier "or pay" the supplier a penalty if they do not take the product. Take-or-pay contracts are common in the energy industry, especially gas products.

program was designed to be fully self-sufficient and self-liquidating to cover all operating costs, helium cost, and interest on the Treasury loans. It was estimated that the Bureau of Mines could stockpile 52 billion cubic of feet of helium by 1985, thus solving any long-term helium demand issues. Section 15 of the Helium Act reads:

It is the sense of the Congress that it is in the national interest to foster and encourage individual enterprise in the development and distribution of supplies of helium, and at the same time provide, within economic limits, through the administration of this act, a sustained supply of helium which, together with supplies available were expected to become available otherwise, will be sufficient to provide 40 central government activities.⁷⁷

The plan, at first glance, was a very simple one. After the crude helium was purchased by the U.S. Bureau of Mines, the helium would enter Cliffside field for storage and some would be processed by Government helium plants to produce Grade-A helium. In order to fully service the Treasury debt, the wholesale price the Bureau would sell helium was raised from \$19 (for Federal Customers⁷⁸) to \$35 per thousand cubic feet. This price increase, established to pay off the helium debt in 25 years, essentially *doubled* the price any user would pay for helium. The Bureau would also nearly maintain a Government monopoly on helium production because the contracted crude helium refiners on the pipeline (contractually) could not sell any commercial helium to end users. However, any private plant that was not under contract with the Bureau of Mines could sell to any third party. The Bureau's primary (and flawed) assumptions with the passing of this Act were:

- 1. All U.S. helium produced would be purchased and sold by the Federal Government.
- 2. Both Federal and private demand would continue to escalate.

The first five plants were awarded to four different companies in mid 1961 with construction beginning immediately. The contracts were awarded to:

- 1. Northern Helex Company (a subsidiary of Northern Natural Gas Company) was awarded a contract August 15, 1961 to be located in Bushton, Kansas.
- 2. Cities Service Helex, Inc. (a subsidiary of Cities Service Company) was awarded a contract August 22, 1961 to be located in Ulysses, Kansas
- 3. **National Helium Corporation** (a subsidiary of Panhandle Eastern Pipe Line Company and National Distillers & Chemical Corporation) was awarded a contract on September 13, 1961 to be located in Liberal, Kansas.
- 4. **Phillips Petroleum Company** was awarded contracts for two plants on November 13, 1961 to be located in Dumas, Texas and Sherman County, Texas.

In order to connect these private plants to the Cliffside field where crude helium would be stored, the Bureau of Mines contracted for an \$8 million, 450-mile

⁷⁷ Unique Helium Resources are Wasting, Report to Congress, March 7, 1979.

 $^{^{78}}$ In 1960, 75 % of all helium consumption was by the Federal Government. The price established for private parties was \$15.50 prior to the 1960 Act.

pipeline in September 1961 which was expected to become functional by July 1962. The plants along this pipeline would first extract helium from the natural gas stream then return the helium-free natural gas back to the companies to sell to the company's customers.

Northern Helex at Bushton, Kansas and Phillips at Sherman County, Texas were the first two conservation plants to come on stream in December 1962, delivering over 2 million cubic feet of crude helium to the Government pipeline before the end of the year. The three other plants would come on stream in 1963, the largest being National Helium's Liberal, Kansas plant which was designed to produce 5.8 million cubic feet of helium per day. The price that the Bureau of Mines paid for their crude helium product ranged from \$10.30 to \$11.78 per thousand cubic feet.⁷⁹

By November 1962, the private Kerr-McGee plant in Pinta Dome, Arizona came online representing the only company who did not have any contract with the Federal Government over the sales of helium. The helium produced by Kerr-McGee would ultimately find its way to non-Government users on the west coast of the United States.

Another resource outside the United States, representing the first non-U.S. helium resource to be revealed outside U.S. borders,⁸⁰ was a non-combustible gas was found near the town of Swift Current, in southwest Saskatchewan. The discovery well (B.A. Wilhelm #1–9), drilled in October 1958, revealed a helium content of 1.9 % with the residual being primarily nitrogen (96.6 % Nitrogen). A small plant with 12 million cubic feet of gas annual capacity was built by Canadian Helium Ltd. (company formed by British Oxygen Company "BOC" and Air Liquide) which came on stream in December 1963. Another Canadian discovery by Texaco in the Wood Mountain⁸¹ (1.38 % helium) area of Saskatchewan province coupled with the Swift Current reserves were believed to satisfy all Canadian demand through the year 2000.⁸² The Swift Current plant would shut down permanently in 1977 after 14 years in operation. The Wood Mountain helium would never be produced.

The increased United States helium activity due to the 1960 Act resulted in enormous volumes of crude helium to be injected into Cliffside field. Although Government demand was increasing rapidly, especially due to the nation's space race, the \$35 per thousand cubic feet charged by the Bureau of Mines was high enough to create private competition which could produce and sell Grade-A helium at lower cost. By 1964, construction was underway on a new private plant

⁷⁹ Worlds biggest helium plant opens, Oil and Gas Journal, Gene Kinney, September 30, 1963, pp. 54–66.

 $^{^{80}}$ It was believed that the U.S.S.R. had their own helium resource and were capable of meeting all Russian demand.

⁸¹ The Saskatchewan Wood Mountain project is soon to be on production by our company, Weil Helium, LLC.

⁸² Canadian helium to lose present markets in Europe, Oilweek, November 1, 1965, p. 14.

in Otis, Kansas that would produce 1–2 % helium gas from the Reichel field in Rush County, Kansas. The plant, owned by Kansas Refined Helium Company, was designed to produce 180 million cubic feet of helium per year. Later, in 1966 another private plant in Elkhart, Kansas was built and operated by Alamo Chemical Company and Gardner Cryogenics to process gas from the Greenwood field in Southeastern Colorado/Southwestern Kansas.

By 1967, three private plants (Navajo, Otis, and Elkhart) which were capable of producing Grade-A helium (gaseous and liquid), were selling helium to commercial users at a significant discount to Bureau's price of \$35 per thousand cubic feet helium. Under the terms of the 1960 Helium Act, all Government agencies were obligated to purchase helium from the Bureau of Mines at the established \$35. Government demand during the late 1960s would begin to wane due to Government cutbacks related to the Vietnam War. In addition, the January 1967 fire in the Apollo 1 at Cape Kennedy⁸³ (later Cape Canaveral) which claimed the lives of three astronauts, would sharply reduce NASA's helium requirements for the remainder of the year. Virtually all of the helium supplied to non-Government users was purchased from the three private helium plants. The Swift Current, Saskatchewan plant was also enlarged to a capacity of 36 million cubic feet per year to meet Canadian demand (some of this gas was exported to Japan and other Asian countries⁸⁴).

All five of the Government-owned helium plants were in operation at the beginning of 1968 but due to dwindling reserves and associated high costs, the Government Otis, Kansas plant ceased operations in April 1968 and ownership of the Shiprock, New Mexico plant was transferred to the Navajo tribe in July 1968. During the year, four more private plants would come on stream making a total of 16 plants producing both crude and Grade-A helium. Cities Service Cryogenics built a crude helium facility in Scott City, Kansas which utilized a private pipeline to carry crude helium to the company's facility in Ulysses, Kansas, where it would be further refined to Grade-A. (Cities Service installed a purification and liquefaction facility in Ulysses during the year). The other three private plants, two in Arizona and one in Amarillo, Texas were also in operation by the end of the year. With seven private plants in operation in 1968, the likelihood of any purchaser (besides Government agencies) to buy expensive \$35 helium from the Bureau of Mines was unlikely. The established \$35 price mandated by the 1960 Act did not take into account advances in technology which allowed private companies the opportunity to offer a better price.

By the end of 1969, it was readily apparent that helium sales were continually declining with the peak helium sales occurring in 1966. Although exports had increased to roughly 60 million cubic feet, operations at four private plants would cease by the end of 1969. All three private Arizona plants and the new Linde Amarillo plant would

⁸³ The Apollo I had a cabin fire during launch rehearsal on January 27, 1967 claiming the lives of Virgil I. "Gus" Grissom, Edward H. White II, and Roger B. Chaffee.

⁸⁴ USGS Minerals Yearbook 1967.

either be abandoned or non-operating. The following year, the Government Amarillo Helium Plant which had been in operation since 1929 was closed on April 15, 1970. A portion of the facility was still used for loading smaller helium canisters for distribution.

Termination of Contracts

The early 1970s would see a dramatic increase in United States helium exports to foreign countries. A 130 % increase in exports occurred from 1970 to 1971. Helium demand in foreign countries would ultimately result in foreign helium extraction units for the first time since Canada's entry in 1963. A helium-bearing field in Poland was discovered (0.4 % helium) and a contract to design a plant was signed by the end of 1971 (The Odalanow Poland plant came on stream in 1977). The same year another plant near Paris, France was producing 7 million cubic feet per year.⁸⁵

Despite the aggressive foreign demand for helium, the United States which was suffering from an economic slowdown in the early 1970s, would continue to see declines in domestic helium sales. In addition, a lowering of the borrowing allotments by the Treasury to the Department of the Interior resulted in delayed payments to the Conservation plants (which would spark a lawsuit by Northern Helex in December 1970 for breach of contract). Without the large federal demand for helium, the Bureau of Mines helium program debt burden grew to \$210 million by the end of the fiscal year 1970. The forecasted revenues in 1961 were roughly \$120 million short in 1970 due to the presence of lower-cost private helium producers and lower Government demand.⁸⁶ Private producers were able to sell Grade-A helium to private end-users for about \$21, which was \$14 lower (per thousand cubic feet) than the Government sales price.

It became clear that the Department of the Interior could not continue with the Conservation program established in 1960. As the former Bureau of Mines director John F. O'Leary put it, "the program is a goddam waste of money. Its that simple."⁸⁷

On January 26, 1971, the Secretary of the Interior made a determination that the conservation program was no longer necessary to meet the objectives of the U.S. helium program. All Government helium requirements had been fulfilled by Government plants which meant that the primary purpose of the 1960 Act had been satisfied. The 1960 Act which read, "a sustained supply of helium which, together with supplies available were expected to become available otherwise, will be *sufficient to provide for essential government activities.*" A total of 28.5 billion

⁸⁵ USGS Minerals Yearbook 1971.

⁸⁶ Federal sales were 264 thousand cubic feet in 1970 compared with 684 thousand cubic feet in 1967.

⁸⁷ The Great Balloondoggle, Time Magazine, June 7, 1971 (online).

cubic feet of crude helium had been stored in Cliffside since the conservation program began thus allowing the interpretation of the Act being "sufficient to provide for essential government activities". The four conservation companies were notified that their contracts would terminate on March 28, 1971.

The termination of the conservation contracts would ignite a flurry of lawsuits both by the four companies directly affected by the termination and by landowners who would no longer be receiving royalty payments⁸⁸ for helium extracted. The damages estimated by the conservation companies were roughly \$375 million, of which they felt the Government should be held responsible. Despite two years of legal wrangling, the Bureau of Mines discontinued accepting helium on November 12, 1973, thus officially terminating the conservation contracts. This termination would result in the unfortunate loss of 2.2 billion cubic feet of helium per year through either venting or wasted in the burning of fuel gas. In order to prevent the wastage of precious helium gas, the Bureau of Mines in 1975 offered the use of Cliffside field, for a storage fee, for private storage of helium gas (a description of the Cliffside Field is located at the end of this chapter). Northern Helex would be the first to take advantage of this arrangement in September 1975, storing about 600 million cubic feet of helium per year.

From the mid 1970s until the end of the decade, the United States would no longer maintain the status of sole world exporter of helium. Although the helium content was quite low, new production was established near Paris, France and a new facility in Odolanow, Poland became operational in 1977 (Odolanow is still in operation today). Another small plant in Orenburg, Russia would come online in the same year. As United States exports continued to grow throughout the late 1960s and 1970s, economic extraction of low concentration helium became feasible due to the quantities of gas being processed. Production at the Swift Current, Saskatchewan plant would come to an end in 1977 due to water invasion⁸⁹ and reserve depletion.

In the United States, the Kerr-McGee Navajo, Arizona plant would be shut down in 1976 because of diminished reserves but a new helium resource was identified in the newly discovered Dineh-bi-Keyah field in Apache County, Arizona which was estimated to contain 1.3 billion cubic feet of recoverable helium. In addition, a large (world's largest in 1979) helium purification plant developed by Union Carbide Corporation (now Praxair) was brought on production in 1979 in Bushton, Kansas to process crude helium from the Northern Helex Company.

⁸⁸ Landowners who own the "mineral rights" on their property are entitled to negotiated royalties on any product produced from their land free of cost. In many cases, the landowner (surface owner) does not own the mineral rights under the surface and is thus not entitled to royalty payments. Only the mineral owner earns royalties. On Federal lands, the United States Government owns the minerals and are entitled to royalty payments as well.

⁸⁹ In many cases, near the end of a field's productive life, more and more water is produced out of the formation displacing gas. When this happens, the wells are usually plugged because the cost of separating the water from the gas exceeds the revenue derived from the gas sales.

While tremendous advances were being made by private helium producers, the helium debt incurred by the Federal Government by July 1, 1976 would reach a staggering \$412 million (and interest of \$24 million) to be serviced by a mere Government net income of \$1 million from helium sales.

Near the end of the decade, the most important American helium industry event to occur since the Hugoton, Kansas production was the discovery of the Tip Top field in Sublette County, Wyoming by Mobil Oil. The field had actually been discovered in 1962 but had been shut-in due to the poor composition of the gas (66% CO₂, 21 % Methane, and 5 % Hydrogen Sulfide). The helium content, a relatively high 0.6 %, was (on average) higher than the giant Hugoton field and the estimated recoverable helium in this field was over 42 billion cubic feet of gas. As a result of this discovery, Mobil (later ExxonMobil), the developer of the field and manufacturer of the processing plant would become the largest single domestic producer in the United States since production began in 1986.

Mobil began drilling the Tip Top field in 1978 for methane recovery but extensive processing was required to make the gas marketable. First the hydrogen sulfide (H₂S), which is a very poisonous gas, had to be removed, then CO₂, and lastly nitrogen before any methane sales could be monetized. At the time, there was no market in the area for CO₂, which is used for enhanced oil recovery,⁹⁰ meaning that all non-combustible gases (including the CO₂) were vented into the atmosphere during processing. Negotiations between Exxon and the Federal Government (the ExxonMobil field is located on Federal Lands and royalties are owed to the U.S. Government) began in the early 1980s to pursue the extraction of helium.

Helium extracted from Federal lands, as per the Minerals Leasing Act of 1920 required that all helium found on Federal Lands must be sold to the United States Government at a stipulated price. This 1920 Act was written shortly after World War I when helium was still considered of extreme military importance. Section 181 of Chapter 3A, Subchapter 1 reads:

The United States reserves the ownership of and the right to extract helium from all gas produced from lands leased or otherwise granted under the provisions of this chapter, under such rules and regulations as shall be prescribed by the Secretary of the Interior: Provided further, That in the extraction of helium from gas produced from such lands it shall be so extracted as to cause no substantial delay in the delivery of gas produced from the well to the purchaser thereof.

Therefore, no incentive existed to produce helium from Federal lands unless the price paid for the gas was high enough to warrant extraction. After years of negotiations between Exxon and the U.S. Bureau of Mines, a contract was established and Exxon began construction of a helium extraction and purification plant at their Shute Creek facility in Lincoln County, Wyoming in the early 1980s. Helium production at

 $^{^{90}}$ Enhanced oil recovery is a method to enhance oil production by injecting CO₂ (or Nitrogen) into the flanks of a field to lower the viscosity of the oil to make it "flow" into the producing wellbores. Many oil fields who use CO₂ for enhanced oil recovery are able to extract sizable additional reserves which would otherwise not be producible.

Shute Creek began in October 1986 with the capacity to produce 1.5 million cubic feet of helium per day (roughly 540 million cubic feet of helium per year).

By the end of the 1980s, Government involvement in the helium industry was beginning to appear irrelevant and a push began to privatize the industry. Although many factors played a part in the desire to rid Government involvement in helium, the fact that private usage far exceeded Government usage must have played a large role (recall that at the time of the 1960 Act, 75 % of helium consumption was by the Federal Government). On January 28, 1986 when the Space Shuttle Challenger disaster occurred, NASA demands dropped precipitously meaning even fewer Government demands. Therefore by 1987, the Office of Management and Budget (OMB) established the notion that Government should no longer have role in helium production. The main asset in question was the stalwart U.S. Bureau of Mines Exell plant which had been in operation since 1943. In 1988, however, the House of Representatives Appropriations Committee prohibited the sale of the plant. A further due diligence study of the Governments helium assets and operations would need to be addressed. By the late 1980s, the prices that the Bureau of Mines received for Grade-A helium and those received by private companies were approaching parity, around \$37 per thousand cubic feet.

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Chapter 6 Helium Today

Helium Privatization Act of 1996

At the beginning of the 1990s, it became clear that change was needed in the United States helium industry. Proposed legislation to amend the 1960 Helium Act allowing Government agencies to purchase helium from private producers was recognized. In the 1993 Minerals Yearbook, the Vice Presidents National Performance Review (NPR) revealed (excerpt from the Minerals Yearbook 1993):

...it was determined that the Federal Government needed to reexamine its role in the Federal Helium Program. The report states that the program can be run more efficiently, reducing outlays by Federal helium customers and increasing revenue. Suggestions were made to cancel the helium debt, reduce the selling price for USBM (U.S. Bureau of Mines) helium, discontinue nonrevenue-producing functions, increase efficiencies of helium operations, and begin sales of crude helium as market conditions permit. The USBM is implementing these suggestions into the operation of the Helium Program.

Clearly, much debate was needed in order to tackle the privatization issue, not least of which was finding a reasonable, non-competitive Government agreement with energy giants like Exxon and the major industrial gas companies who were firmly established in the private helium industry. If the Government were to reduce the price of Government-sold helium in order to clear their helium inventory, then a likely public relations campaign against the Government would ensue.

In 1995, a bill was introduced to Congress highlighting various points to be addressed (paraphrased from the Minerals Yearbook 1994):

- 1. Discontinue Bureau of Mines helium sales and allow Government purchases of privately-produced helium.
- 2. Dispose of Government helium assets.
- 3. Establish an orderly sales program of Cliffside reserves.
- 4. Maintain operations of Cliffside and associated 425-mile Government pipeline.

5. Continue leasing of federal lands where helium-bearing reserves exist.

6. Eliminate the helium debt.

By the next year, President Clinton signed into law on October 9, 1996, the Helium Privatization Act of 1996. This law mandated that the U.S. Government terminate the production and sale of Grade-A helium by 1998, dispose of all Government helium-related assets, and sell the helium reserve held in Cliffside Field by 2015 (except for 600 million cubic feet ordered maintained by the Government). In March 1998, the last Federal helium plant, the Excel plant was shut down as mandated by the Act and was later sold to a private buyer.

Approximately 30 billion cubic feet of helium stored in the Cliffside Field was ordered to be sold on a straight-line basis no later than January 1, 2015 and in such a manner as to prevent "minimum market disruption".¹ The price to be charged for the Cliffside helium was formulated in order to completely pay down the U.S. helium debt by 2015, when Cliffside was mandated to close (or when the Helium Debt was repaid; whichever came first). The formula derived for pricing this helium was simply the total helium reserves stored in Cliffside divided by the remaining helium debt (and adjusted for the Consumer Price Index, CPI). In 2000 (in 1996 dollars²), this price was calculated to be \$43 per thousand cubic feet while privately produced helium was then selling for \$32 per thousand cubic feet (roughly 34 % higher than privately-produced helium). Due to this price differential, it was believed that any helium sold from Cliffside would represent a supply of last resort. At this time, the helium stored in Cliffside field was the highest priced helium in the world and refiners primarily relied on private producers of helium. Thus, at the time of the passage of the 1996 Act, the formulaic price established by the Act seemed to be a prudent one.

Shortly after the passing of this Act, a feasibility study by the National Academies Press titled, *The Impact of Selling the Federal Helium Reserve*,³ was released highlighting current government role and any potential harmful consequences which might arise as a result of this Act. During the time of this study, the helium industry was relatively stable and it was not believed that Cliffside with-drawals would exceed estimated projections. In 1998, roughly 98 % of all domestic helium demand was met by private industry while the remaining 2 % was supplied by the Government. Of this 2 % supplied by the Government, most of that amount was allocated to the Department of Defense, Department of Energy, and NASA.⁴ At this time, it was widely believed that enough helium existed from private sources that withdrawals would not begin from Cliffside until much later

¹ Impact of Selling the Federal Helium Reserve, National Academies Press, 2001.

² The price of \$43 represents dollar value in 1996. The posted price for the year was \$49.50. Government posted helium prices can be found at the following resource: http://www.blm.gov/nm/st/en/prog/energy/helium/helium_operators_information/crude_helium_price.html.

³ This publication can be found online: http://www.nap.edu/catalog/9860.html.

⁴ Helium, Minerals Yearbook 1998, David V. Hayes, Jr., p. 36.2.

than anticipated. All current domestic demand and a portion of international demand was adequately met by U.S. helium producers and the remaining foreign demand was supplied by plants operating in Poland, Russia, and Algeria during the decade of the 1990s.

Almost immediately after the feasibility study in 2000, nearly every aspect of the Act mentioned above was no longer relevant due primarily to much higher than expected demand coupled with decreasing private domestic supply. As private helium resources from the Hugoton Field were depleting by the end of the decade, soon the Cliffside Field represented the least expensive helium resource in the country thanks to the very low, formulaic price mentioned above. What was designed to be a resource of last resort for industrial gas companies soon became a resource of first resort and in so doing hampered the impetus to locate new domestic sources. Ever since, the Cliffside field helium reserves have been sold at far below market prices thus resulting in less revenue derived from a resource owned by the U.S. taxpayer.

Due to ever-increasing demand, foreign supplies of helium began to gather momentum when in 1994, helium production began from the Helios Plant in Arzew, Algeria out of the giant offshore Hassi R'Mel Field. Helium production from this field, which represented the first "large" foreign helium resource, was (and is) exported to foreign markets principally in the Far East. U.S. demand was met by U.S. supply and none of this helium was (or is) exported to North America.

Foreign demand began to increase in 2000 and 2001 by 38 % and 16 %,⁵ respectively, signaling a growing trend in international consumption (especially in Asia). This growing demand led to the establishment of a new helium facility to be constructed in Skikda, Algeria (production began in 2007) and another in Ras Laffan, Qatar which came online in 2005. Like the Arzew plant, these two projects were (and are) able to produce helium because they were already taking their vast volumes of natural gas to liquid for the LNG (Liquefied Natural Gas) export market. The helium concentrations were actually much lower than what might be considered economical in the United States and elsewhere but because all of the natural gas was taken to liquid, the helium (which will not liquefy at natural gas temperatures) would come off the top in relatively pure form. Further helium processing and liquefaction from these facilities would go on to meet regional and far eastern end-users. Start-up problems with both of these facilities led to lengthy delays prior to any helium production resulting in increased U.S. export.

The period from the 1996 Act to today noticed ever increasing demand for helium and the 2008–2009 recession was the only period where helium demand stabilized. After the economic recovery, however, demand grew and once again, the primary resource for global helium remained the U.S. Cliffside Helium Reserve where the most inexpensive helium in the world resided. Soon, after everalarming withdrawal rates from the Reserve, it became clear that these helium reserves were being sold at far below market prices and was providing no incentive

⁵ Helium, Minerals Yearbook 2000 and 2001, Norbert Pacheco.

for the exploration of new molecules.⁶ As the supply situation grew more dire during 2012–2013, the United States Congress acted, on behalf of the end-users of helium and the U.S. Taxpayer, to correct the problem of (1) keeping the BLM Cliffside Field operational past its eminent closure, (2) fixing the issue of the U.S. Taxpayer selling helium at very low, non-market prices, and (3) encourage the development of new domestic resources.

Due to faster than expected repayment of the Helium Debt, the Cliffside Field was scheduled to close in late 2013 which was over a year before scheduled by the 1996 Act.⁷ If Cliffside had closed, a global crisis would have manifested due to Cliffside's role in the global helium market. Immediately before the mandated U.S. Government Reserve closure in late 2013, President Obama signed into law on October 2, 2103, the Helium Stewardship Act of 2013. The Act, which was a bi-partisan effort, was designed to keep the Cliffside Field open and maintained so as not to disrupt the world helium market and adversely affecting important end-users, especially domestic users. The 2013 Act also sought to help other "nonrefiners" have access to the BLM pipeline which had previously been controlled by only three refining companies. In addition, it secured access to Federal users of helium who might otherwise be severely impacted by severed supply. More importantly, however, the Act recognized that helium from the Cliffside field was being sold at below market prices at U.S. taxpayer expense. As a result, the Act installed a staged auction for helium reserves in order to establish a market-based price to the benefit of the U.S. taxpayer.

The passage of the Helium Stewardship Act has gone mostly according to plan but there have been several issues raised since it was passed. One of the major issues currently at stake is the lack of tolling arrangements negotiated between the refiners and non-refiners. As per the 2013 Act, refiners on the BLM pipeline must "toll" production for non-refiners at "commercially reasonable rates" if they have excess capacity. These tolling agreements today, however, are still a point of contention with the refiners on the pipeline. That is, the refiners do not believe they should have to toll any gas through any processing plant owned by the refiner in order to help competitors.

In order to solve some of these tolling issues, the United States Bureau of Land Management held a scoping meeting on March 6, 2014 in order to hear from refiners and non-refiners alike to help resolve this important issue. A non-refiner spoke of the troubles of negotiating a tolling arrangement with the following statement:

Since this sale, responses from the Refiners on the federal system continue to raise serious questions about whether the reforms contained in the Act will be effectively implemented and whether Congress' goals will be achieved. To date, no Refiner has replied to our requests for tolling with adequate committed available tolling services at commercially reasonable rates for volumes purchased in the recent IFO. If these issues are not addressed, up to 40 MMcf of helium could be effectively withheld from domestic

⁶ Although helium does not form molecules, the industry refers to helium as "molecules", not atoms.

⁷ The 1996 Act was to terminate by the 2015 deadline or the full repayment of the Helium Debt, whichever came first. The Helium Debt repayment occurred before the 2015 deadline.

end-users—a total that will only increase with each subsequent sale. [The non refiner], however, stands ready to serve the end user community upon finding a Refiner who is willing to toll this helium on a steady committed basis and at a true commercially reasonable rate.

Despite the inability to tackle the tolling issues, the U.S. BLM held the first-ever Federal Helium Auction on July 31, 2014. A total of 92.814 million cubic feet of crude helium, which represented 10 % of the total volume made available by the BLM for fiscal year 2015, was auctioned and purchased by two "refiners" on the BLM pipeline. This purchase by the refiners, of course, eliminated the need to have tolling contracts in place but rather deferred it until the next auction date. The U.S. BLM generated a total of \$14.9 million dollars for the U.S. Treasury with an average price of \$161.32 per thousand cubic feet of helium. Had the auction not taken place, this helium would have sold at the traditional "formulaic" price of \$95 per thousand cubic feet resulting in the elimination of the extra \$6.16 million for the U.S. Treasury generated by the auction.

The Federal Helium Reserve is owned by the U.S. taxpayer meaning that taxpayers received a fair market price for this auctioned helium, albeit small amount, which had traditionally been sold at below-market prices. At issue, however, is the difference in price between this auctioned helium and the remaining reserves that are still sold at formulaic, non-market driven prices. That is, the average auctioned helium price of \$161.32 was far higher than the formulaic price of \$95 per thousand cubic feet. Using a weighted average of the 10 % auctioned helium multiplied by the average auction price and the 90 % of the remaining reserves multiplied by the formulaic price of \$95 resulted in a "new" formulaic price of \$106 per thousand cubic feet. As a result, the U.S. taxpayer is still not getting anywhere near fair market prices for the remaining helium left in the Reserve.

This discrepancy in price is currently being studied by lawmakers so that the U.S. taxpayer can get a fair price on the remaining helium left in the Reserve but we are still a long way off from reaching any sort of remedy that would cause the taxpayers to get a fair shake on this resource. The refiners believe that helium should continue to be sold for the formulaic price in order to reap larger margins. This, of course, is a detriment for other companies wanting to identify and explore for new helium sources all over the world, especially in the United States. If true market forces are allowed to operate, new helium resources will be sought and processed ultimately leading to higher supplies than we are currently seeing.

The pricing of helium has been the primary reason why supply issues have continued for the last decade or so. Because the United States Government has kept artificially low prices for taxpayer owned helium, it has hampered true market forces to work which help solve supply issues. As mentioned before and still today, the helium supplies in the Governments Cliffside field still represent the lowest priced helium available anywhere in the world which has severely impacted end-users who rely on helium for which there is no substitute. Lawmakers are currently addressing this issue but progress has been slow. The only way future supply concerns can be dealt with is by employing a full market priced mechanism where new supplies can be sought to meet escalating demand. Today, the helium supply issue is still very tight but hope is still high for new projects in Canada, the United States, Russia, Algeria, and Qatar. The United States, which has historically been an exporter of helium, will soon become an importer for the first time in its history in the coming years. As this text goes to print, the Qatar II helium project with an annual capacity of 1.3 billion cubic feet of helium (not including Qatar I capacity of 700 million cubic feet per year) became the largest helium hub in the world when it came online in 2013 representing 25 % of total global demand. As the U.S. Cliffside Field continues to decline, the primary resource for global helium will effectively cease to exist as a prime player sometime in the early 2020s, which is only 6 years away from now. New sources must come on stream sooner rather than later and with ever-higher helium prices, soon the impetus to locate and drill for new sources will be underway.

As the U.S. Cliffside Helium Reserve is drawn down to virtually nothing in the next few years, future helium supply will be at risk unless new reserves are located, even beyond the ones mentioned above. It is interesting to think about the current low supply situation in terms of the U.S. Helium Act of 1960 which sought to store helium in the Cliffside Reserve to primarily handle NASA's needs. What if that Act was never passed? It is entirely possible that all of the uses mentioned in Chap. 1 would be severely impacted, if there would be some of these industries at all. The MRI market would have certainly been impacted and most certainly the semiconductor and fiber optic industries. What would our economy look like without advancements in these technologies? It is only because of the 1960 Act that we have helium to draw from now but it was the 1996 Act which, although unintended, squandered these reserves and sold helium at far-below-market prices.

Helium is, indeed, a finite resource just like coal, oil, and natural gas. Although more is being produced within the Earth than is extracted, it still takes a tremendous amount of risk capital to bring new supplies to the market. If a true market system is able to operate, as the 2013 Act hopes to achieve, the incentive will arise to search for more molecules. As it stands today, however, the price of U.S. Cliffside helium (the primary supplier of helium in the world) is still too low to bring new players into field of helium exploration.

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