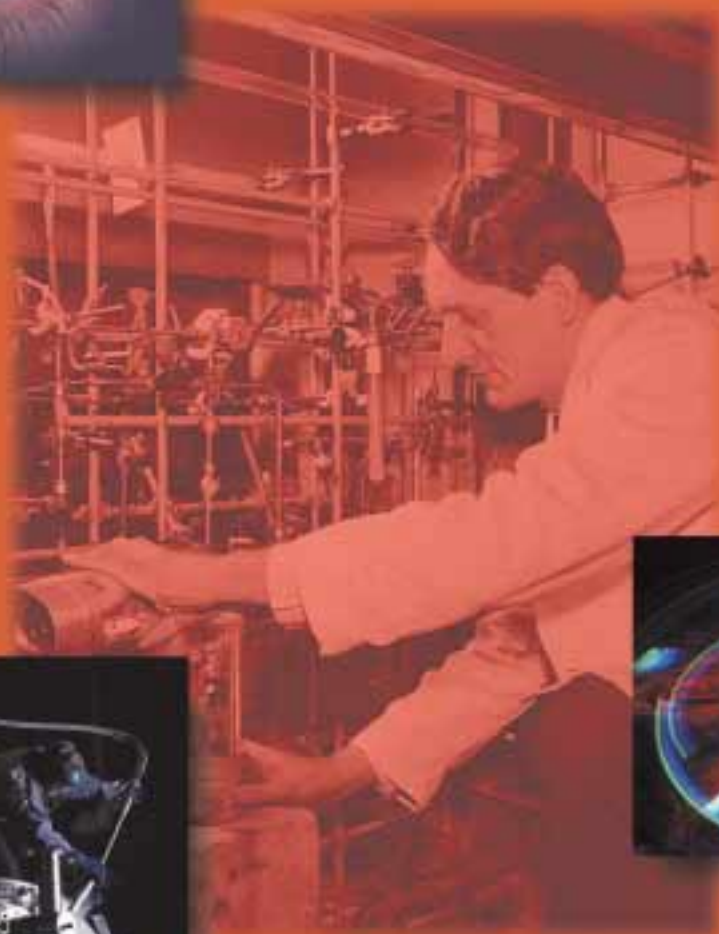


Neil Bartlett and the
Reactive Noble Gases
May 23, 2006

International Historic Chemical Landmark



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“I think I identified at times with the inert gases, and at other times anthropomorphized them, imagining them lonely, cut off, yearning to bond. Was bonding, bonding with other elements, absolutely impossible for them?”

—Oliver Sacks, *Uncle Tungsten* (New York: Alfred A. Knopf, 2001), p. 202, fn. 8.

noble gases

Forbidden union

Scientists had always believed that noble gases, also known as inert or rare gases, were chemically unable to react. Helium, neon, argon, krypton, xenon, and radon (all gases at room temperature) were viewed as the “loners” of the Periodic Table. Their inertness became a basic tenet of chemistry, published in textbooks and taught in classrooms throughout the world.

Conventional scientific wisdom held that the noble gas elements could not form compounds because their electronic structure was extremely stable. For all except helium, the maximum capacity of the outer electron shell of the noble gas atom is eight electrons. For helium, that limit is just two electrons. These electron arrangements are especially stable, leaving the noble gases without a tendency to gain or lose electrons. This led chemists to think of them as totally unreactive.

A few chemists questioned the absolute inertness of the noble gases. Among those scientists were Walter Kossel in 1916 and Nobel-prize winning chemist Linus Pauling in 1933. They predicted that highly reactive atoms such as fluorine might form compounds with xenon, the heaviest of the noble elements and whose electrons, they observed, were not as tightly bound as those of the lighter gases.

Mysterious compound

In 1961 Neil Bartlett was teaching chemistry at the University of British Columbia in Vancouver, Canada. Some years earlier, while experimenting with fluorine and platinum, he had accidentally produced a deep-red solid whose exact chemical composition remained a mystery. With the assistance of his graduate student Derek Lohmann, he vigorously pursued the identity of the red solid. After much research they eventually established that the known gaseous fluoride, platinum hexafluoride

(PtF₆), had reacted with some oxygen impurity to produce the red solid. The same solid, which he and Lohmann subsequently identified as O₂⁺PtF₆⁻, was easily obtained by simply mixing the two gases.

What was most unusual about this compound was that it contained oxygen in the form of positively charged ions, although oxygen usually has a net negative charge. Oxygen normally pulls electrons from other atoms and is thus called an oxidizing agent or oxidant. But Bartlett believed that, in this case, the PtF₆ component was a more powerful oxidizing agent than even oxygen and was extracting electrons from oxygen, leaving oxygen with a net positive charge. Even though PtF₆ was first prepared some years earlier by



researchers at Argonne National Laboratory, its oxidizing power had not been recognized until Bartlett's research. It was this development that led Bartlett to theorize that if PtF₆ could oxidize oxygen, then it might also be able to achieve the “impossible” task of oxidizing xenon, whose ionization potential (energy required to remove an electron) was very similar to that of oxygen.

Simple experiment

In March of 1962, Bartlett concocted a simple experiment to test his hypothesis. He set up a glass apparatus containing PtF₆ — a red gas — in one

container and xenon — a colorless gas — in an adjoining container, separated by a seal. Here is his recollection of the ensuing experiment, which he conducted alone in his laboratory:

Because my co-workers at that time (March 23, 1962) were still not sufficiently experienced to help me with the glassblowing and the preparation and purification of PtF₆ [platinum hexafluoride] necessary for the experiment, I was not ready to carry it out until about 7 p.m. on that Friday. When I broke the seal between the red PtF₆ gas and the colorless xenon gas, there was an immediate interaction, causing an orange-yellow solid to precipitate. At once I tried to find someone with whom to share the exciting finding, but it appeared that everyone had left for dinner!

—Neil Bartlett, “Forty Years of Fluorine Chemistry” in *Fluorine Chemistry at the Millennium*, ed. R.E. Banks; (Amsterdam: Elsevier Science, 2000), p. 39.

The reaction took place at room temperature “in the twinkling of an eye” and was “extraordinarily exhilarating,” recalls Bartlett. He was certain that the orange-yellow solid was the world's first noble gas compound. But convincing others would prove somewhat difficult. The prevailing attitude was that no scientist could violate one of the basic tenets of chemistry: the inertness of noble gases. Bartlett insisted that he had, to the disbelief of some of his colleagues! The proof was in the new compound he had made. That orange-yellow solid was subsequently identified in laboratory studies as xenon hexafluoroplatinate (XePtF₆), the world's first noble gas compound.

Within months, other chemists successfully repeated the experiment. Although the intricate chemical details behind the reaction would take years to clarify and the formula of the colorful solid was later modified as [XeF]⁺[PtF₅]⁻, the significance of the experiment remained clear. Spurred by Bartlett's success, other scientists soon began to make new compounds from xenon and

later, radon and krypton. With Bartlett's simple experiment, the old "law" of the unreactivity of the noble gases had been vanquished. The new field of noble gas chemistry, with its exciting possibilities, had been launched.

Powerful tool

Bartlett's experiment opened the door to a better understanding of the oxidation states of atoms and their possible reactions. Today, noble gas chemistry has become a powerful tool for developing new compounds with useful properties. "The important aspect of my discovery," Bartlett says, "was to draw attention to fundamental chemical considerations — especially that quantitative energy differences are important when considering variations in the chemistry of the elements in a Periodic Table framework."

Bartlett estimates that more than

100 noble gas compounds are known today. These fragile compounds are energy rich: they tend to be extremely unstable and therefore highly reactive. More are being discovered every year. In 2002, researchers at the University of Helsinki in Finland reported the formation of the first and only known argon compound (produced at extremely low temperatures). Of the six known noble gases, only helium and neon have not formed compounds to date.

Noble gas compounds have already made an impact on our daily lives. XeF₂ has been used to convert uracil to 5-fluorouracil, one of the first anti-tumor agents. The reactivity of radon means that it can be chemically scrubbed from the air in uranium mines and other mines. Excimer lasers use compounds of argon, krypton, or xenon to produce precise beams of ultraviolet light (when electrically stimulated)

that are used to perform eye surgery for vision repair.

Compounds of the gases are poised to play an even bigger role in the future. Researchers recently succeeded in combining noble gases with hydrocarbons, a development that could lead to new and better synthetic approaches to some organic materials. Noble gas compounds also show promise as green chemistry reagents that allow for more environmentally-friendly manufacturing processes. Bartlett believes even the highly fragile compounds being produced in Helsinki will provide benefits as yet unforeseen. All trace their legacy back to the pivotal moment in a chemistry lab at the University of British Columbia, when a clever young scientist turned conventional wisdom upside down with the help of a memorable experiment and changed the face of chemistry forever.

Beginnings

Neil Bartlett was born September 15, 1932, in Newcastle-upon-Tyne, United Kingdom. One of his earliest, formative memories was of a laboratory experiment he conducted in a grammar school class as a twelve-year-old. In the experiment, he mixed a solution of aqueous ammonia (colorless) with copper sulfate (blue) in water, causing a reaction which would eventually produce "beautiful, well-formed crystals." From that moment "I was hooked," writes Bartlett, who yearned to know why the transformation took place. He could not have known that the event would vaguely foreshadow his famous experiment decades later in which he produced the world's first noble gas compound following a similarly stunning chemical reaction.

He began to immerse himself in chemistry to the extent that he built his own makeshift laboratory in his parent's home, complete with flasks and beakers and chemicals he purchased at a local supply store. That curiosity carried over into academic success and eventually earned him a scholarship for his undergraduate education.

Bartlett attended King's College in Durham (U.K.), where he received his Bachelor of Science degree in 1954 and his doctorate in 1958. That year Bartlett was appointed a lecturer in chemistry at the University of British Columbia, where he remained until 1966, eventually reaching the rank of full professor. In 1966 he became a professor of chemistry at Princeton



University while also serving as a member of the research staff at Bell Laboratories. In 1969, he joined the University of California, Berkeley, as a professor of chemistry, retiring in 1993. From 1969 to 1999 he also served as a scientist at the Lawrence Berkeley National Laboratory. Bartlett

became a naturalized U.S. citizen in 2000.

Bartlett's fame goes beyond the inert gas research to include the general field of fluorine chemistry. He holds a special interest in the stabilization of unusually high oxidation states of elements and applying these states to advance chemistry. Bartlett is also known for his contributions toward understanding thermodynamic, structural, and bonding considerations of chemical reactions. He helped develop novel synthetic approaches, including a low-temperature route to thermodynamically unstable binary fluorides, including NiF₄ and AgF₃. He discovered and characterized many new fluorine compounds and also produced many new metallic graphite compounds, including some that show promise as powerful battery materials.

The American Chemical Society designated the research of Neil Bartlett on the noble gases as an International Historic Chemical Landmark on May 23, 2006. The commemorative plaque at the University of British Columbia in Vancouver reads:

In this building in 1962 Neil Bartlett demonstrated the first reaction of a noble gas. The noble gas family of elements – helium, neon, argon, krypton, xenon, and radon – had previously been regarded as inert. By combining xenon with a platinum fluoride, Bartlett created the first noble gas compound. This reaction began the field of noble gas chemistry, which became fundamental to the scientific understanding of the chemical bond. Noble gas compounds have helped create anti-tumor agents and have been used in lasers.

About the National Historic Chemical Landmarks Program

The American Chemical Society, the world's largest scientific society with more than 158,000 members, has designated landmarks in the history of chemistry since 1993. The process begins at the local level. Members identify milestones in their cities or regions, document their importance, and nominate them for landmark designation. In addition, the Society designates international landmarks in conjunction with other national societies. In either case, an international committee of chemists, chemical engineers, museum curators, and historians evaluates each nomination. For more information, please call the Office of Communications at 202-872-6274 or 800-227-5558, e-mail us at nhclp@acs.org, or visit our web site: www.chemistry.org/landmarks.

A nonprofit organization, the American Chemical Society publishes scientific journals and databases, convenes major research conferences, and provides educational, science policy, and career programs in chemistry. Its main offices are in Washington, DC, and Columbus, Ohio.

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Photo credits: The University of British Columbia

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