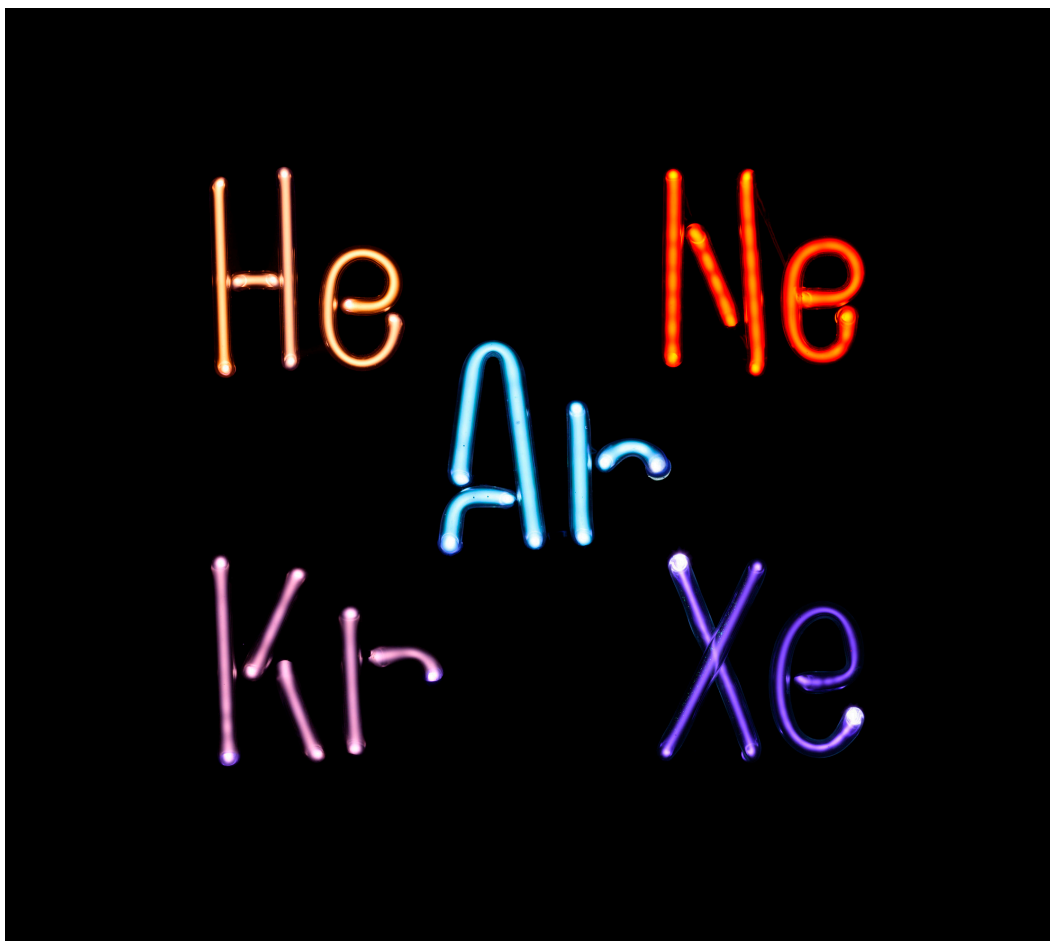


INTERCHAPTER K

The Noble Gases



When an electric discharge is passed through a noble gas, light is emitted as electronically excited noble-gas atoms decay to lower energy levels. The tubes contain helium, neon, argon, krypton, and xenon.

2	0	He	4.002602	$1s^2$
10	0	Ne	20.1797	$2s^2 2p^6$
18	0	Ar	39.948	$3s^2 3p^6$
36	0	Kr	83.798	$4s^2 4p^6$
54	0	Xe	131.293	$5s^2 5p^6$
86	0	Rn	(222)	$6s^2 6p^6$

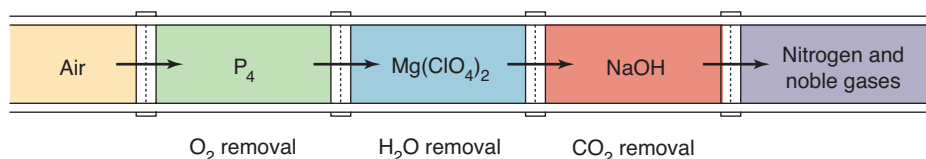


Figure K.1 A schematic illustration of the removal of $O_2(g)$, $H_2O(g)$, and $CO_2(g)$ from air. First the oxygen is removed by allowing the air to pass over phosphorus, $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$. The residual air is passed through anhydrous magnesium perchlorate to remove the water vapor, $Mg(ClO_4)_2(s) + 6H_2O(g) \rightarrow Mg(ClO_4)_2 \cdot 6H_2O(s)$, and then through sodium hydroxide to remove the carbon dioxide, $NaOH(s) + CO_2(g) \rightarrow NaHCO_3(s)$. The gas that remains is primarily nitrogen with about 1% noble gases.

The Group 18 elements—helium, neon, argon, krypton, xenon, and radon—are called the **noble gases** and are noteworthy for their relative lack of chemical reactivity. Only xenon and krypton are known to enter into chemical compounds, and even then only with the two most electronegative compounds, fluorine and oxygen. The principal source of the noble gases, except for helium, is the atmosphere, where they are thought to have arisen as by-products of the decay of radioactive elements in the earth's crust. Because of its low mass, however, helium escapes from the earth's atmosphere into outer space. Properties of the noble gases are given in Table K.1. The data in Table K.1 nicely illustrate trends in physical properties with increasing atomic size.

K-1. The Noble Gases Were Not Discovered until 1893

In 1893, the English physicist Lord Rayleigh noticed a small discrepancy between the density of nitrogen obtained by the removal of oxygen, water vapor, and carbon dioxide from air and the density of nitrogen prepared by chemical reaction, such as the thermal decomposition of ammonium nitrite:



One liter of nitrogen at $0^\circ C$ and 1 atm obtained by the removal of all the other known gases from air has a mass of 1.2572 grams (Figure K.1), whereas one liter of dry nitrogen obtained from ammonium nitrite has a mass of 1.2505 grams under the same conditions. This slight difference led Lord Rayleigh to suspect that some other gas was present in the sample of nitrogen from air.

TABLE K.1 Properties of the noble gases

Element	Symbol	Atomic mass	Atomic radius/pm	Ionization energy/MJ·mol ⁻¹	Concentration in air/ppm	Melting point/ $^\circ C$	Boiling point/ $^\circ C$
helium	He	4.002602	32	2.3723	5.2	—	-268.93
neon	Ne	20.1797	69	2.0806	18.2	-248.609	-246.053
argon	Ar	39.948	97	1.5205	9340	-189.36	-185.847
krypton	Kr	83.798	110	1.3507	1.1	-157.38	-153.34
xenon	Xe	131.293	130	1.1704	0.08	-111.745	-108.09
radon	Rn	(222)	145	1.0370	$\sim 1 \times 10^{-15}$	-71	-61.7

The English chemist William Ramsay found that if hot calcium metal is placed in a sample of nitrogen obtained from air, about 1% of the gas fails to react. Pure nitrogen should react completely. Because of the inertness of the residual gas, Ramsay gave it the name argon (Greek, idle). Ramsay then liquefied the residual gas and, upon measuring its boiling point, discovered that it consisted of five components, each with its own characteristic boiling point (Table K.1). The component present in the greatest amount retained the name argon. The others were named helium (sun), neon (new), krypton (hidden), and xenon (stranger). Helium was named after the Greek word for sun (*helios*) because its presence in the sun had been determined earlier by spectroscopic methods. All the noble gases are colorless, odorless, and relatively inert. For their work in discovering and characterizing an entire new family of elements, Rayleigh received the 1904 Nobel Prize in Physics and Ramsay received the 1904 Nobel Prize in Chemistry (Figure K.2).

K-2. Helium Is the Second Most Abundant Element in the Universe

Helium is the second lightest element and the second most abundant element in the universe, after hydrogen. Despite the fact that helium is denser and hence has less lifting power than hydrogen, it is used in lighter-than-air aircraft because it is nonflammable. Helium is used in welding to provide an inert atmosphere around the welding flame and thus reduce corrosion of the heated metal. An inert helium environment is used for growing silicon and germanium crystals in the semiconductor industry. Helium is used as an inert carrier gas in gas chromatography (an analytical method used to separate mixtures). It is also used to replace nitrogen in deep-sea-diving breathing mixtures to help reduce the formation of nitrogen bubbles in the blood, a condition known as the bends (see Section 16-7).

Because helium boils at 4.22 K, liquid helium is often used as a coolant for superconducting magnets such as those used in MRI (magnetic resonance imaging) and in other cryogenic applications. For example, the recently constructed Large Hadron Collider uses 96 metric tons of liquid helium for cooling.

On earth helium is produced from the radioactive decay of α -emitters (alpha-emitters) such as naturally occurring uranium and thorium. Recall from

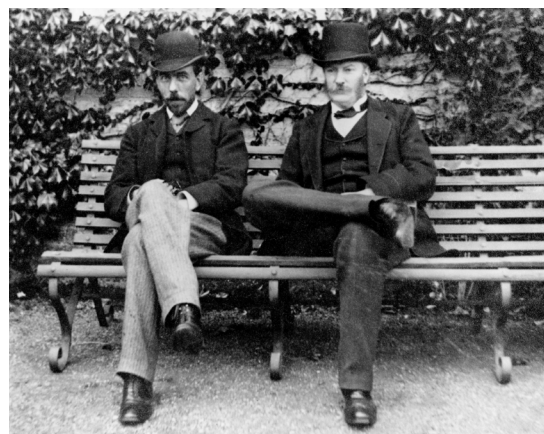


Figure K.2 The two discoverers of the noble gases. (*left*) Sir William Ramsay was a professor of chemistry at the University College of London and (*right*) Lord Rayleigh, born John William Strutt, was Cavendish Professor of Physics at Cambridge University.

Chapter 2 that α -particles are energetic helium nuclei. An estimated 3000 metric tons of helium are formed each year in this way. Naturally occurring helium is trapped in nonpermeable rock layers beneath the earth. Helium is obtained by separation from natural gas (which is also trapped in such layers) using fractional distillation. The largest producer of helium is the United States, which has extensive quantities of helium in its natural gas deposits. Starting in 1925, when the use of lighter-than-air aircraft yielded a military advantage, and continuing through the space race and the cold war, when helium was needed as a coolant for military and space applications, the United States government maintained a strategic helium reserve. In 1996 the U.S. government began phasing out this reserve.

The speed of sound in helium is nearly three times that in air because of its low atomic mass (see Chapter 13). For this reason, if helium is inhaled, say, from a small balloon, it can cause a temporary change in the fundamental frequency of the vocal cavity, making the voice sound high-pitched. However, this must be done cautiously as helium is an asphyxiant and inhaling too much helium and no oxygen can cause respiratory distress or even death.

Never inhale a gas directly from a high-pressure tank, as lung damage can result.

K-3. Excited Neon Gas Emits an Orange-Yellow Glow

Neon is the fifth most abundant element in the universe, but is relatively rare on earth due to its low mass, which means that, like helium, it also escapes from the upper atmosphere into space (although at a much slower rate than helium). When placed in a discharge tube, neon emits an orange-yellow glow that penetrates fog very well (Frontispiece). Neon is used in neon signs, which are essentially discharge tubes filled with neon or a gas mixture containing neon. In fact, because of its high cost, very few “neon” signs actually contain pure neon and some contain no neon at all. Neon has traditionally been used in a variety of electronics such as vacuum tubes and television tubes and in some cryogenic applications. Neon is also used in helium-neon lasers, which operated as bar-code scanners and optical disk readers before the development of less costly diode lasers.

K-4. Argon Is the Third Most Abundant Gas in Our Atmosphere and Has a Wide Range of Industrial Uses

Argon is the most plentiful and least expensive noble gas. Not considering water vapor, argon is the third most abundant gas in the earth’s atmosphere (Table K.2). Worldwide, about 700000 metric tons of argon are isolated annually from air using fractional distillation. Because it is relatively inexpensive compared to the other inert gases, argon has a wide variety of industrial uses. It is used in fluorescent and incandescent lightbulbs because it does not react with the discharge electrodes or the hot filament. Argon is used to provide an inert atmosphere in welding; in sealed museum cases to help preserve specimens that are subject to oxidation in air; in special fire extinguishers; for growing silicon and germanium crystals; and to fill the space above wines and pharmaceuticals to prevent oxidation. The gas is also used in argon lasers, which are used predominantly in laser surgery.

The most abundant isotope of argon is argon-40, which is produced by the radio decay of potassium-40. Because potassium-40 has a half-life of 1.248×10^9 years, the ratio of argon-40 to potassium-40 can be used to determine the age of rocks, a method called potassium-argon dating (we discuss radiodating of materials in Chapter 17). The radio isotope argon-39 is also used in some radiodating applications.

TABLE K.2 Composition of the earth’s atmosphere below 100 km

Major constituents	Content in fraction of total molecules (and percent by mass)
nitrogen (N ₂)	0.7808 (75.51%)
oxygen (O ₂)	0.2095 (23.14%)
argon	0.0093 (1.28%)
water vapor	0–0.04
Minor constituents	Content in parts per million (ppm)*
carbon dioxide	385 ppm (2009 data)
neon	18 ppm
helium	5 ppm
methane	2 ppm
krypton	1 ppm
hydrogen (H ₂)	0.5 ppm
dinitrogen oxide	0.5 ppm
xenon	0.1 ppm

*The unit ppm denotes parts per million parts, for example, 385 ppm of carbon dioxide means that 385 of each 1 million molecules are CO₂.

K-5. Krypton and Xenon Form a Small Number of Stable Compounds

Krypton and xenon are scarce and costly, which limits their applications, although they are used in lasers, flashtubes for high-speed photography, and automobile-engine timing lights (Figure K.3). Xenon arc lamps produce an intense white light and are used in applications such as IMAX projectors and high-intensity headlights. Xenon is also used as a propellant in ion thrusters on spacecraft. In the early 1940s it was discovered that xenon gas could be used as a general anesthetic, although its medical use has been limited to date.

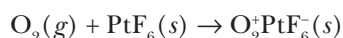
Prior to 1962 most chemists believed, and all chemistry textbooks proclaimed, that the noble gases did not form any chemical compounds. In fact, the gases helium through xenon were called the inert gases, indicating that they did not undergo any chemical reactions.

In 1962, Neil Bartlett, then of the University of British Columbia, was working with the extremely strong oxidizing agent platinum hexafluoride,



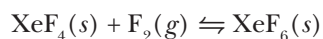
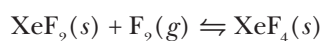
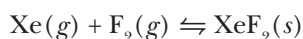
Figure K.3 Xenon flash lamps.

$\text{PtF}_6(s)$, which oxidizes $\text{O}_2(g)$ to produce the ionic compound $\text{O}_2^+\text{PtF}_6^-(s)$ according to



Bartlett realized that the ionization energy of $\text{O}_2(g)$ ($1164.6 \text{ kJ}\cdot\text{mol}^{-1}$) is about the same as the ionization energy of $\text{Xe}(g)$ ($1170.4 \text{ kJ}\cdot\text{mol}^{-1}$), so he reasoned that xenon might react with $\text{PtF}_6(s)$ in an analogous manner. When he mixed xenon and $\text{PtF}_6(s)$ in a reaction chamber, he obtained a definite chemical reaction that at the time was thought to be the formation of $\text{Xe}^+\text{PtF}_6^-(s)$. It has since been found that the product of the reaction is more complex than $\text{Xe}^+\text{PtF}_6^-(s)$, but nevertheless Bartlett showed that xenon will react with a strong oxidizing agent under the right conditions of temperature and pressure. Bartlett's discovery prompted other research groups to investigate reactions of xenon, and within a year or so several other compounds of xenon were synthesized.

Three xenon fluorides can be prepared by the direct combination of xenon and fluorine in a nickel vessel according to the equations



As these three equations indicate, the reaction of a mixture of xenon and fluorine yields a mixture of $\text{XeF}_2(s)$, $\text{XeF}_4(s)$, and $\text{XeF}_6(s)$ (Figure K.4). The chief difficulty is the separation of the products. A favorable yield of $\text{XeF}_2(s)$ can be obtained by using a large excess of xenon. Xenon difluoride forms large, colorless crystals that melt at 129.03°C . It is a linear molecule, as predicted by VSEPR theory (AX_2E_3). Xenon difluoride is soluble in water and evidently exists as XeF_2 molecules in solution. Xenon tetrafluoride can be obtained in quantitative yield by reacting a 1:5 mixture of $\text{Xe}(g)$ and $\text{F}_2(g)$ at 400°C and 6 bar in a nickel vessel. Xenon tetrafluoride forms colorless crystals that melt at 117.10°C . The molecule is square planar, as predicted by VSEPR theory (AX_4E_2). Xenon hexafluoride forms colorless crystals that melt at 49.48°C and has an octahedral structure, as predicted by VSEPR theory (AX_6).

Xenon forms chemical bonds with the most electronegative elements, fluorine and oxygen, and exhibits oxidation states (see Chapter 24) of +2, +4, +6, and +8 (Table K.3). Xenon, having the greatest atomic size of any of the nonradioactive noble gases, has the smallest ionization energy. Hence, except for radon, xenon is the most "reactive" noble gas, and we expect the reactivity of the noble gases to decrease from xenon to helium. Only a few molecules containing



Figure K.4 Xenon tetrafluoride crystals. Xenon tetrafluoride was first prepared in 1962 by the direct combination of $\text{Xe}(g)$ and $\text{F}_2(g)$ at 6 bar and 400°C .

TABLE K.3 The principal compounds of xenon

Compound	Oxidation state	Physical state	Molecular shape
XeF ₂	+2	colorless crystals	linear
XeF ₄	+4	colorless crystals	square planar
XeOF ₄	+6	colorless liquid	square pyramidal
XeO ₂ F ₂	+6	colorless crystals	seesaw
XeO ₃	+6	colorless crystals	trigonal pyramidal
XeO ₄	+8	colorless gas	tetrahedral

krypton, such as KrF₂(s), have been isolated, and the only argon compound synthesized to date is HArF(s), but this is only stable at temperatures below 40 K.

K-6. Radon Is a Major Health Hazard

Radon is a naturally occurring, radioactive noble gas formed in the radioactive decay of radium-226, which in turn arises from the radioactive decay of uranium ores. Because it is radioactive and inert, radon sees few commercial or academic uses. However, it is a major health hazard.

We are constantly being exposed to natural and man-made radiation, called **background radiation**. About 55% of natural background radiation results

from radon decay. Indoor levels of radon are generally higher than outdoor levels, because radon enters a house through the ground and indoor airflow is much more restricted than outdoor airflow. The existence of radioactive radon gas in the air in homes in the United States was brought sharply into focus in 1984 when an engineer at the Limerock nuclear power plant in Pennsylvania repeatedly triggered the plant's radioactivity detectors. The source of the radioactivity was found to be the engineer's home, which registered a radioactivity level 675 times the maximum level the Environmental Protection Agency recommends for indoor air. Figure K.5 is a map of the United States showing regions of the country where radon gas is most prevalent in indoor air samples.

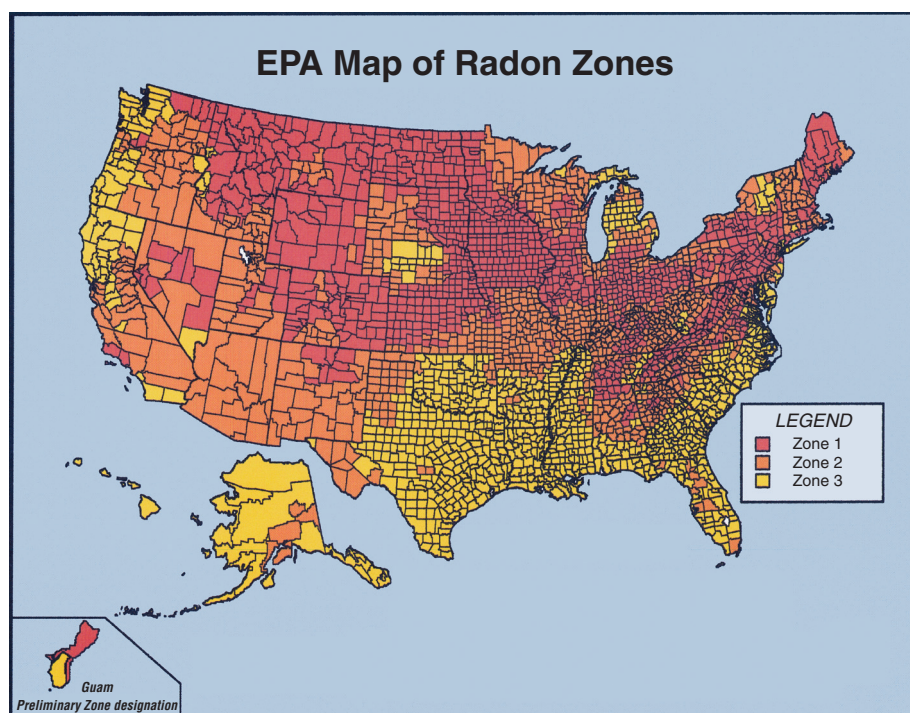


Figure K.5 A map of the United States showing average indoor radon gas levels by region. Zone 1 represents regions with the greatest concentrations of radon gas and Zone 3 represents regions with the lowest concentrations.

Three radon isotopes are produced in the decay of uranium ores—radon-219, radon-220, and radon-222. The half-lives of radon-219 and radon-220 are on the order of a few seconds; hence, these two radioisotopes decay before they can leave the ground. In contrast, radon-222 has a half-life of 3.8 days and is an α -emitter. The decay products of radon-222 are called radon daughters or progeny. Two of the radon-222 progeny are polonium-218 and polonium-214, which are also α -emitters with half-lives of 3.1 minutes and 2×10^{-4} seconds, respectively. Radon is a noble gas and is thus chemically inert and diffuses out of the ground in which it is formed. Similarly, inhaled radon is generally exhaled unless it decays to polonium-218 and polonium-214 while in the lungs. These polonium isotopes are fairly chemically reactive and bind to lung tissue. They emit α -particles, which damage cells and trigger the development of lung cancers. Although α -particles have a fairly short penetration range of about 70 μm , this distance is roughly twice the thickness of cell walls in the lungs. The U.S. Environmental Protection Agency (EPA) estimates that radon causes 5000 to 20 000 annual deaths from lung cancer in the United States. Because of this, radon is now recognized as a major cause of lung cancers, comparable in significance to smoking cigarettes, and especially deadly in combination. The presence of radon can be detected using commercially available test kits (Figure K.6).



Figure K.6 A home radon detector.

Provided the structure itself is not built from radioactive mine tailings or highly radioactive materials such as uranium-rich granites, it is usually not difficult to reduce radon levels within the structure. The basic procedure is to seal off the points of entry of radon gas into the structure. Common avenues of entry are cracks in the basement walls and floor, openings around pipes, and so forth. Good ventilation, particularly of basements, is also recommended. It is advisable to avoid a tightly sealed structure that has a low level of outside airflow into the structure.

The sources and principal commercial uses of the noble gases are given in Table K.4.

TABLE K.4 Sources and uses of the noble gases

Element	Principal Source	Uses
helium	natural gas wells	provide an inert atmosphere for welding, inflation of meteorological balloons and blimps, carrier gas for chromatography, high vacuum leak detection, cryogenics, coolant for superconducting magnets, nitrogen substitute for deep-sea diving, pressurize liquid rocket fuels, helium dating of rocks
neon	fractional distillation of liquid air	fluorescent tubes, lasers, vacuum tubes, high-voltage indicators, cryogenics
argon	fractional distillation of liquid air	provide an inert atmosphere for welding, fluorescent tubes, blanketing material for the production of titanium and other metals, lasers, deaeration of solutions
krypton	fractional distillation of liquid air	fluorescent tubes, high-speed photographic lamps, lasers
xenon	fractional distillation of liquid air	fluorescent tubes, lasers, stroboscopic lamps, high intensity headlights
radon	uranium ores	rarely used commercially

TERMS YOU SHOULD KNOW

noble gas *K1*

α -emitters (alpha-emitters) *K2*

background radiation *K5*

QUESTIONS

K-1. What is the principal chemical property of the noble gases?

K-2. Discuss how the noble gases were discovered by Lord Rayleigh.

K-3. What is the principal source of helium?

K-4. Why did Rayleigh and Ramsey place the newly discovered noble gases in a new group in the periodic table?

K-5. What is the source of $\text{He}(g)$ in natural gas deposits?

K-6. Sketch an experimental setup for removing $\text{O}_2(g)$, $\text{H}_2\text{O}(l)$, and $\text{CO}_2(g)$ from air.

K-7. Describe the important role that the noble gases played in the theories of chemical bonding and electronic structure of atoms.

K-8. Nitrogen is also a relatively inert gas. Suggest an experiment to demonstrate the difference between nitrogen and argon.

K-9. When Bartlett prepared $\text{O}_2^+\text{PtF}_6^-$ in 1962, what reasoning did he use to conjecture that it might be possible to prepare $\text{Xe}^+\text{PtF}_6^-$?

K-10. Use VSEPR theory to predict the structures of the following compounds:

- | | |
|--------------------|--------------------|
| (a) RnF_2 | (b) RnF_4 |
| (c) RnO_3 | (d) RnO_4 |