# 6.3: Periodicity

The elements within the same group of the periodic table tend to exhibit similar physical and chemical properties. Four major factors affect reactivity of metals: nuclear charge, atomic radius, shielding effect and sublevel arrangement (of electrons). Metal reactivity relates to ability to lose electrons (oxidize), form basic hydroxides, form ionic compounds with non-metals. In general, the bigger the atom, the greater the ability to lose electrons. The greater the shielding, the greater the ability to lose electrons. Therefore, metallic character increases going down the table, and decreases going across -- so the most active metal is towards the left and down.

## Group 1: The Alkali Metals

The word "alkali" is derived from an Arabic word meaning "ashes". Many sodium and potassium compounds were isolated from wood ashes ($Na_2CO_3$ and $K_2CO_3$ are still occasionally referred to as "soda ash" and "potash"). In the alkali group, as we go down the group we have elements Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). Several physical properties of these elements are compared in Table $6.3.1$. These elements have all only one electron in their outermost shells. All the elements show metallic properties and have valence +1, hence they give up electron easily.

Table 6.3.1: General Properties of Group I Metals

| Element | Electronic Configuration | Melting Point (°C) | Density (g/cm³) | Atomic Radius | Ionization Energy (kJ/mol) |
|---|---|---|---|---|---|
| Lithium | $[He]2s^1$ | 181 | 0.53 | 1.52 | 520 |
| Sodium | $[Ne]3s^1$ | 98 | 0.97 | 1.86 | 496 |
| Potassium | $[Ar]4s^1$ | 63 | 0.86 | 2.27 | 419 |
| Rubidium | $[Kr]5s^1$ | 39 | 1.53 | 2.47 | 403 |
| Cesium | $[Xe]6s^1$ | 28 | 1.88 | 2.65 | 376 |

As we move down the group (from Li to Fr), the following trends are observed (Table $6.3.1$):

- All have a single electron in an 's' valence orbital
- The melting point decreases
- The density increases
- The atomic radius increases
- The ionization energy decreases (first ionization energy)

> *The alkali metals have the lowest $I_1$ values of the elements*

This represents the relative ease with which the lone electron in the outer 's' orbital can be removed.

***The alkali metals are very reactive, readily losing 1 electron to form an ion with a 1+ charge***:
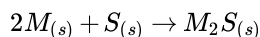
$$M \rightarrow M^+ + e-$$
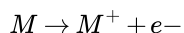
Due to this reactivity, the alkali metals are found in nature only as compounds. The alkali metals combine directly with most nonmetals:
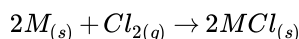
- React with hydrogen to form solid *hydrides*

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH(s)$$
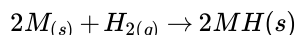
(Note: hydrogen is present in the metal hydride as the **hydride** H⁻ ion)

- React with sulfur to form solid *sulfides*

$$2M_{(s)} + S_{(s)} \rightarrow M_2S_{(s)}$$

React with chlorine to form solid *chlorides*

$$2M_{(s)} + Cl_{2(g)} \rightarrow 2MCl_{(s)}$$

Alkali metals react with water to produce hydrogen gas and alkali metal hydroxides; this is a very exothermic reaction (Figure 6.3.1).

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2MOH_{(aq)} + H_{2(g)}$$
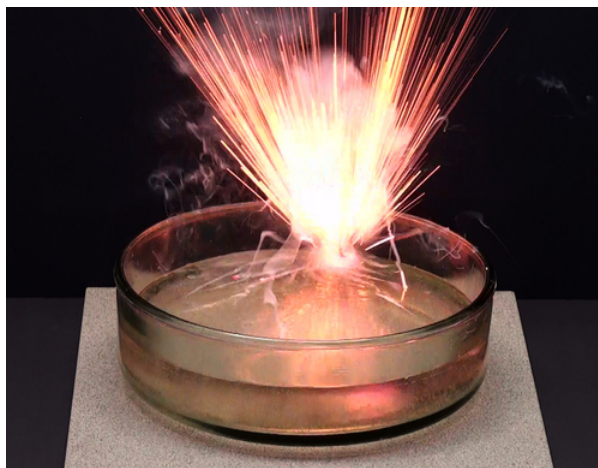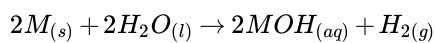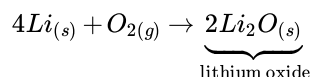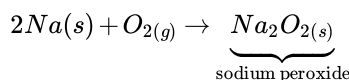


Figure 6.3.1: A small piece of potassium metal explodes as it reacts with water. (CC SA-BY 3.0; Tavoromann)

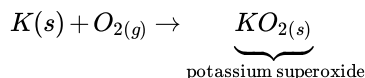**The reaction between alkali metals and oxygen is more complex:**

- A common reaction is to form metal oxides which contain the $O^{2-}$ *ion*

$$4Li_{(s)} + O_{2(g)} \rightarrow \underbrace{2Li_2O_{(s)}}_{\text{lithium oxide}}$$

Other alkali metals *can* form metal peroxides (contains $O_2^{2-}$ ion)

$$2Na(s) + O_{2(g)} \rightarrow \underbrace{Na_2O_{2(s)}}_{\text{sodium peroxide}}$$

K, Rb and Cs *can* also form superoxides ($O_2^-$ ion)

$$K(s) + O_{2(g)} \rightarrow \underbrace{KO_{2(s)}}_{\text{potassium superoxide}}$$

📌 Colors via Absorption

The color of a chemical is produced when a valence electron in an atom is excited from one energy level to another by visible radiation. In this case, the particular frequency of light that excites the electron is ***absorbed***. Thus, the remaining light that you see is white light devoid of one or more wavelengths (thus appearing colored). Alkali metals, having lost their outermost electrons, have no electrons that can be excited by visible radiation. Alkali metal salts and their aqueous solution are colorless unless they contain a colored anion.

📌 Colors via Emission

When alkali metals are placed in a flame the ions are reduced (gain an electron) in the lower part of the flame. The electron is excited (jumps to a higher orbital) by the high temperature of the flame. When the excited electron falls back down to a lower orbital a photon is released. The transition of the valence electron of sodium from the 3p down to the 3s subshell results in release of a photon with a wavelength of 589 nm (yellow)

Flame colors:

- Lithium: crimson red
- Sodium: yellow
- Potassium: lilac

## Group 2: The Alkaline Earth Metals

Compared with the alkali metals, the alkaline earth metals are typically harder, more dense, melt at a higher temperature. The first ionization energies ($I_1$) of the alkaline earth metals are not as low as the alkali metals. The alkaline earth metals are therefore less reactive than the alkali metals (Be and Mg are the least reactive of the alkaline earth metals). Several physical properties of these elements are compared in Table $6.3.2$.

Table $6.3.2$: General Properties of Group 2 Metals

| Element | Electronic Configuration | Melting Point (°C) | Density (g/cm$^3$) | Atomic Radius | Ionization Energy (kJ/mol) |
|---|---|---|---|---|---|
| Beryllium | $[He]2s^2$ | 1278 | 1.85 | 1.52 | 899 |
| Magnesium | $[Ne]3s^2$ | 649 | 1.74 | 1.60 | 738 |
| Calcium | $[Ar]4s^2$ | 839 | 1.54 | 1.97 | 590 |
| Strontium | $[Kr]5s^2$ | 769 | 2.54 | 2.15 | 549 |
| Barium | $[Xe]6s^2$ | 725 | 3.51 | 2.17 | 503 |

Calcium, and elements below it, react readily with water at room temperature:

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$
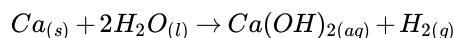
The tendency of the alkaline earths to lose their two valence electrons is demonstrated in the reactivity of Mg towards chlorine gas and oxygen:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$
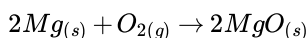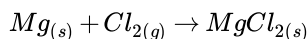
The 2+ ions of the alkaline earth metals have a noble gas like electron configuration and are thus form colorless or white compounds (unless the anion is itself colored). Flame colors:

- Calcium: brick red
- Strontium: crimson red
- Barium: green

## Contributors and Attributions

- Mike Blaber (Florida State University)

> **Learning Objectives**
>
> - To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all $O_2$, $CO_2$, and water vapor from air and showed that this residual gas was slightly denser than pure $N_2$ obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new "substance" (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning "lazy." Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the −1 of the halogens.

> **📌 J. W. Strutt (Lord Rayleigh) (1842–1919)**
>
> Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.
>
> **Sir William Ramsay (1852–1916)**
>
> Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning "hidden," was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning "new," had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning "strange," had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than $N_2$, so scuba divers often use gas mixtures that contain these gases, rather than $N_2$, to minimize the likelihood of the "bends," the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

## Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either $ns^2np^6$ or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 6.3.1 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 6.3.1: Selected Properties of the Group 18 Elements

| Property | Helium | Neon | Argon | Krypton | Xenon | Radon |
|---|---|---|---|---|---|---|
| atomic symbol | He | Ne | Ar | Kr | Xe | Rn |
| atomic number | 2 | 10 | 18 | 36 | 54 | 86 |
| atomic mass (amu) | 4.00 | 20.18 | 39.95 | 83.80 | 131.29 | 222 |
| valence electron configuration* | $1s^2$ | $2s^22p^6$ | $3s^23p^6$ | $4s^24p^6$ | $5s^25p^6$ | $6s^26p^6$ |
| | | | | | | |

*The configuration shown does not include filled d and f subshells. [†]This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

| Property | Helium | Neon | Argon | Krypton | Xenon | Radon |
|---|---|---|---|---|---|---|
| triple point/boiling point (°C) | —/−269[†] | −249 (at 43 kPa)/−246 | −189 (at 69 kPa)/−189 | −157/−153 | −112 (at 81.6 kPa)/−108 | −71/−62 |
| density (g/L) at 25°C | 0.16 | 0.83 | 1.63 | 3.43 | 5.37 | 9.07 |
| atomic radius (pm) | 31 | 38 | 71 | 88 | 108 | 120 |
| first ionization energy (kJ/mol) | 2372 | 2081 | 1521 | 1351 | 1170 | 1037 |
| normal oxidation state(s) | 0 | 0 | 0 | 0 (+2) | 0 (+2, +4, +6, +8) | 0 (+2) |
| electron affinity (kJ/mol) | > 0 | > 0 | > 0 | > 0 | > 0 | > 0 |
| electronegativity | — | — | — | — | 2.6 | — |
| product of reaction with $O_2$ | none | none | none | none | not directly with oxygen, but $XeO_3$ can be formed by Equation 6.3.5. | none |
| type of oxide | — | — | — | — | acidic | — |
| product of reaction with $N_2$ | none | none | none | none | none | none |
| product of reaction with $X_2$ | none | none | none | $KrF_2$ | $XeF_2$, $XeF_4$, $XeF_6$ | $RnF_2$ |
| product of reaction with $H_2$ | none | none | none | none | none | none |

*The configuration shown does not include filled d and f subshells. [†]This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

## Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 6.3.1).
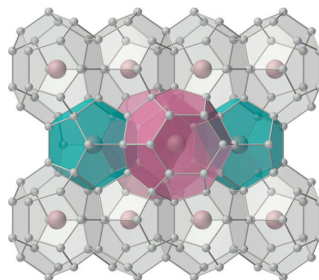


Figure 6.3.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or $CH_4$ can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe \cdot 5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules ($H_2O$, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

📌 Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.
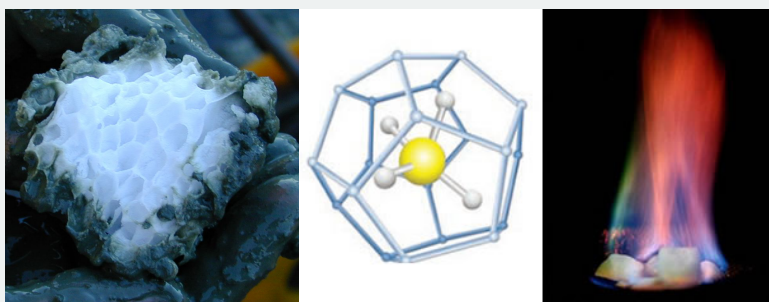


Figure 6.3.2: "Burning snowballs." Like xenon, methane ($CH_4$) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that $PtF_6$, a compound used in the Manhattan Project, could oxidize $O_2$. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of $O_2$, Bartlett recognized that $PtF_6$ should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red $PtF_6$ vapor, yellow-orange crystals immediately formed (Figure 6.3.3). Although Bartlett initially postulated that they were $Xe^+PtF_6^-$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the $XeF^+$ ion:

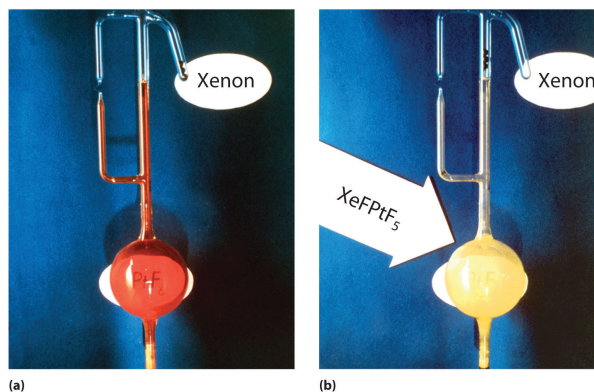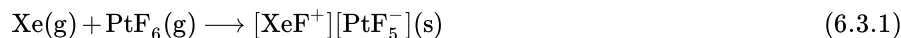$$Xe(g) + PtF_6(g) \longrightarrow [XeF^+][PtF_5^-](s) \tag{6.3.1}$$



Figure 6.3.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^+PtF_5^-$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give $XeF_2$, $XeF_4$, or $XeF_6$, depending on conditions; one such reaction is as follows:

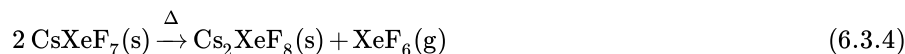$$Xe(g) + 2\,F_2(g) \longrightarrow XeF_4(s) \tag{6.3.2}$$

The ionization energies of helium, neon, and argon are so high (Table 6.3.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: $F_2$ and $Cl_2$. Although $XeCl_2$ and $KrF_2$ can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

> *The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.*

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with $XeF_6$ produces $CsXeF_7$, which gives $Cs_2XeF_8$ when heated:

$$XeF_6(s) + CsF(s) \longrightarrow CsXeF_7(s) \tag{6.3.3}$$

$$2\,CsXeF_7(s) \xrightarrow{\Delta} Cs_2XeF_8(s) + XeF_6(g) \tag{6.3.4}$$

The $XeF_8^{2-}$ ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the $IF_8^-$ ion. $Cs_2XeF_8$ is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of $Cs_2XeF_8$ are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of $SF_6$.)



$XeF_8{}^{2-}$
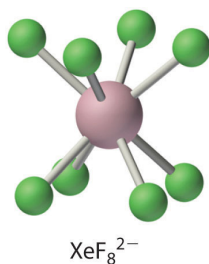
For a previously "inert" gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between $O$ and $Xe$. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either $XeF_4$ or $XeF_6$ produces $XeO_3$, an explosive white solid:

$$XeF_6(aq) + 3\,H_2O(l) \longrightarrow XeO_3(aq) + 6\,HF(aq) \tag{6.3.5}$$

Treating a solution of $XeO_3$ with ozone, a strong oxidant, results in further oxidation of xenon to give either $XeO_4$, a colorless, explosive gas, or the surprisingly stable perxenate ion ($XeO_6^{4-}$), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, $XeO_3$ is isoelectronic with the iodate ion ($IO_3^-$), and $XeF_8^{2-}$ is isoelectronic with the $IF_8^-$ ion.

> *Xenon has a high affinity for both fluorine and oxygen.*

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

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✔ **Example 6.3.1**

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

**Given:** nonradioactive isotope of radon

**Asked for:** summary of its chemistry

**Strategy:**

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

**Solution**

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We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including $RnF_2$, $RnF_4$, $RnF_6$, and possibly $RnF_8$ (due to its large radius). The ion $RnF_8^{2-}$ should also exist. We expect radon to form a series of oxides similar to those of xenon, including $RnO_3$ and possibly $RnO_4$. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

### ? Exercise 6.3.1

Predict the stoichiometry of the product formed by reacting $XeF_6$ with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

**Answer**

$KXeF_7$; the xenon atom in $XeF_7^-$ has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

## Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

## Contributors and Attributions

- o Anonymous

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