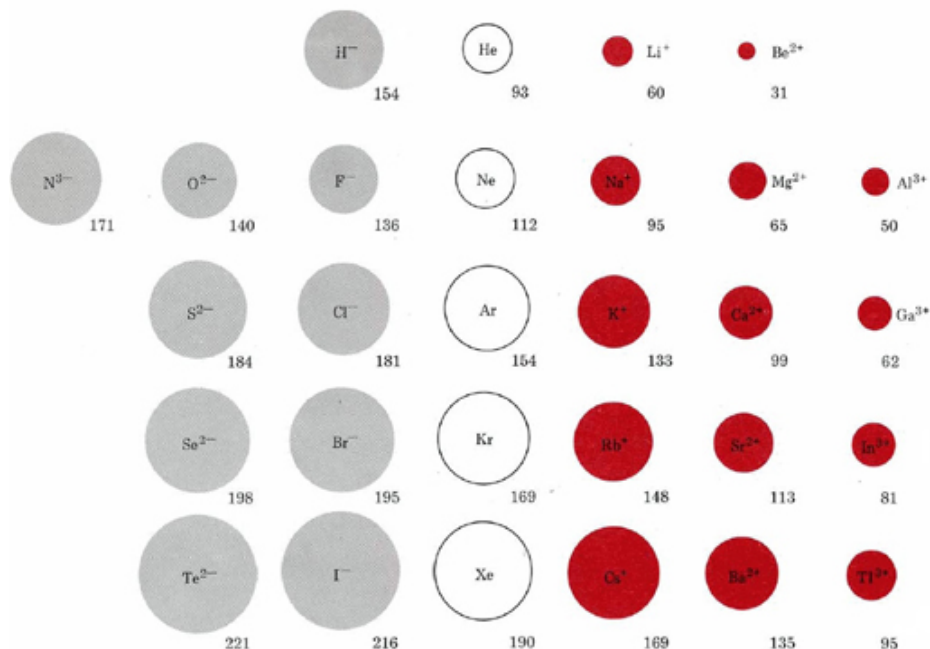


6.20: Ionic Sizes

The size of an ion is governed not only by its electronic structure but also by its *charge*. This relationship is evident in the following figure comparing ionic radii. Ions in the first row of this figure, H^- , Li^+ , and Be^{2+} , all have the same $1s^2$ electronic structure as the helium (He) atom, but differ in size due to the different number of protons each has in their nucleus.



The elements of the periodic table are shown as circles with different radius. Each row consists of elements as well as ions which have the same number of electrons. The first row is H negative to B e superscript 2 positive. The second row is N superscript 3 negative to A l superscript 3 positive. Third row has S superscript 2 negative to G a superscript 3 positive. Fourth row has S e superscript 2 negative to I n superscript 3 positive. The final row has T e superscript 2 negative to T l superscript 3 positive. As we move across each row, the radius of each circle decreases.

Species which have the same electronic structure but different charges are said to be *isoelectronic*. For any electronic series, such as H^- , He, Li^+ , Be^{2+} , in which the nuclear charge increases by 1 each time, we find a progressive decrease in size due to the increasingly strong attraction of the nucleus for the electron cloud. Each row in the figure corresponds to an isoelectronic series involving a different noble-gas electron configuration.

As we move from the more negative to the more positive ions in each row, there is a steady decrease in size. If we move *down* any of the columns, ionic sizes increase due to the increasing principal quantum number of the outermost electrons. The sizes of singly charged cations, for example, increase in the following order: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.

A further point of interest is the size of an ion relative to the atom from which it was formed. Recall the electron dot density diagram showing the formation of LiH . when the Li atom lost its electron and became a Li^+ ion, its size decreased dramatically. Comparing atomic radii to the ionic radii above reveals that this is also true for the other alkali metals. For example, check out the image below, which compares the atomic radii of the uncharged element to its ion. On the left are cations, which have lost an electron to become an ion and show decreases in size.


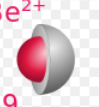
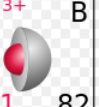

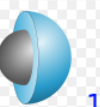


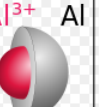



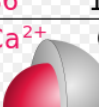
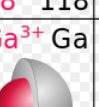


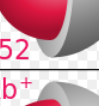
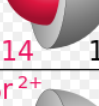
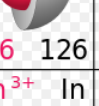
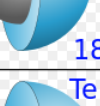
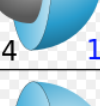
Li^+  90 134	Be^{2+}  59 90	B^{3+}  41 82	O^{2-}  126 73	F^-  119 71
Na^+  116 154	Mg^{2+}  86 130	Al^{3+}  68 118	S^{2-}  170 102	Cl^-  167 99
K^+  152 196	Ca^{2+}  114 174	Ga^{3+}  76 126	Se^{2-}  184 116	Br^-  182 114
Rb^+  166 211	Sr^{2+}  132 192	In^{3+}  94 144	Te^{2-}  207 135	I^-  206 133

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On the right side of the figure are the anions, which form when an element gains an electron. The added electron, as can be observed from the pattern above, increases the atomic radii. Since the added electron goes into a subshell that already has occupants, rather than starting on a new subshell, there is often very little change in size. This is clearly seen in the electron dot density diagram mentioned above, where the formation of an H^- ion from an H atom produces no perceptible increase in size. Comparing the figure of atomic radii to ionic radii above, we also find that the van der Waals radii of nonmetals are only slightly smaller than the radii of their anions. However, some ions still experience fairly significant size changes, as can be seen in the figure above (anions are on the right side).

The sizes of the ions involved have a considerable influence on both the chemical and physical properties of ionic compounds. There is a strong correlation, for example, between ionic size and the melting point of an ionic compound. Among the halides of sodium the melting point decreases in the order of NaF (995°C) > NaCl (808°C) > NaBr (750°C) > NaI (662°C). The larger the anion, the farther it is from the sodium ion, and the weaker the coulombic force of attraction between them. Hence the lower the melting point. When a very small cation combines with a very large anion, the resulting compound is less likely to exhibit the characteristic macroscopic properties of an ionic substance.

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