

Tendencies of ionic and atomic radii in the periodic table

Tendencies:

1. The atomic radii increase down a group (e.g. first group 157 – 272 pm) and within the s and p blocks, decrease from left to right across a period (e.g. second period 157 – 64 pm).
2. The atomic radii for elements following the f block decrease because of the lanthanide contractions
3. All anions are larger and all cations are smaller than their parent atoms, but the ionic radii have generally the same tendencies like atomic radii.
4. The radius of an ion depends on the coordination number!

Explanations:

1. By descending a group, the valence electrons occupy orbitals of increasing quantum numbers. Consequently atoms within the group have a greater number of completed shells of electrons so that the radii increase down the group. Across the period the valence electrons enter the same shell, but the increasing effective charge in a shell across the period lead to a draw in of the electrons that results in a decrease of the radius.
2. The elements in the third row of the d block elements (period 6) are very similar to those of the second row (period 5). This is unusual because of their larger number of electrons in comparison with the d-elements in period 5. Example: tungsten ($Z = 74$; $r = 141$ pm) and molybdenum ($Z = 42$; $r = 140$ pm). The reason for this behaviour is the lanthanide contraction. The lanthanides are the first row of the f-blocks in which the 4f orbitals are occupied. These orbitals have less shielded properties by which the valence electrons suffer a stronger attraction of the nucleus charge Z_{eff} . The result is the contraction of the atom. The effect influences the following d-block elements (period 6) with the same result.
3. The increase of anionic radii has its origin in higher electron-electron repulsions, due to additional electrons and a decrease of Z_{eff} . The smaller radius of a cation in comparison with its parent atom is introduced by reduced electron-electron repulsions and due to the loss of valence electrons, less shells and an increase of Z_{eff} . When we take the favour of some atoms to form anions or cations into considerations, the variation in ionic radii through the periodic table mirrors that of the atomic radius.

Use of atomic radii tendencies

Chemical properties like ionization energy and electronegativity can directly be derived from the atomic radii. E.g. the higher the atomic radius (Cs) the lower is the electronegativity or the ionization energy. General: Atomic radii and electronegativity or ionization energy respectively have opposite behaviour in the periodic table across the period and the group. The knowledge of the atomic radii helps to identify elements in X-ray structure analyses.

Source:

Shriver, Atkins, *Inorganic Chemistry*, OXFORD University Press, **2006**, 4, 23 – 31.