

### 1.1.1: Atomic and Ionic Radius

Atomic radii is useful for determining many aspects of chemistry such as various physical and chemical properties. The [periodic table](#) greatly assists in determining atomic radius and presents a number of trends.

#### Definition

Atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of electron. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change.

The effective nuclear charge  $Z_{\text{eff}}$  of an atom is the net positive charge felt by the valence electron. Some positive charge is shielded by the core electrons therefore the total positive charge is not felt by the valence electron. A detailed description of shielding and effective nuclear charge can be found [here](#).  $Z_{\text{eff}}$  greatly affects the atomic size of an atom. So as the  $Z_{\text{eff}}$  decreases, the atomic radius will grow as a result because there is more screening of the electrons from the nucleus, which decreases the attraction between the nucleus and the electron. Since  $Z_{\text{eff}}$  decreases going down a group and right to left across the periodic table, the atomic radius will *increase* going down a group and right to left across the periodic table.

#### Types of Radius with Respect to Types of Bonds

Determining the atomic radii is rather difficult because there is an uncertainty in the position of the outermost electron – we do not know exactly where the electron is. This phenomenon can be explained by the [Heisenberg Uncertainty Principle](#). To get a precise measurement of the radius, but still not an entirely correct measurement, we determine the radius based on the distance between the nuclei of two bonded atoms. The radii of atoms are therefore determined by the bonds they form. An atom will have different radii depending on the bond it forms; so there is no fixed radius of an atom.

#### Covalent Radius

When a [covalent bond](#) is present between two atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, but you want the radius which is half the diameter.

Covalent radii will increase in the same pattern as atomic radii. The reason for this trend is that the bigger the radii, the further the distance between the two nuclei. See explanation for  $Z_{\text{eff}}$  for more details.

The covalent radius depicted below in Figure 1 will be the same for both atoms because they are of the same element as shown by X.

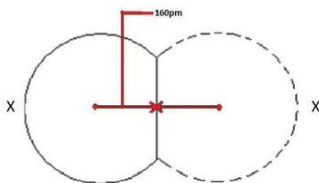


Figure 1: Covalent radii

#### Ionic Radius

The ionic radius is the radius of an atom forming [ionic bond](#) or an ion. The radius of each atom in an ionic bond will be different than that in a covalent bond. This is an important concept. The reason for the variability in radius is due to the fact that the atoms in an ionic bond are of greatly different size. One of the atoms is a cation, which is smaller in size, and the other atom is an anion which is a lot larger in size. So in order to account for this difference, one must get the total distance between the two nuclei and divide the distance according to atomic size. The bigger the atomic size, the larger radius it will have. This is depicted in Figure 2 as shown below where the cation is displayed on the left as  $X^+$ , and clearly has a smaller radius than the anion, which is depicted as  $Y^-$  on the right.

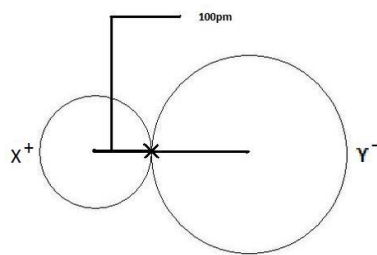


Figure 2: Ionic radii

### ✓ Example 1: Cadmium Sulfide

If we were able to determine the atomic radius of an atom from experimentation, say Se, which had an atomic radius of 178 pm, then we could determine the atomic radius of any other atom bonded to Se by subtracting the size of the atomic radius of Se from the total distance between the two nuclei. So, if we had the compound CaSe, which had a total distance of 278 pm between the nucleus of the Ca atom and Se atom, then the atomic radius of the Ca atom will be 278 pm (total distance) - 178 pm (distance of Se), or 100 pm. This process can be applied to other examples of ionic radius.

Cations have **smaller** ionic radii than their neutral atoms. In contrast, anions have **bigger** ionic radii than their corresponding neutral atoms.

A detailed explanation is given below:

- The cation, which is an ion with a positive charge, by definition has fewer electrons than protons. The loss in an electron will consequently result in a change in atomic radii in comparison to the neutral atom of interest (no charge).
- The loss of an electron means that there are now more protons than electrons in the atom, which is stated above. This will cause a *decrease* in atomic size because there are now fewer electrons for the protons to pull towards the nucleus and will result in a stronger pull of the electrons towards the nucleus. It will also decrease because there are now less electrons in the outer shell, which will decrease the radius size.
- An analogy to this can be of a magnet and a metallic object. If ten magnets and ten metallic objects represent a neutral atom where the magnets are protons and the metallic objects are electrons, then removing one metallic object, which is like removing an electron, will cause the magnet to pull the metallic objects closer because of a decrease in number of the metallic objects. This can similarly be said about the protons pulling the electrons closer to the nucleus, which as a result *decreases* atomic size.

Figure 3 below depicts this process. A neutral atom X is shown here to have a bond length of 180 pm and then the cation  $X^+$  is smaller with a bond length of 100 pm.

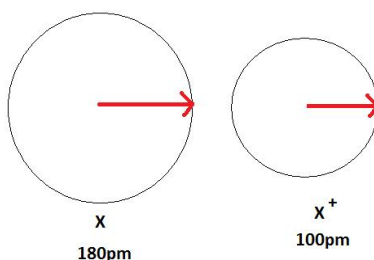


Figure 3: The ionic radius decreases for the generation of positive ions.

An **anion**, on the other hand, will be bigger in size than that of the atom it was made from because of a gain of an electron. This can be seen in the Figure 4 below. The gain of an electron adds more electrons to the outermost shell which *increases* the radius because there are now more electrons further away from the nucleus and there are more electrons to pull towards the nucleus so the pull becomes slightly weaker than of the neutral atom and causes an *increase* in atomic radius.

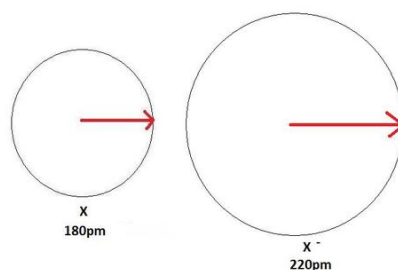


Figure 4: The ionic radius increases for the generation of negative ions.

## Metallic Radius

The metallic radius is the radius of an atom joined by metallic bond. The metallic radius is half of the total distance between the nuclei of two adjacent atoms in a metallic cluster. Since a metal will be a group of atoms of the same element, the distance of each atom will be the same (Figure 5).

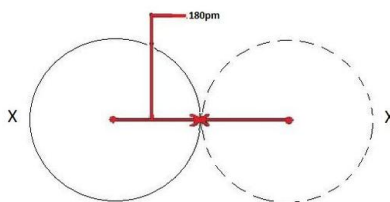


Figure 5: Metallic radii from metallic bonding

## Periodic Trends of Atomic Radius

- An atom gets larger as the number of electronic shells increase; therefore the radius of atoms increases as you go down a certain group in the periodic table of elements.
- In general, the size of an atom will decrease as you move from left to the right of a certain period.

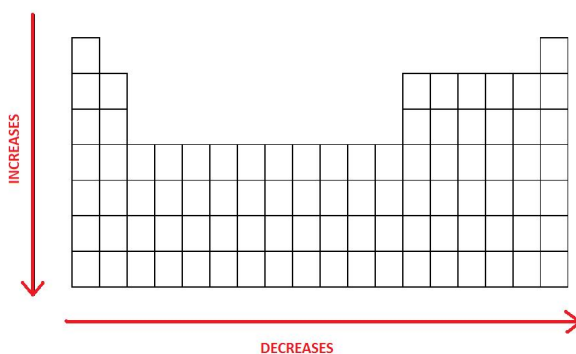
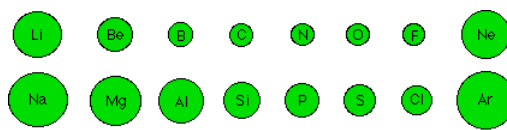


Figure 6: Periodic Trend in atomic radii

The exact pattern you get depends on which measure of atomic radius you use - but the trends are still valid. The following diagram uses metallic radii for metallic elements, covalent radii for elements that form covalent bonds, and van der Waals radii for those (like the noble gases) which don't form bonds.

### Trends in atomic radius in Periods 2 and 3



### Trends in atomic radius down a group

It is fairly obvious that the atoms get bigger as you go down groups. The reason is equally obvious - you are adding extra layers of electrons.

### Trends in atomic radius across periods

You have to ignore the noble gas at the end of each period. Because neon and argon don't form bonds, you can only measure their van der Waals radius - a case where the atom is pretty well "unsquashed". All the other atoms are being measured where their atomic radius is being lessened by strong attractions. You aren't comparing like with like if you include the noble gases.

Leaving the noble gases out, atoms get smaller as you go across a period. If you think about it, the metallic or covalent radius is going to be a measure of the distance from the nucleus to the electrons which make up the bond. (Look back to the left-hand side of the first diagram on this page if you aren't sure, and picture the bonding electrons as being half way between the two nuclei.)

From lithium to fluorine, those electrons are all in the 2-level, being screened by the  $1s^2$  electrons. The increasing number of protons in the nucleus as you go across the period pulls the electrons in more tightly. The amount of screening is constant for all of these elements.

In the period from sodium to chlorine, the same thing happens. The size of the atom is controlled by the 3-level bonding electrons being pulled closer to the nucleus by increasing numbers of protons - in each case, screened by the 1- and 2-level electrons.

### Trends in the transition elements



Although there is a slight contraction at the beginning of the series, the atoms are all much the same size. The size is determined by the 4s electrons. The pull of the increasing number of protons in the nucleus is more or less offset by the extra screening due to the increasing number of 3d electrons.

#### Vertical Trend

The radius of atoms increases as you go down a certain group.

#### Horizontal Trend

The size of an atom will decrease as you move from left to the right of a period.

### Ionic Radius

Ionic radii are difficult to measure with any degree of certainty, and vary according to the environment of the ion. For example, it matters what the co-ordination of the ion is (how many oppositely charged ions are touching it), and what those ions are. There are several different measures of ionic radii in use, and these all differ from each other by varying amounts. It means that if you are going to make reliable comparisons using ionic radii, they have to come from the same source.

What you have to remember is that there are quite big uncertainties in the use of ionic radii, and that trying to explain things in fine detail is made difficult by those uncertainties. What follows will be adequate for UK A level (and its various equivalents), but detailed explanations are too complicated for this level.

### Trends in ionic radius in the Periodic Table

**Trends in ionic radius down a group:** This is the easy bit! As you add extra layers of electrons as you go down a group, the ions are bound to get bigger. The two tables below show this effect in Groups 1 and 7.

	electronic structure of ion	ionic radius (nm)
$\text{Li}^+$	2	0.076
$\text{Na}^+$	2, 8	0.102
$\text{K}^+$	2, 8, 8	0.138
$\text{Rb}^+$	2, 8, 18, 8	0.152
$\text{Cs}^+$	2, 8, 18, 18, 8	0.167

	electronic structure of ion	ionic radius (nm)
$\text{F}^-$	2, 8	0.133
$\text{Cl}^-$	2, 8, 8	0.181
$\text{Br}^-$	2, 8, 18, 8	0.196
$\text{I}^-$	2, 8, 18, 18, 8	0.220

### Trends in ionic radius across a period

Let's look at the radii of the simple ions formed by elements as you go across Period 3 of the Periodic Table - the elements from Na to Cl.

	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$		$\text{P}^{3-}$	$\text{S}^{2-}$	$\text{Cl}^-$
no of protons	11	12	13		15	16	17
electronic structure of ion	2,8	2,8	2,8		2,8,8	2,8,8	2,8,8
ionic radius (nm)	0.102	0.072	0.054		(0.212)	0.184	0.181

The table misses out silicon which does not form a simple ion. The phosphide ion radius is in brackets because it comes from a different data source, and I am not sure whether it is safe to compare it. The values for the oxide and chloride ions agree in the different source, so it is probably OK. The values are again for 6-co-ordination, although I can't guarantee that for the phosphide figure.

First of all, notice the big jump in ionic radius as soon as you get into the negative ions. Is this surprising? Not at all - you have just added a whole extra layer of electrons. Notice that, within the series of positive ions, and the series of negative ions, that the ionic radii fall as you go across the period. We need to look at the positive and negative ions separately.

- **The positive ions:** In each case, the ions have exactly the same electronic structure - they are said to be **isoelectronic**. However, the number of protons in the nucleus of the ions is increasing. That will tend to pull the electrons more and more towards the center of the ion - causing the ionic radii to fall. That is pretty obvious!
- **The negative ions:** Exactly the same thing is happening here, except that you have an extra layer of electrons. What needs commenting on, though is how similar in size the sulphide ion and the chloride ion are. The additional proton here is making hardly any difference.

The difference between the size of similar pairs of ions actually gets even smaller as you go down Groups 6 and 7. For example, the  $\text{Te}^{2-}$  ion is only 0.001 nm bigger than the  $\text{I}^-$  ion.

As far as I am aware there is no simple explanation for this - certainly not one which can be used at this level. This is a good illustration of what I said earlier - explaining things involving ionic radii in detail is sometimes very difficult.

## Trends in ionic radius for some more isoelectronic ions

This is only really a variation on what we have just been talking about, but fits negative and positive isoelectronic ions into the same series of results. Remember that isoelectronic ions all have exactly the same electron arrangement.

	$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$		$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$
no of protons	7	8	9		11	12	13
electronic structure of ion	2, 8	2, 8	2, 8		2, 8	2, 8	2, 8
ionic radius (nm)	(0.171)	0.140	0.133		0.102	0.072	0.054

**Note:** The nitride ion value is in brackets because it came from a different source, and I don't know for certain whether it relates to the same 6-co-ordination as the rest of the ions. This matters. My main source only gave a 4-coordinated value for the nitride ion, and that was 0.146 nm.

You might also be curious as to how the neutral neon atom fits into this sequence. Its van der Waals radius is 0.154 or 0.160 nm (depending on which source you look the value up in) - bigger than the fluoride ion. You can't really sensibly compare a van der Waals radius with the radius of a bonded atom or ion.

## References

1. Pauling, Linus. Atomic Radii and Interatomic Distances in Metal, *Journal of the American Chemical Society* 194769 (3), 542-553
2. Petrucci, Ralph H., William S. Harwood, Geoffery F. Herring, and Jeffry D. Madura. *General Chemistry*. 9th ed. New Jersey: Pearsin Prentice Hall, 2007.

## Problems

1. Which atom is larger: K or Br?
2. Which atom is larger: Na or Cl?
3. Which atom is smaller: Be or Ba?
4. Which atom is larger:  $\text{K}^+$  or K?
5. Put in order of largest to smallest: F, Ar, Sr, Cs.
6. Which has a bigger atomic radius:  $\text{Sr}^{2+}$  or  $\text{Se}^{2-}$ ?
7. If Br has an ionic radius of 100 pm and the total distance between K and Br in KBr is 150 pm, then what is the ionic radius of K?
8. Which has a smaller atomic radius:  $\text{Cs}^+$  or Xe?
9. If the distance between the nuclei of two atoms in a metallic bond is 180 pm, what is the atomic radius of one atom?
10. If Z effective is increasing, is the atomic radius also increasing?

**\*Hint\*** When solving a radius-bond problem, identify the bond first and then use the standard method of finding the radius for that particular bond. Also remember the trend for the atomic radii.

## Answers

1. K
2. Na
3. Be
4. K
5. Cs, Sr, Ar, F
6.  $\text{Se}^{2-}$
7. 50 pm
8.  $\text{Cs}^+$
9. 90 pm

10. No

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