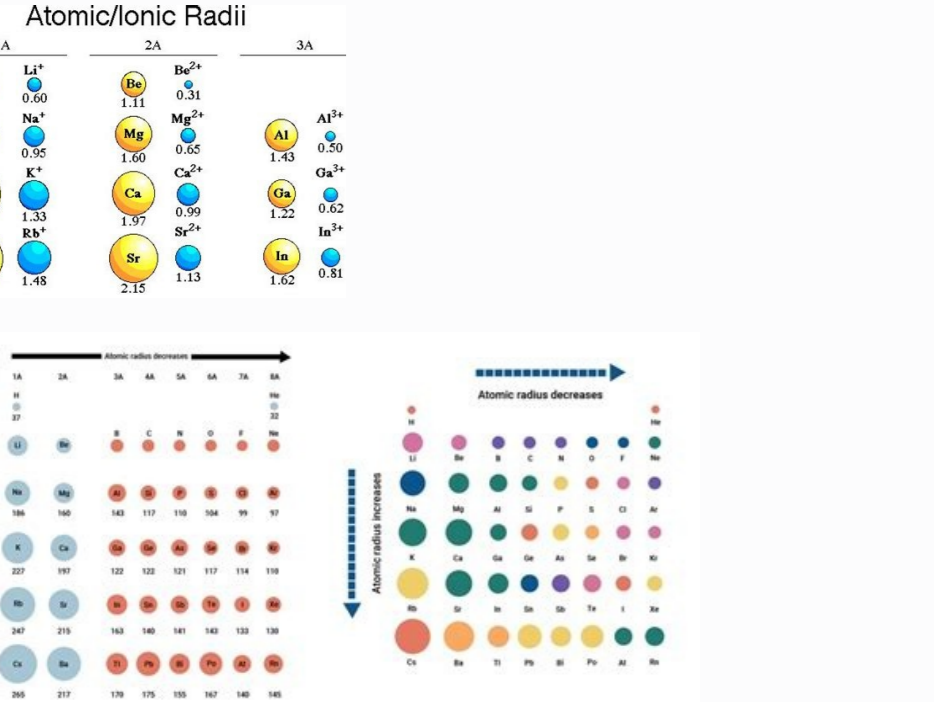
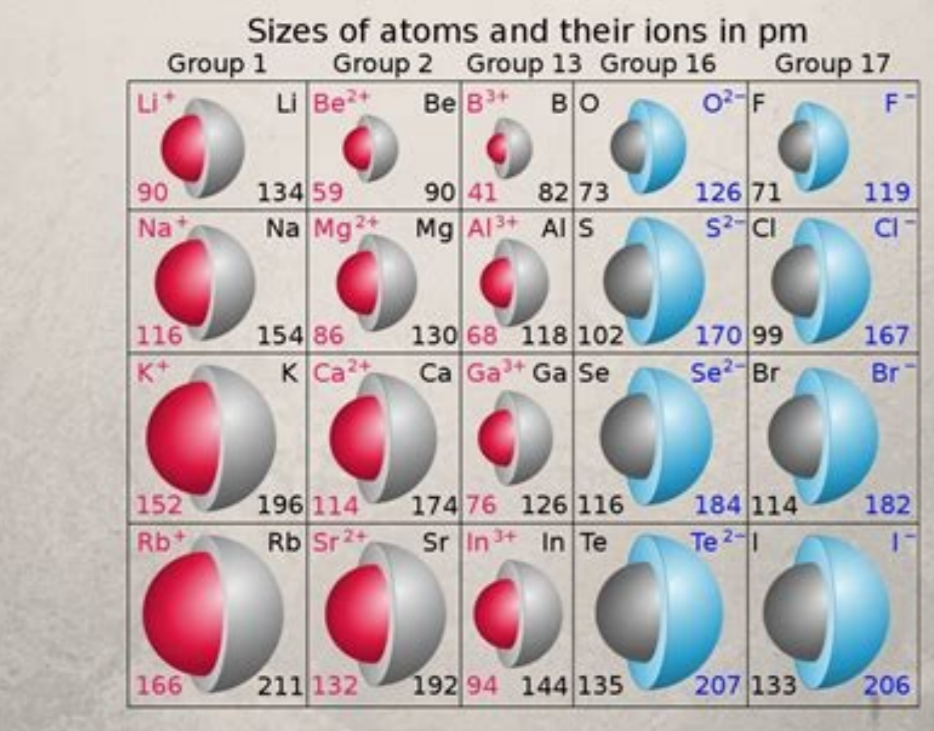
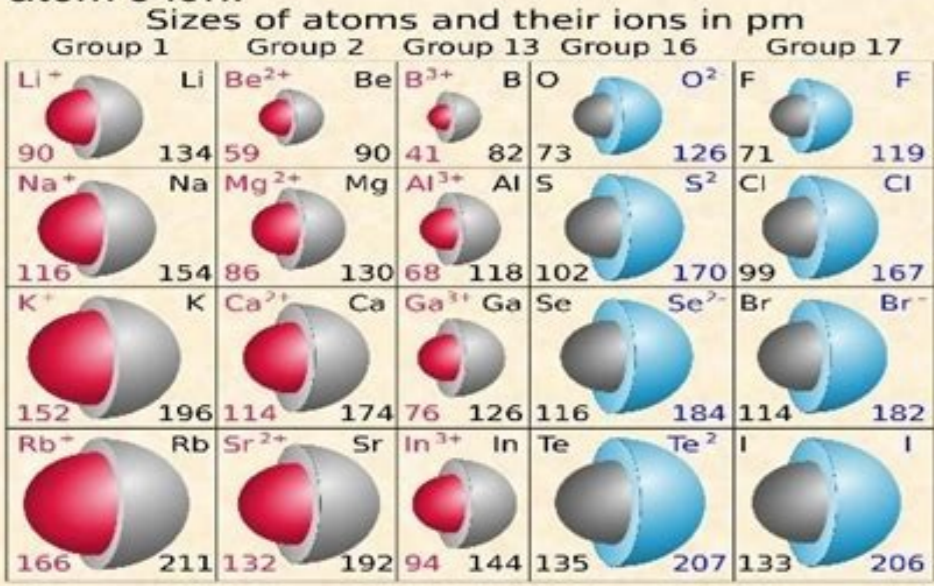


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Ionic Radius

Ionic radius, r_{ion} , is the radius of an atom's ion.



Atomic and Ionic Radius



Ionic and atomic radius trend. Ionic and atomic radius difference. Ionic and atomic radius size. What does atomic radius and ionic radius mean. Is ionic radius and atomic radius the same. How to compare ionic and atomic radius. Difference between ionic and atomic radius. Ionic radius and atomic radius worksheet answers.

You can see that as the number of protons in the nucleus of the ion increases, the electrons get pulled in more closely to the nucleus. The radii of the isoelectronic ions therefore fall across this series. The relative sizes of ions and atoms you probably won't have noticed, but nowhere in what you have read so far has there been any need to talk about the relative sizes of the ions and the atoms they have come from. Neither (as far as I can tell from the syllabuses) do any of the current UK-based exams for 16-18 year olds ask for this specifically in their syllabuses. However, it is very common to find statements about the relative sizes of ions and atoms. I am fairly convinced that these statements are faulty, and I would like to attack the problem head-on rather than just ignoring it. Important! For 10 years, until I rewrote this ionic radius section in August 2010, I included what is in the box below. You will find this same information and explanation in all sorts of books and on any number of websites aimed at this level. At least one non-UK A level syllabus has a statement which specifically asks for this. However, I was challenged by an experienced teacher about my explanation, and that forced me to think about it carefully for the first time. I am now convinced that the facts and the explanation relating to negative ions are simply illogical. As far as I can tell, no UK-based syllabus mentions the relative sizes of atoms and ions (as of August 2010), but you should check past papers and mark schemes to see whether questions have sneaked in. The rest of this page discusses the problems that I can see, and is really aimed at teachers and others, rather than at students. If you are a student, look carefully at your syllabus, and past exam questions and mark schemes, to find out whether you need to know about this. If you don't need to know about it, stop reading now (unless, of course, you are interested in a bit of controversy!). If you do need to know it, then you will have to learn what is in the box, even if, as I believe, it is wrong. If you like your chemistry to be simple, ignore the rest of the page, because you risk getting confused about what you need to know. If you have expert knowledge of this topic, and can find any flaws in what I am saying, then please contact me via the address on the about this site page. Choosing the right atomic radius to compare with this is at the heart of the problem. The diagrams in the box above, and similar ones that you will find elsewhere, use the metallic radius as the measure of atomic radius for metals, and the covalent radius for non-metals. I want to focus on the non-metals, because that is where the main problem lies. You are, of course, perfectly free to compare the radius of an ion with whatever measure of atomic radius you choose. The problem comes in relating your choice of atomic radius to the "explanation" of the differences. It is perfectly true that negative ions have radii which are significantly bigger than the covalent radius of the atom in question. And the argument then goes that the reason for this is that if you add one or more extra electrons to the atom, inter-electron repulsions cause the atom to expand. Therefore the negative ion is bigger than the atom. This seems to me to be completely inconsistent. If you add one or more extra electrons to the atom, you aren't adding them to a covalently bound atom. You can't simply add electrons to a covalently-bound chlorine atom, for example - chlorine's existing electrons have reorganised themselves into new molecular orbitals which bind the atoms together. In a covalently-bound atom, there is simply no room to add extra electrons. So if you want to use the electron repulsion explanation, the implication is that you are adding the extra electrons to a raw atom with a simple uncombined electron arrangement. In other words, if you were talking about, say, chlorine, you are adding an extra electron to chlorine with a configuration of 2,8,7 - not to covalently bound chlorine atoms in which the arrangement of the electrons has been altered by sharing. That means that the comparison that you ought to be making isn't with the shortened covalent radius, but with the much larger van der Waals radius - the only available measure of the radius of an uncombined atom. So what happens if you make that comparison? Group 7 As we have already discussed above, measurements of ionic radii are full of uncertainties. That is also true of van der Waals radii. The table uses one particular set of values for comparison purposes. If you use data from different sources, you will find differences in the patterns - including which of the species (ion or atom) is bigger. These ionic radii values are for 6-co-ordinated ions (with a slight question mark over the nitride and phosphide ion figures). But you may remember that I said that ionic radii changes with co-ordination. Nitrogen is a particularly good example of this. 4-co-ordinated nitride ions have a radius of 0.146 nm. In other words, if you look at one of the co-ordinations, the nitride ion is bigger than the nitrogen atom; in the other case, it is smaller. Making a general statement that nitride ions are bigger or smaller than nitrogen atoms is impossible. So what is it safe to say about the facts? For most, but not all, negative ions, the radius of the ion is bigger than that of the atom, but the difference is nothing like as great as is shown if you incorrectly compare ionic radii with covalent radii. There are also important exceptions. I can't see how you can make any real generalisations about this, given the uncertainties in the data. And what is it safe to say about the explanation? If there are any additional electron-electron repulsions on adding extra electrons, they must be fairly small. This is particularly shown if you consider some pairs of isoelectronic ions. You would have thought that if repulsion was an important factor, then the full radius of, say a sulphide ion, with two negative charges would be significantly larger than a chloride ion with only one. The difference should actually be even more marked, because the sulphide electrons are being held by only 16 protons rather than the 17 in the chlorine case. On this repulsion theory, the sulphide ion shouldn't just be a little bit bigger than a chloride ion - it should be a lot bigger. The same effect is shown with selenide and bromide, and with telluride and iodide ions. In the last case, there is virtually no difference in the sizes of the 2- and 1- ions. So if there is some repulsion playing a part in this, it certainly doesn't look as if it is playing a major part. What about positive ions? Whether you choose to use van der Waals radii or metallic radii as a measure of the atomic radius, for metals the ionic radius is smaller than either, so the problem doesn't exist to the same extent. It is true that the ionic radius of a metal is less than its atomic radius (however vague you are about defining this). The explanation (at least as long as you only consider positive ions from Groups 1, 2 and 3) in terms of losing a complete layer of electrons is also acceptable. Conclusion It seems to me that, for negative ions, it is completely illogical to compare ionic radii with covalent radii if you want to use the electron repulsion explanation. If you compare the ionic radii of negative ions with the van der Waals radii of the atoms they come from, the uncertainties in the data make it very difficult to make any reliable generalisations. The similarity in sizes of pairs of isoelectronic ions from Groups 6 and 7 calls into question how important repulsion is in any explanation. Having spent more than a week working on this, and discussing it with input from some very knowledgeable people, I don't think there is any explanation which is simple enough to give to most students at this level. It would seem to me to be better that these ideas about relative sizes of atoms and ions are just dropped. At this level, you can describe and explain simple periodic trends in atomic radii in the way I did further up this page, without even thinking about the relative sizes of the atoms and ions. Personally, I would be more than happy never to think about this again for the rest of my life! © Jim Clark 2000 (last modified January 2022) Learning Objectives To understand periodic trends in atomic radii. To predict relative ionic sizes within an isoelectronic series. Although some people like the idea of visualising atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion "sizes" are defined and obtained. Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure (1) which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom. Figure (1): Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm. Figure (2) also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks. Argon, with filled n = 1, 2, and 3 principal shells, has three peaks. The peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the 1s2 shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the n = 1 shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the n = 1 shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled n = 2 shell in argon is located closer to the nucleus and has a lower energy than the n = 2 shell in neon. Figure (3) illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure (2a)). Figure (2b): Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl2 is half the distance between the two chlorine atoms in a single molecule of Cl2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl2 molecules. Which do you think is larger? Why? In a similar approach, we can use the lengths of carbon-carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon-chlorine distance of 77 pm + 99 pm = 176 pm for a C-Cl bond, which is very close to the average value observed in many organochlorine compounds. Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure (2b)). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure (2c)). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a (Cl2) molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, (Cl2(s)) at low temperatures). These radii are generally not the same (Figure (2d)). Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure (3)). A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure (4)). Figure (4): Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties. Trends in atomic size result from differences in the effective nuclear charges (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always less than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius. Atomic radii decrease from left to right across a row and increase from top to bottom down a column. The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled 1s inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2s and 2p orbitals, electrons in the same principal shell are not very effective at shielding one another from the nuclear charge. Thus the single 2s electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled 1s2 shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2s electrons in beryllium do not shield each other very well, although the filled 1s2 shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2s electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2s and 2p orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure (5)). Figure (5): The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group. The increase in atomic size going down a column is also due to electron shielding, but the nuclear charge is more complex because the principal quantum number n is not constant. As we saw in Chapter 2, the size of the orbitals increases as n increases, provided the nuclear charge remains the same. In group 1, for example, the size of the atoms increases substantially going down the column, although the nuclear charge increases from +1 to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the most positive charge in the series (Al3+) is the smallest, and the ion with the smallest nuclear charge (Na+) is the largest. The neon atom in this isoelectronic series is not listed in Table (3), because neon forms no covalent or ionic compounds and hence its radius is difficult to measure. Ion Radius (pm) Atomic Number Table (Table (3)). Radius of ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon. "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751-767. N3- 146 7 O2- 140 8 F- 133 9 Na+ 98 11 Mg2+ 79 12 Al3+ 57 13 Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl-, K+, S2-, and Se2-. Given: four ions Asked for: order by increasing radius Strategy: Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table. Determine the relative sizes of the ions based on their principal quantum numbers n and their locations within a row. A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K+, Cl-, and S2- form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S2- with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se2- ion to be even larger than S2-. B The order must therefore be K+ < Cl- < S2- < Se2-. Based on their positions in the periodic table, arrange these ions in order of increasing size: Br-, Ca2+, Rb+, and Sr2+. Answer Ca2+ < Sr2+ < Rb+ < Br- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The covalent atomic radius (r_{cov}) is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The van der Waals radius (r_{vdW}) of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The ionic radii of cations and anions are always smaller or larger, respectively, than the parent due to changes in electron-electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an isoelectronic series, shows a clear correlation between increasing nuclear charge and decreasing size. Modified by Joshua Halpern (Howard University)

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