THE COMPARATIVE SIZES OF ATOMS V’s IONS.

These notes are a direct result of question 7 (iii) of Assignment 3.

The reference for these notes comes from Silberberg, 3rd Ed., 2003 (!!sic!!), p 318/319.

From the relation between effective nuclear charge ($Z_{\text{eff}}$) and atomic size, the following is easily understood:

- Cations are smaller than their parent atoms……here the electrons are removed from the outer shell. The resulting decrease in electron repulsions allows the nuclear charge to pull the remaining electrons closer.
- Anions are larger than their parent atoms……here the electrons are added to the outer level. The increased repulsions cause the electrons to occupy more space.

It is therefore obvious that ionic size increases down a group!! However, across a period the pattern is much more complex: size decreases among the cations, then increases tremendously when we reach the anions, and then finally decreases again among the anions. This pattern results from changes in $Z_{\text{eff}}$ and electron-electron repulsions. The decrease in size of the cations eg in Period 3, $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$ is obvious (QED). Now on producing anions, the huge jump in size can be seen by the following analysis: $\text{P}^{3–}$ has $\text{EIGHT}$ more electrons than $\text{Al}^{3+}$. Then, the ongoing rise in $Z_{\text{eff}}$ makes $\text{P}^{3–}$ larger than $\text{S}^{2–}$ (why?) which is larger than $\text{Cl}^–$ (why?). These factors lead to some striking effects even among ions with the same number of electrons (isoelectronic): All the following ions are isoelectronic with Neon and even though the cations form from elements in the next period, the anions are still much larger….  

<table>
<thead>
<tr>
<th>Period 2</th>
<th>N$^{3–}$ (146pm); O$^{2–}$ (140pm); F$^–$ (133pm)</th>
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<tbody>
<tr>
<td>Period 3</td>
<td>Na$^+$ (102pm); Mg$^{2+}$ (72pm); Al$^{3+}$ (54pm)</td>
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Now the problem with q.7 (iii):

The ‘size’ of O is 73 pm, while that of O$^{2–}$ is 140pm; while F is 72 pm and F$^–$ is 133pm.

From the discussion above you would expect F$^–$ to be smaller than O$^{2–}$ (F$^–$ has one more proton (and therefore a higher $Z_{\text{eff}}$) and one less electron than O$^{2–}$ (less electron repulsion)). But the question asks you to qualitatively compare the size of O V’s F$^–$….. 

…..F$^–$ > F….; O > F ….; BUT O v’s F$^–$ ????

So, on one level it is possible to think/relate sizes of atoms and ions as by the above discussion, but really on another level, some prerequisite information is needed. So therefore in the exam, you will not be asked to compare ions and atoms of different elements!!!!!