Chapter 23   CONFIGURATIONS AND CONSEQUENCES, Part 1

Now we will see how to read electron configurations straight from the Periodic Table. Again, be ready to flip to the inside front cover for the full Table. I'll only show parts here.

23.1 Reading the Periodic Table

To do a configuration for some element, you simply locate the element in the Table and read the configuration to that point. All configurations start at H. You walk through the Table, passing through each subshell, writing each subshell down as you go. The type of subshell corresponds to the block you are in, whether it be s-block, p-block, d-block or f-block. When you get to the subshell with the element you want, then you count over by the individual squares. As you walk through the Table, the tricky part is the shell number, n: it's related to the row (Period) number. Keep in mind how we started all this and how the Period numbers came out in the end. I repeat this at left. Notice that for all s and p subshells, the n value is the Period (row) number. For example, $2s$ and $2p$ are in Period $\underline{2}$. For a d subshell, its value of n is the Period number minus one. For example, $3d$ is in Period $\underline{4}$. For an f subshell, its value of n is the Period number minus two. For example, $4f$ is in Period $\underline{6}$.

Period 1	$1s^2$
2	$2s^2\ 2p^6$
3	$3s^2\ 3p^6$
4	$4s^2\ 3d^{10}\ 4p^6$
5	$5s^2\ 4d^{10}\ 5p^6$
6	$6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$
7	$7s^2\ 5f^{14}\ 6d^{10}\ 7p^6$

Time for some examples. Let's redo some configurations from the last Chapter but using only the Periodic Table. Let's do carbon again. Locate it in the Table.

Start at the beginning at H ($1s^1$) and cut across to He; that's $1s^2$. Go to the next row, beginning with $2s$. Pass through the first two squares, which adds $2s^2$. Hop over to the p-block, starting into $2p$. You go two squares to land on C, which adds $2p^2$. Now string it together: $1s^2 2s^2 2p^2$. That's it.

Let's do chlorine. Locate it.

Start at the beginning: buzz through the two squares of H and He, giving $1s^2$. Go to the Second Period. The two s squares give us $2s^2$. Hop over to p: the six squares give us $2p^6$. Now go to the Third Period. The two s squares give us $3s^2$. Go again over to p: you go five squares to hit Cl, giving $3p^5$. Put it together: $1s^2 2s^2 2p^6 3s^2 3p^5$.

Vanadium. Locate it.

Start off again with $1s^2$. Drop down, go through $2s^2$. Hop over and go through $2p^6$. Go to the Third Period. Two s squares will get you $3s^2$, then the six p squares will add $3p^6$. Drop down to the next row.

Two *s* squares get you $4s^2$. Now enter the *d*-stretch: go in three squares to land on V. That adds $3d^3$. Put it all together: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$.

This is really all you have to do. Just walk through the Table, one subshell section at a time, writing them down as you go.

I'm going to introduce another notation for writing configurations. This version is an abbreviated format, using symbolism for the noble gas elements, Group 18. Why do we choose a format based on Group 18? There is a very good reason for this. The configurations of the Group 18 elements are among the best and most favorable of all configurations possible. This is really important here, in the next Chapter and into later Chapters. In fact, I think I'll repeat it.

THE CONFIGURATIONS OF THE GROUP 18 ELEMENTS ARE AMONG THE BEST AND MOST FAVORABLE OF ALL CONFIGURATIONS POSSIBLE.

These even get a specific term: "noble gas configuration". The abbreviated format for configurations uses a noble gas symbol in [brackets]. The bracket term means the configuration for that noble gas element. For example,

> ‣ The configuration of He is $1s^2$. The bracket notation [He] means $1s^2$.
> ‣ The configuration of Ne is $1s^2 2s^2 2p^6$. The bracket notation [Ne] means $1s^2 2s^2 2p^6$.
> ‣ The configuration of Ar is $1s^2 2s^2 2p^6 3s^2 3p^6$. The bracket notation [Ar] means $1s^2 2s^2 2p^6 3s^2 3p^6$.

Etc. You can only put a noble gas symbol into [brackets], but you can use this notation for any element whatsoever. Let's go back to our examples above.

Carbon was $1s^2 2s^2 2p^2$. Since [He] means $1s^2$, we can abbreviate carbon as [He]$2s^2 2p^2$.

This is not much of an abbreviation, is it? The advantage becomes more obvious as we go down the Periodic Table.

Chlorine: $1s^2 2s^2 2p^6 3s^2 3p^5$

[Ne]   ➡ We can abbreviate chlorine's configuration as [Ne]$3s^2 3p^5$.

Vanadium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

[Ar]   ➡ We can abbreviate vanadium's configuration as [Ar]$4s^2 3d^3$.

The noble gas abbreviated configurations are even easier to read off the Periodic Table than the full forms. Again, you first locate the element you want. Now, instead of going all the way back to H, you only go back to the prior noble gas element: write its symbol in [brackets], and continue from that point. Let's do an example, something different. How about cadmium? Cadmium is one of the important elements in common, rechargeable, nickel-cadmium batteries known as "Nicads" (NiCd). They're phasing these out, however, as newer technology batteries are becoming more readily available. Much of this is because cadmium compounds tend to be toxic, so there are exposure problems and environmental problems, despite the recycle programs. Let's see how well you remember the tour from Chapter 2 through the Periodic Table: I told you at that time about many different elements and their compounds and how some are necessary for life and how some are toxic to life. I also told you how Nature throws a whammy, making even some toxics essential for life. Cadmium has been regarded as toxic for many years and yet, recently, an organism was discovered that uses cadmium compounds to live. This was a first for Cd as a new biometal. These kinds of findings really serve to point out how significant discoveries continue to be made. Often, the more we learn, the more we realize we don't know.

In order to do the configuration for cadmium, first locate it in the Table.

	1	2											13	14	15	16	17	18
1	H																	He
2																		Ne
3			3	4	5	6	7	8	9	10	11	12						Ar
4																		Kr
5											**Cd**							Xe

Identify the prior noble gas and start from there. The prior noble gas is Kr, so we begin writing the configuration with [Kr]. From there, we proceed to the next row, Period 5. Two *s* squares leave us with $5s^2$. We then move over all ten squares into the *d* stretch to land on Cd. That gives us $4d^{10}$. Put it all together and you get $[Kr]5s^24d^{10}$. That's it. Like I said, as you get lower in the Periodic Table, the abbreviation method gets much easier to work with than the full format. The full configuration for cadmium is $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}$.

Let's do something from the *f* block. How about Pu? That's plutonium. Locate it.

	1	2											13	14	15	16	17	18
1	H																	He
2																		Ne
3			3	4	5	6	7	8	9	10	11	12						Ar
4																		Kr
5																		Xe
6		56	57	72														Rn
7		88	89	104														118

58													71
90			**Pu**										103

There's a catch to doing a configuration which involves an *f* stretch, so watch how this works. Pu has $Z = 94$ and it is in Period 7. The prior noble gas is Rn in Period 6; thus, the configuration begins with [Rn].

[Rn]

After that we start into Period 7 with $7s^2$, which puts us at $Z = 88$ (Ra).

$[Rn]7s^2$

Here's where you need to remember that the next element, $Z = 89$ (Ac), is not standard fill sequence. The standard fill sequence in Period 7 is actually $7s^25f^{14}6d^{10}7p^6$; we just filled up $7s^2$ to end at $Z = 88$. Pu has 94 electrons, six more. Just put six into the next subshell, which is 5*f*. The final configuration is

$[Rn]7s^25f^6$

That's it.

Final example: let's see what happens after an *f* portion in the configuration. We'll do Hg, $Z = 80$, right below Cd. Locate it.

	1	2											13	14	15	16	17	18
1	H																	He
2																		Ne
3			3	4	5	6	7	8	9	10	11	12						Ar
4																		Kr
5																		Xe
6		56	57	72								**Hg**						Rn
7		88	89	104														118

58													71
90													103

Notice that mercury will include the whole $4f$ part in its configuration. The prior noble gas is Xe, so the configuration begins with [Xe].

> [Xe]

After that we add $6s^2$, which puts us at Z = 56 (Ba).

> $[Xe]6s^2$

24 electrons remain. The next element, Z = 57 (La), does not follow standard fill sequence. The actual standard fill sequence for Period 6 is $6s^2 4f^{14} 5d^{10} 6p^6$, so $4f$ should follow $6s$. $4f$ can handle 14 of the 24 remaining electrons.

> $[Xe]6s^2 4f^{14}$

We are now at 70 electrons and Hg needs ten more; those will go to $5d$.

> $[Xe]6s^2 4f^{14} 5d^{10}$

Done.

Remember: if you go down into either the $4f$ or $5f$ stretch, start filling it right after the $6s^2$ or $7s^2$ part. Keep track of your number of electrons as you go.

By the way, I've been saying for some time now that there are several other exceptions to the standard fill sequence besides La and Ac. Here they are.

> d-block: Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt, Au
> f-block: Ce, Gd, Pa, U, Cm

I will not detail those configurations here. Technically, La and Ac are exceptions but these two were moved to their correct final configuration block in the Periodic Table. Thus, you can still read the configurations for La and Ac right off the Periodic Table. Out of all of the exceptions, notice that none are in the Main Groups, so those elements will always follow the general fill sequence. The exceptions only occur within the d-block or f-block.

In general, configurations are very important and that is why I am spending a lot of time with them. They tell us a lot. You need to practice them and get a good handle on doing them. Here're a few for you.

. . . .

Example. Complete the following configurations.

> As: [_____] $4s^2$ _____ _____
>
> Sr: $1s^2 2s^2$ _____ _____ $3p^6$ $4s^2$ _____ $4p^6$ _____
>
> Ra: [_____] _____

. . . .

If you need help, go back through the prior illustrations.

Now, having come this far, we need to pause for a moment. We have come a long way since Chapter 2. We are finally able to answer the questions first posed at that time regarding the location and energies of electrons in atoms. The answers lie in electron configurations. All chemical properties depend on this. The entire Periodic Table depends on this. We'll see more of the importance of this as we go further in this Chapter and into the following Chapters. For now, there is still more to do with configurations, since we have only done neutral atoms. We need to do ions.

23.2 Ions

Configurations for many ions follow the same general principles as for neutral atoms but there are some twists. Anions are straightforward. Some cations are straightforward but some are not. As before, all configurations are the result of the balance between electron-nuclear attractions and electron-electron repulsions. Both of these are affected by adding electrons to form anions and by subtracting electrons to form cations. We shall see the outcomes as we go.

Anion configurations follow the general fill sequence nicely, so there's nothing new here. You can start with the configuration of the neutral element and add electrons to it according to charge. We did

chlorine's configuration earlier; now let's do chloride. The configuration of neutral Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$. Cl⁻ has one more electron; this evenly fills out $3p$ to give $1s^2 2s^2 2p^6 3s^2 3p^6$. That part is simple to see but there is a catch for the noble gas abbreviation which I need to point out. The abbreviated configuration of neutral Cl is [Ne]$3s^2 3p^5$. For the configuration of Cl⁻, we might be tempted to write [Ne]$3s^2 3p^6$ but this is the same as the configuration for argon! Both Cl⁻ and Ar have the same number of electrons and the same configuration; both would be written in abbreviated format as simply [Ar]. This is a good generality to be aware of: all common anions have the configuration of the <u>following</u> noble gas. The configuration of nitride is [Ne]. For sulfide, it's [Ar], just like chloride. For iodide, it's [Xe]. Etc.

Notice that I said this applies for the <u>common</u> anions. The common anions are all in the p-block. There are <u>un</u>common anions from other blocks which don't follow a noble gas configuration, like Au⁻. Be aware that this can happen.

Now for cations.

This is where we run into different twists because we encounter a number of variations within the overlap regions. First of all, let me say that all cations from the s-block follow the normal fill sequence, so you never have to worry about these. For cations from the other blocks, variations can happen. The most common variation involves the s and d subshells and this is the only variation which I will cover here: generally, if electrons are available for d, then they go to d before going to s. I'll give you an example of this variation along with a normal case for comparison. Let's work with the 3+ and 2+ cations of scandium. Neutral scandium has 21 electrons and follows the general fill sequence.

Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ OR   [Ar]$4s^2 3d^1$
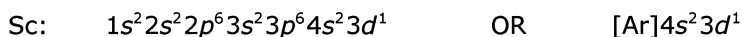
Sc³⁺ has 18 electrons and Sc²⁺ has 19 electrons. Sc³⁺ <u>does follow</u> the general fill sequence for 18 electrons.

Sc³⁺: $1s^2 2s^2 2p^6 3s^2 3p^6$ OR   [Ar]

The oddball in this comparison is Sc²⁺: the nineteenth electron goes into $3d$, not into $4s$ as would be expected by the usual fill sequence.

Sc²⁺: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ OR   [Ar]$3d^1$
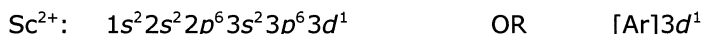
The overall result is this: for many cations, the total energy outcome places the d subshell ahead of the outermost s subshell. This gives a different fill sequence in those cases. Notice that I said this occurs for many cations; <u>it does not occur for all cations</u>. (See the technicality below.) Sometimes, it just doesn't matter anyway. For example, it mattered for Sc²⁺ but it didn't matter for Sc³⁺. It also does not matter for s-block cations, as I already mentioned.

There is a trick for getting around this without getting bogged down in memorizing a separate sequence for some cations. You start with the configuration of the neutral atom. Then, you remove electrons from the configuration according to the cation charge but you remove them from the <u>highest n-shell first</u>. This gives the correct answer in the great majority of cases. Let's run through several examples.

‣ Al³⁺

Start with the configuration for neutral aluminum.

Al: [Ne]$3s^2 3p^1$

Compared to the neutral atom, the 3+ cation has three fewer electrons. Remove three from the configuration, beginning with the highest n-shell. Here, the highest n is $n = 3$. There happen to be three electrons in $n = 3$ ($3s^2 3p^1$), so drop those.

Al³⁺:   [Ne]

This is the same as the general fill sequence.

‣ Ga⁺

Start with the configuration for neutral gallium.

Ga: [Ar]$4s^2 3d^{10} 4p^1$
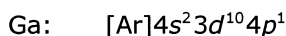
The 1+ cation has one less electron. Remove one from the above configuration, beginning with the highest n-shell. That would be $n = 4$. Within $n = 4$, we have electrons in $4s$ and in $4p$. Which subshell loses? Remember: within a shell, electrons like s better than p, so p loses. That leaves us with the following.

Ga$^+$:   [Ar]$4s^2 3d^{10}$

Ga$^+$ also follows the general fill sequence. Compare this to the next case.

▸ Ga^{3+}

　　Start with the configuration for neutral gallium, as above.

Ga: [Ar]$4s^2 3d^{10} 4p^1$
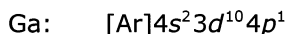
The 3+ cation has three less electrons. Remove three from the above configuration, beginning again with $n = 4$. As for Ga$^+$, the first electron comes from $4p^1$; the next two come from $4s^2$.

Ga^{3+}:   [Ar]$3d^{10}$

This does NOT follow the general fill sequence, but our method produced the correct answer.

▸ V^{2+}

　　We did neutral vanadium earlier. You do the 2+ cation.

V^{2+}:   [____] ____

　　That takes care of the cations. Remember! For cations, take electrons out of the <u>highest n-shell</u> first, corresponding to charge. Out of all of the errors which students make for configurations of ions, this is one of the most common.

　　OK, now for the technicality which I mentioned above. When the total energies switch over from the sequence *s*-before-*d* (as in the general fill sequence) to the sequence *d*-before-*s* (for many cations), the switchover is incomplete for some 1+ cations in the *d*-block. This is just a consequence of the subtle factors that are involved. To illustrate this, let's compare the actual configurations of Sc$^+$, Y$^+$ and La$^+$. These three elements are right on top of each other in Group 3.

　　▸ The actual configuration of Sc$^+$ is [Ar]$4s^1 3d^1$. This configuration would be obtained by our steps outlined above.
　　▸ The actual configuration of Y$^+$ is [Kr]$5s^2$. This configuration follows the normal fill sequence for neutrals. It would not be obtained by our steps above.
　　▸ The actual configuration of La$^+$ is [Xe]$5d^2$. This configuration follows the switch-over to the sequence of *d*-before-*s*, but it would not be obtained by our steps above.

All three of these elements are in the same Group but all three of these do something different for their 1+ cation. If you ask me why this is so, I really don't know. Fortunately, by the time you hit 2+ or higher charge, the switchover is fairly complete and our prior steps apply. This 1+ mixup is only in the *d*-block anyway, so don't worry about 1+ cations from the *s*- or *p*-blocks. I'll simply avoid configurations for 1+ cations from the *d*-block. Your instructor may cover them, in which case follow whatever steps s/he tells you to do.

　　This completes our discussion of how to do configurations. We now turn to the significance of configurations and various relationships within the Periodic Table. Most of the following discussion deals with neutrals again but we'll bring in more stuff about ions also.

23.3 Consequences and trends

　　One direct consequence of the setup of the Periodic Table is related to the Group arrangements: each member of a Group ends in a similar configuration. I'll illustrate with several halogens.

F　　[He]$2s^2 2p^5$
Cl　　[Ne]$3s^2 3p^5$
Br　　[Ar]$4s^2 3d^{10} 4p^5$
Etc.
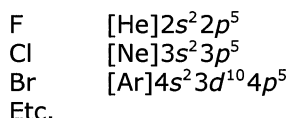
All end in np^5. In order to see the significance of this, I have to remind you of something old and I have to introduce something new. The old part is that ELECTRONS DO CHEMISTRY. The new part is a bit more specific: it is primarily the electrons in the outermost shell that do chemistry. Why those? It's because they are in the biggest orbitals, so they are more reachable and they are held more weakly than those in lower (smaller) n-shells. Because of this, these electrons are the most available to be lost to form cations and/or these electrons are the most available for sharing in covalent bonds. Catch the significance here; I'm setting you up for ionic and covalent bonding in compounds. This will be incredibly important, as we shall see starting in Chapter 25 when we cover those aspects. For now, just remember that

ELECTRONS IN THE OUTERMOST SHELL OF THE NEUTRAL ATOM ARE THE "MOST AVAILABLE" TO DO CHEMISTRY.

If we focus only on the highest n-shell in each case, all of our halogens have two electrons in ns and five in np.

		highest n-shell
F	$[He]2s^2 2p^5$	$2s^2 2p^5$
Cl	$[Ne]3s^2 3p^5$	$3s^2 3p^5$
Br	$[Ar]4s^2 3d^{10} 4p^5$	$4s^2 4p^5$
Etc.		

All halogens have seven "most available" electrons and these electrons are all in the same kinds of orbitals, s and p (although they are in different shells). Because of this similarity, all halogens will share similarities in chemical properties. This is very general and it is a common theme for the Periodic Table. It's also very important.

▸ All elements in a Group will have similar configurations for their most available electrons.
▸ Because of this, all elements within a Group will have similar chemical properties.

Notice that I'm saying "similar". I'm not saying "same". There are going to be some differences and, besides, there will be some effect from the differences in the shells involved. Nevertheless, the generalities remain true and they remain very important.

The distinction between those electrons which are "most available" to do chemistry and those which are not leads to two new terms. The terms are "valence electrons" and "core electrons". I'll define these terms for you but I am only going to use Main Group definitions. These Main Group definitions only cover s and p valence electrons. This will easily cover the most important cases for our purposes here but they do not cover d and f valence electrons. If your instructor is doing d and f valence, then be sure to follow her/his definition for those cases.

With this specification in mind, valence electrons are defined as those in the highest n-shell of the neutral atom. Core electrons are simply all electrons which are not valence. So, if you want to know what's core, then first figure out what's valence. Let's apply these terms to our halogen configurations from above.

		valence electrons (highest n-shell)	core electrons (not valence)
F	$[He]2s^2 2p^5$	$2s^2 2p^5$	$[He]$
Cl	$[Ne]3s^2 3p^5$	$3s^2 3p^5$	$[Ne]$
Br	$[Ar]4s^2 3d^{10} 4p^5$	$4s^2 4p^5$	$[Ar]$ and $3d^{10}$

The total number of valence electrons is an important aspect. Each of the above has seven valence electrons. They have different numbers of core electrons, but that is less important to the chemical properties.

For Main Group cases, valence electrons are also called outer shell electrons. Core electrons are also called inner shell electrons. These are just alternate terms.

Since the total number of valence electrons is such an important aspect, it will be extremely useful to you to determine that number without going through a configuration all the time. This information can be taken directly off the Periodic Table. Here's how.

▸ For any s-block element, the number of valence electrons is equal to the Group number.
▸ For p-block elements except He, the number of valence electrons is equal to Group number minus ten. (Helium is only $1s^2$ with two valence electrons.)

Know these two points. Continuing with the halogens as examples, all of these are in Group 17. All have $17 - 10 = 7$ valence electrons. Let's do a new example: how many valence electrons are in silicon? Locate it.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2																		Ne
3														**Si**				Ar

Silicon is in Group 14, so it has four valence electrons. If you need to, you can still do a full breakdown.

	valence electrons	core electrons
Si $[Ne]3s^23p^2$	$3s^23p^2$	$[Ne]$
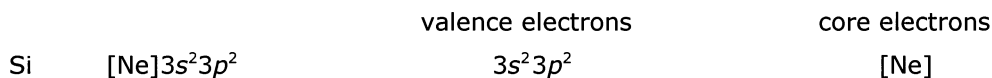
By the way, the number of core electrons is the total number of electrons minus the number of valence electrons. The total number is the same as the atomic number (Z) for the neutral atom. This allows us to equate the number of core electrons as follows.

number of core electrons = atomic number – number of valence electrons

For silicon ($Z = 14$), there are $14 - 4 = 10$ core electrons.

While the number of valence electrons is very important by itself, sometimes we also want to know which shell the valence electrons are in. That's easy: it's Period number. Si is in Period 3, so we know immediately that its valence electrons are in $n = 3$.

Now we turn to several properties of the elements which depend on electron configuration; it's really the trends in these properties which are of interest right now. Since the Periodic Table is based on configurations, then these trends will be apparent from the Table. In fact, these are typically called "Periodic Trends".

As we go, keep in mind that these are trends. These are not perfect rules to go by. There will be exceptions but the trends are very good in general. I will again restrict to Main Groups. The *d*-block and *f*-block elements are more erratic in their properties. There are more subtleties involved in those blocks and, besides, those blocks contain all of the exceptions to the general fill sequence. Thus, we'll stick to Main Groups. We'll cover three Periodic Trends for now: atomic size, ionization energy and electron affinity. We'll add a fourth in Chapter 25.

• ATOMIC SIZE

Let me return to the very beginning of Chapter 2 and explain the last two points which we listed about atoms at that time.

  ❝ 8. The electrons are widely spread out in a volume surrounding the nucleus. This volume is actually very large (by many thousands of times) when compared to the size of the nucleus. Although this volume is large compared to the nucleus, "large" to an atom is still very small compared to anything we can normally see.

     9. IMPORTANT RESULT FOR SIZE: The size of the atom is almost entirely determined (~99.99%) by the volume in space which is occupied by the electrons. ❞

We now know that electrons are in orbitals and that these constitute field regions in three dimensional space. Orbitals are not hard objects, so they don't have a fixed size. Nevertheless, the electrons in the orbitals of one atom will avoid the electrons in orbitals of another atom if they get too close. This means that there is a practical limit of approach for atoms and we use this to judge the size of the atoms. There's a technicality here: this practical limit of approach has different ways of being measured, such as the distance between two atoms within a covalent bond or the distance between separate chemical units in a solid phase. We don't need this technical distinction for our purposes right now, and we'll just stick with the general trend.

When we talk about size, we will talk about the radius (not the diameter) of the atom. Thus, we use atomic radii for size. Here's what you need to know.

  ▸ Electrons in orbitals determine size. Therefore, size is related to electron configuration.
  ▸ Electron configuration is related to position in the Periodic Table. Therefore, size is related to position in the Periodic Table.

Here are some numbers. Since there are different methods of measuring these, you may find different numbers in other sources. That's OK; they'll follow the same general trends anyway.

ATOMIC RADII (pm)

		1	2		13	14	15	16	17	18
1		H 37								He
2		Li 134	Be 90.		B 82	C 77	N 75	O 73	F 71	Ne
3		Na 154	Mg 130.		Al 118	Si 111	P 106	S 102	Cl 99	Ar
4		K 196	Ca 174		Ga 126	Ge 122	As 119	Se 116	Br 114	Kr
5		Rb 211	Sr 192		In 144	Sn 141	Sb 138	Te 135	I 133	Xe
6		Cs 225	Ba 198		Tl 148	Pb 147	Bi 146	Po	At	Rn
7		Fr	Ra							

smallest atoms

LARGEST ATOMS

Notice that there are some blanks. The heaviest members of the Main Groups starting with Po are not as well studied because they are all radioactive. For this reason, not all of their properties are fully characterized. This chart also does not have values for Group 18. That's because the numbers given here are derived from covalent bonds in various compounds, and most elements of Group 18 do not form compounds (although there are quite a few for Xe). Other methods of measurement of atomic radii do include Group 18 and they are consistent with the trend. Overall, He is the smallest of all atoms.

Let's now focus on the trends which are seen in the above numbers. The relationship between size and position in the Periodic Table has two parts, one vertical and one horizontal: atoms get larger going down one Group and atoms get smaller to the right in one Period.

Hopefully you will readily understand the reason for the vertical part of the trend. As you go down one Group, there are electrons in higher *n*-shells. These have bigger orbitals; therefore, the atom is bigger. That's all there is to it. Pick a Group, any Group. Look at the numbers. As you go down the Group, the atoms are bigger.

Now consider the horizontal part of the size trend. This part is a bit trickier. As you go through the elements left-to-right in a row, more electrons are being added but so also are more protons being added to the nucleus. The additional electrons are going into *s* and *p* orbitals of the same shell, and shielding effects are small for electrons in the same shell. The overall outcome is that the increasing nuclear charge (either as Z itself or as Z_{eff}) has an increasing pull on all electrons. This greater electron-nuclear attraction dominates over the small increase in electron-electron repulsion. The net result is the orbitals shrink a bit and the atoms get smaller left-to-right in the row. So pick a Period, any Period. Look at the numbers. As you go left-to-right within the Period, the atoms are smaller.

Now combine the vertical and horizontal parts of the trend to get the overall diagonal relationship: the smallest atoms are in the upper right of the Periodic Table; the largest atoms are at the lower left of the Periodic Table. This is the final, grand result and it's an essential one to know. The sizes of atoms play immensely important roles in many things. We will see some of these aspects in this Chapter and in later Chapters.

• IONIZATION ENERGY

"Ionization" is the process of removing electrons from an atom or molecule. The ionization energy (IE) is the energy required for the process. Technically, IE is for one electron at a time and it is measured in the gas phase. We can write this process for an atom as an equation.

$$\text{neutral atom}(g) \rightarrow \text{cation}^+(g) + e^- \qquad \Delta E = \text{ionization energy}$$
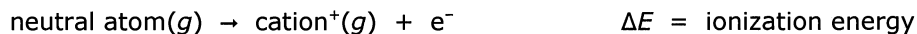
It will always cost you to take an electron out of a neutral atom. Thus, all IEs are positive kJ's.

The important concept for IE is the following. If the atom has a strong grip on its electrons, then more energy is needed to remove them. In other words, if the atom has a strong grip on its electrons,

then it has a high IE. For this reason, IE is a measure of how well the atom holds onto its electrons: a higher IE means a stronger hold, and a lower IE means a weaker hold.

The equation above is for the "first ionization" and its energy is called the "first ionization energy". The numbering of ionizations begins with the neutral atom and proceeds from there. The "second ionization" is the next step.

$$cation^+(g) \rightarrow cation^{2+}(g) + e^- \qquad \Delta E = \text{second ionization energy}$$

Notice that the second ionization ends with the 2+ cation. You can keep going and do third, fourth, fifth, etc. ionizations. Just remember that each step involves one electron at a time.

For purposes of Periodic Trend, we work with first ionization only. Here are some numbers.

IONIZATION ENERGIES (kJ/mol)		1	2		13	14	15	16	17	18	HIGHEST IEs
	1	H 1312								He 2372	STRONGEST HOLD
	2	Li 520.	Be 900.		B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081	
	3	Na 496	Mg 738		Al 578	Si 786	P 1012	S 1000.	Cl 1251	Ar 1520.	
	4	K 419	Ca 590.		Ga 579	Ge 762	As 947	Se 941	Br 1140.	Kr 1351	
	5	Rb 403	Sr 550.		In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170.	
	6	Cs 376	Ba 503		Tl 589	Pb 716	Bi 703	Po	At	Rn	
lowest IEs weakest hold	7	Fr	Ra 509								

The Periodic Trend for first IE has two parts: a vertical part and a horizontal part. IE decreases going down a Group and IE increases to the right in one Period. There's a direct correlation with the previous trend in atomic size. Let's look at this.

The ionization process removes the most readily available electron and this will be from the highest *n*-shell. For elements lower in a Group, those electrons are coming from larger orbitals and so those electrons are held less tightly. In other words, as you go down a Group, an electron is easier to pull out and the IE is smaller. Pick a Group, any Group. The numbers are nice and trendy although not all of the trends are perfect. Group 13 is the most out of whack because Ga and Tl are a bit high, but such imperfections don't change the overall picture. Overall, as you go down a Group, the hold on the electron is weaker and the IE decreases.

For the horizontal part of the trend, we again refer to size. I mentioned earlier that atoms are getting smaller left-to-right in a row because electron-nuclear attraction is winning out overall. Since electron-nuclear attraction is winning out and since things are getting smaller, then it will be harder to pull an electron out of the atom. That will result in higher IE as you go left-to-right. Again, there are some imperfections to the trends. Some of these occur on going from Group 2 to Group 13 due to switching from *s* to *p* subshells. Some imperfections also occur between Groups 15 and 16 due to pairing up an electron in the *p*-subshell of the Group 16 element. Although these imperfections are present in some Periods, they do not occur in all of them. Overall, we'll stick with the generalities.

Just as we did for atomic size, we can combine the vertical and horizontal parts of our IE trend to get an overall diagonal trend: the highest IEs are at the top of a Group and to the right of a Period. Overall, this means that the highest IEs are in the upper right of the Periodic Table. Conversely, the lowest IEs are in the lower left. Remember the significance of all this. Atoms near the upper right of the Periodic Table have the strongest hold on their electrons. Atoms near the lower left have the weakest hold on their electrons.

Keep in mind that the Periodic Trend is for first ionization, so we are really referring to the hold on the first electron which would be lost. Typically, when someone refers to IEs, they are referring to the first IE unless indicated otherwise.

Let me come back to the otherwise cases and talk about additional ionizations steps, since there are two interesting and important points to make here. These are not Periodic Trends, but they do relate to configurations.

The first point is that each successive ionization step is harder to do. "Harder to do" means it will cost you more and that means you must pay more kJ's. In other words, each successive step has a higher IE. To take a second electron out of an atom will cost you more than the first. The third will cost more than the second. Etc. Think about it. Each time you remove one electron, you decrease the total repulsion between all electrons which remain behind. With a bit less repulsion, those which remain can contract a bit and come in closer to the nucleus. The net result is that the remaining electrons are held more tightly, and it will cost more to remove another. For this example, I'll bring in actual numbers using magnesium as an example.

▸ First ionization

$$Mg(g) \rightarrow Mg^+(g) + e^-$$
$$\text{first IE} = 738 \text{ kJ}$$

▸ Second ionization

$$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$$
$$\text{second IE} = 1,450 \text{ kJ}$$

As you can see, the second step is more expensive than the first.

The second point to note is what happens when you start yanking on core electrons. There's a BIG jump in IE when you hit the first core electron. These things are incredibly expensive to pull out of the atom. Let's continue with Mg, but now start over and watch where the electrons are coming from. Neutral Mg has the configuration $[Ne]3s^2$ ($1s^2 2s^2 2p^6 3s^2$); there are two valence electrons.

▸ First ionization --This removes one of the valence electrons from $3s$.

$$Mg(g) \rightarrow Mg^+(g) + e^-$$
$$\text{first IE} = 738 \text{ kJ}$$
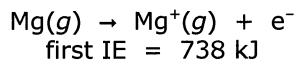
▸ Second ionization --This removes the second valence electron from $3s$.

$$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$$
$$\text{second IE} = 1,450 \text{ kJ}$$
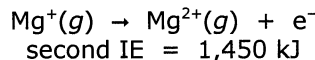
▸ Third ionization --This removes a core electron from $2p$.

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^-$$
$$\text{third IE} = 7,732 \text{ kJ}$$
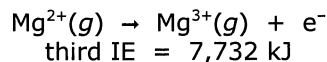
Notice the HUGE difference when you start pulling on core electrons. This will have very important ramifications in the next Chapter.

This is all I need to say about ionization right now. Keep in mind that IE reflects how well an atom holds onto the electrons it has. For our next Periodic Trend, we consider how much an atom wants more electrons than it's got.

• ELECTRON AFFINITY

"Affinity" is used here in its normal dictionary sense as a liking or desire. Electron affinity (EA) refers to the desire by an atom for more electrons. Like IE, EA has a specific reaction which can be measured. Technically, it's the following.

$$\text{neutral atom}(g) + e^- \rightarrow \text{anion}^-(g)$$
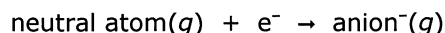
A desire for an electron will be reflected by a negative ΔE. On the other hand, some elements have a positive ΔE, and that means that they don't want another electron at all. For those which do want another electron, a stronger desire will be reflected by a more negative ΔE. This can cause some problems with wording, so be careful with this: the highest EA is now the most negative ΔE.

Here are some numbers.

ELECTRON AFFINITIES (kJ/mol)

Period	1	2		13	14	15	16	17
1	H -73							
2	Li -60.	Be (+)		B -27	C -122	N 7	O -141	F -328
3	Na -53	Mg (+)		Al -42	Si -134	P -72	S -200.	Cl -349
4	K -48	Ca -2		Ga -40.	Ge -119	As -79	Se -195	Br -351
5	Rb -47	Sr -5		In -39	Sn -107	Sb -101	Te -190.	I -295
6	Cs -46	Ba -14		Tl -36	Pb -35	Bi -91	Po -183	At -270.
7	Fr	Ra						

MORE AFFINITY
GREATER DESIRE

less affinity
weaker desire

As far as trends go, this one is not nearly as smooth as the trends for atomic radii and ionization energy. Nevertheless, there is a reasonable, overall pattern. EA is greater (more negative) to the right of the Periodic Table. EA is also a bit better for elements higher in the Table (although Period 2 is not as good as Period 3). These patterns relate somewhat to size again, and smaller atoms tend to have more affinity for an electron, but now there are more idiosyncrasies due to specific configuration effects. We'll just keep it in general terms here without getting more specific.

Notice that the values for Be and Mg are simply given as (+). The (+) means they don't want more electrons, and their value is difficult to measure. Nitrogen also does not want more electrons but its EA is measurable at (+)7 kJ/mol. A bigger point to note is that I left Group 18 completely out of the picture. Group 18 is excluded from this trend. As mentioned earlier in this Chapter, the noble gases already possess some of the most favored configurations and they really don't want more electrons. All of their values would also be positive if measurable. It is traditional to exclude Group 18 from the EA Periodic Trend because the Group itself is an exception. Be aware of this. When we say EAs are better to the right, Group 18 is excluded.

The above Periodic Trend applies for the first EA, which is for the neutral atom gaining one more electron. Like IEs, EAs also come in steps. Also like IE, the Periodic Trend only applies for the first EA. Most values for first EA have a negative ΔE and that means it's favorable. All second (and later) EAs, however, have a positive ΔE; thus, no atom wants to gain a second electron all by itself. All second (and later) electrons will cost energy to acquire.

23.4 Some important conclusions

We can now combine the overall results for IE and EA trends into some important conclusions for chemical properties of the elements. These are essential.

1. Elements near the right of the Periodic Table, especially the upper right, want electrons the most. They very much want to keep their own electrons (high IE, strong hold) and they even want another electron (high EA, strong desire). Because of this, these elements

   • will NOT form cations readily at all;
   • will form anions readily; and,
   • will tend to be more greedy for shared electrons in covalent bonds.

2. Elements near the left of the Periodic Table want electrons the least. They do not hold their own very strongly (low IE, weak hold) and they do not want more electrons very much (low EA, weak desire). Because of this, these elements

   • will form cations readily;
   • will NOT form anions readily at all; and,

• will tend to be weak for shared electrons in covalent bonds. In fact, many will become cations because they are too weak to hold onto a share with another element.

These results are extremely important. They explain a lot about the chemical properties of the elements, as we shall see in later Chapters. Remember these results. Remember that they are derived from the concepts behind the Periodic Trends. Remember that Periodic Trends ultimately relate back to configurations. Remember that configurations determine chemical properties.

We are coming full circle. We are filling in the pieces of the Grand Puzzle as related to the Periodic Table. It's all connected. Nature determines the specific orbitals for electrons in an atom. This gives the configurations of the elements. Configuration gives the properties of the elements. By setting up the Periodic Table according to configurations, the setup of the Periodic Table reflects those properties. This is important. It's important now for elements and it's important when we bond different elements together to make new compounds. You will see this, but that's later. We're not ready for bonds yet. We're not quite done with monatomic things.

Problems

1. True or false.

   a. Valence electrons are the ones which are most available to do chemistry.

   b. For any given atom, the ionizations of core electrons are much more expensive in energy than the ionizations of valence electrons.

   c. The fourth ionization for Si involves a core electron.

   d. The electron affinity is greater for tin than for sulfur.

   e. Elements near the right of the Periodic Table will form cations more readily than they will form anions.

2. Give the full configuration for S and for S^{2-}.

3. Give the full configuration for Ca and Ca^{2+}.

4. Using noble gas abbreviation, give the configuration of each of the following.

   a. N   b. Zr   c. Os   d. Mn

5. Using noble gas abbreviation, give the configuration of each of the following.

   a. B   b. Sc   c. Bi   d. Np

6. Using noble gas abbreviation, give the configuration of each of the following.

   a. K^+ b. Se^{2-} c. Fe^{3+} d. Mg^{2+}

7. Using noble gas abbreviation, give the configuration of each of the following.

   a. Ce^{4+} b. In^{3+} c. Re^{2+} d. P^{3-}

8. Using <u>box</u> notation, show the configuration of the <u>valence</u> electrons for Al.

9. Using <u>box</u> notation, show the configuration of the <u>valence</u> electrons for As.

10. How many valence and core electrons are in each of the following?

    a. Ca   b. Sb   c. Pb   d. F

11. a. What neutral atom from Period 3 has three valence electrons?

    b. What is the shell value (n) for the valence electrons in Br?

    c. What element forms a 3+ cation whose configuration ends in $4d^6$?

12. a. What Main Group element has four valence electrons in the $n = 5$ shell?

    b. What element has 6 valence electrons and 46 core electrons?

    c. What element in Group 15 has ten core electrons?

13. a. What is the shell value (n) for the valence electrons in Bi?

    b. What element has a configuration which ends in $5p^5$?

    c. What element forms a 2+ cation whose configuration ends in $4d^8$?

14. a. What element has the strongest hold on its electrons?

    b. What element has the largest atomic size in Period 4?

    c. What element in Period 3 has the greatest desire for another electron?

15. a. Which element in Group 15 has the strongest hold on its electrons?

    b. What metal element in the s block has the smallest atomic size?

    c. What element in Group 16 has the highest ionization energy?

16. Which one of the following has the greatest desire to gain an electron?

    P   S S^{2-} Cl Cl^- Br

17. Which one of the following has the strongest hold on all of its electrons?

    Na^+ Na   Mg   K K^+ Ca