Chapter 23

CONFIGURATIONS AND CONSEQUENCES, Part 1

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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

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

 $7s^2 5f^{14} 6d^{10} 7p^6$

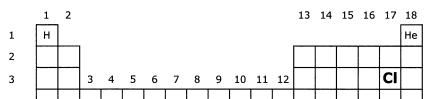
is the shell number, n: it's related to the row (Period) number. Keep in mind how we started all this and how the Period numbers came out in the end. I repeat this at left. Notice that for all s and p subshells, the n value is the Period (row) number. For example, 2s and 2p are in Period 2. For a d subshell, its value of n is the Period number minus one. For example, 3d is in Period 4d. For an d subshell, its value of d is the Period number minus two. For example, 4d is in Period 6d.

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.

	1	2											13	14	15	16	17	18
1	Н		_															Не
2														C				
3			3	4	5	6	7	8	9	10	11	12						

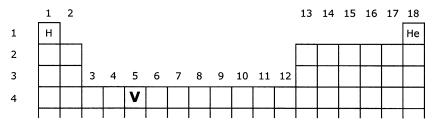
Start at the beginning at H ($1s^1$) and cut across to He; that's $1s^2$. Go to the next row, beginning with 2s. Pass through the first two squares, which adds $2s^2$. Hop over to the p-block, starting into 2p. You go two squares to land on C, which adds $2p^2$. Now string it together: $1s^22s^22p^2$. 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: $1s^22s^22p^63s^23p^5$.

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: $1s^22s^22p^63s^23p^64s^23d^3$.

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 most favorable of all configurations. 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 MOST FAVORABLE OF ALL CONFIGURATIONS.

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 $1s^22s^22p^6$. The bracket notation [Ne] means $1s^22s^22p^6$.
- ▶ The configuration of Ar is $1s^22s^22p^63s^23p^6$. The bracket notation [Ar] means $1s^22s^22p^63s^23p^6$.

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 $1s^22s^22p^2$. Since [He] means $1s^2$, we can abbreviate carbon as [He] $2s^22p^2$.

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

Chlorine:
$$1s^22s^22p^63s^23p^5$$

[Ne]

We can abbreviate chlorine's configuration as [Ne]3 s^23p^5 .

Vanadium:
$$1s^22s^22p^63s^23p^64s^23d^3$$
 \Rightarrow We can abbreviate vanadium's configuration as [Ar] $4s^23d^3$. [Ar]

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, Cd? For many years, Cd was one of the important elements in typical, commercially available, rechargeable batteries known as NiCd (nicad) due to their Ni and Cd content. These have declined in use, however, and have been substantially replaced by nickel metal hydride (NMH) or lithium ion batteries. (We will talk about these battery types in Chapter 64.) Much of the decline was due to the toxicity of cadmium compounds, so there were exposure and environmental problems, despite recycle programs. Although quite toxic to most life forms, I mentioned in Chapter 2 that

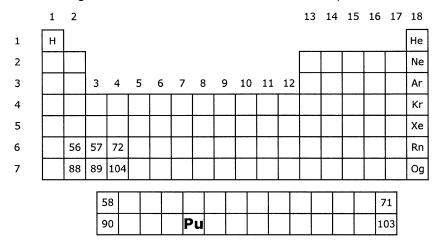
Even cadmium (Cd), which forms highly toxic compounds for many biological organisms, is a biometal for some diatoms.

Thus, Cd is mostly bane, but some boon, to biological systems. Now, in order to do the configuration for cadmium, first locate it in the Table.

	1	2											13	14	15	16	17	18
1	Н																	Не
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.



There's a catch to doing a configuration for an element in 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]

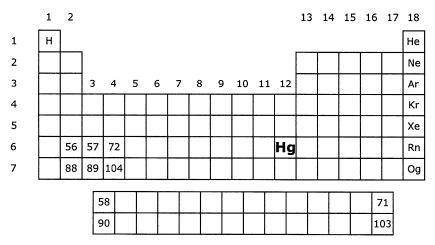
After that we start into Period 7 with $7s^2$, which puts us at Z=88 (Ra).

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 5f. 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.



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

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

[Xe]6
$$s^2$$

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

$$[Xe]6s^24f^{14}$$

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

$$[Xe]6s^24f^{14}5d^{10}$$

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.

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 among the d-block or f-block elements.

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: $1s^2 2s^2 ____ 3p^6 4s^2 ___ 4p^6 ___$

Hf: $[___] ___ 4f^{14} ___$

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 locations 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 also some twists. Anions are straightforward. Some cations are straightforward but some are not. As before, 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 we do chloride. The configuration of neutral Cl is $1s^22s^22p^63s^23p^5$.

Cl⁻ has one more electron; this evenly fills out 3p to give $1s^22s^22p^63s^23p^6$. 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 $[Ne]3s^23p^5$. For the configuration of Cl⁻, we might be tempted to write $[Ne]3s^23p^6$ 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. Except for H^- , 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.

Sc:
$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$$
 OR [Ar] $4s^2 3d^1$

 Sc^{3+} has 18 electrons and Sc^{2+} has 19 electrons. Sc^{3+} does follow the neutral-atom fill sequence for 18 electrons.

$$Sc^{3+}$$
: $1s^22s^22p^63s^23p^6$ OR [Ar]

The oddball in this comparison is Sc^{2+} : the nineteenth electron goes into 3d, not into 4s as would be expected for the neutral-atom general fill sequence.

$$Sc^{2+}$$
: $1s^22s^22p^63s^23p^63d^1$ OR [Ar] $3d^1$

This is a typical result for cations from the d-block elements: if the final electrons are being added into an s-d overlap region, then they typically fill into d before s. Sc^{3+} involves the 4s-3d overlap region, but this holds true also for the 5s-4d overlap region. This notion even extends to cations from the f-block: if electrons are being added to a 6s-4f-5d or 7s-5f-6d overlap region, then they typically fill into f first. Notice the adverb "typically" in all of these cases; there can be exceptions (as to be seen in the technicality below).

So how do we deal with this?

We want a predictive approach to write configurations for cations, but without getting bogged down in remembering all the ins and outs of a separate fill sequence. Fortunately, there is a scheme for doing this which starts with the neutral-atom, general fill sequence: start with the configuration of the neutral atom, and then remove electrons according to the cation charge, but remove them from the <u>highest n-shell first</u>. This gives the correct answer in the majority of cases. Let's run through several examples.

► Al³⁺

Start with the configuration for neutral aluminum.

AI:
$$[Ne]3s^23p^1$$

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 ($3s^23p^1$), so drop those.

This follows the same sequence as the general fill sequence for neutral atoms.

▶ Ga⁺

Start with the configuration for neutral gallium.

Ga:
$$[Ar]4s^23d^{10}4p^1$$

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 are better off in s than in p, so p loses. That leaves us with the following.

Ga⁺:
$$[Ar]4s^23d^{10}$$

Ga⁺ parallels the general fill sequence as for neutral atoms. Now compare this to the next case.

▶ Ga³⁺

Start with the configuration for neutral gallium, as above.

Ga:
$$[Ar]4s^23d^{10}4p^1$$

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]3 d^{10}

This does NOT follow the general fill sequence as for neutral atoms, but our scheme produced the correct answer.

▶ V²⁺

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

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 fill sequence switches over from s-before-d (as in the general fill sequence for neutral atoms) to d-before-s (for many cations), the switchover is incomplete for 1+ cations in the d-block. Thus, quite a few 1+ cations still follow s-before-d while others follow d-before-s. This is just a consequence of the subtle factors that are involved in the overlap regions. 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]4s¹3d¹. This configuration would be obtained by our steps outlined above.
- ▶ The actual configuration of Y^+ is $[Kr]5s^2$. This configuration follows the general fill sequence for neutral atoms. 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. Fortunately, by the time you hit 2+ and higher charge cations, the switchover is fully complete and our prior steps apply. This 1+ cation irregularity also occurs in cations from the f-block, and it's even messier for those. So how do we deal with this? Simple: we avoid it. We will not work with 1+ cations from the d- or f-blocks. We have plenty to work with otherwise. We can still do any cation of 2+ or higher charge, and we can still do cations of 1+ charge from the s- or p-blocks.

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 neutral atoms 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] $2s^22p^5$ Cl [Ne] $3s^23p^5$ Br [Ar] $4s^23d^{10}4p^5$ 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 <i>n-</i> shell
F	[He]2 <i>s</i> ² 2 <i>p</i> ⁵	$2s^22p^5$
Cl	[Ne] $3s^23p^5$	$3s^23p^5$
Br	[Ar]4s ² 3d ¹⁰ 4p ⁵	$4s^24p^5$
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 some 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 somewhat similar chemical properties.

Notice that I'm saying "somewhat 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 d 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 <u>neutral</u> 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 <i>n-</i> shell)	core electrons (not valence)
F	[He] $2s^22p^5$	$2s^22p^5$	[He]
Cl	[Ne]3 <i>s</i> ² 3 <i>p</i> ⁵	$3s^23p^5$	[Ne]
Br	$[Ar]4s^23d^{10}4p^5$	$4s^24p^5$	[Ar] and 3 <i>d</i> ¹⁰

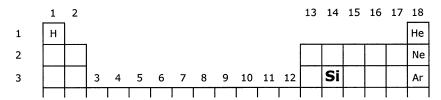
The total number of valence electrons is an important aspect. Each of the above has seven valence electrons. They have different numbers of core electrons, but that is less important to the chemical properties.

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. (Except helium which 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.



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. The radius of this volume can be tens of thousands of times the radius of the nucleus. Although the electron 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 determined by the volume in space which is occupied by the electrons. **

You 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 the orbitals of another atom if the atoms 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 general trends anyway.

ATOMIC SIZES		1	2	13	14	15	16	17	18	
(pm)	1	H 37							Не	smallest atoms
	2	Li 134	Be 90.	B 82	C 77	N 75	0 73	F 71	Ne	
	3	Na 154	Mg 130.	Al 118	Si 111	P 106	S 102	CI 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	Ро	At	Rn	
LARGEST ATOMS	7	Fr	Ra	Nh	FI	Мс	Lv	Ts	Og	

Notice that there are some blanks. The numbers provided here are representative values derived from covalent bonds in a considerable variety of compounds of each element. Group 18 is blank because most elements of Group 18 do not form a considerable variety of compounds (although there are hundreds of Xe compounds known). The elements Po through Og are all very radioactive and, in fact, these elements have to be made for study by nuclear reactions. While some compounds are known for Po through Ra, the study of those elements and their compounds are limited (although you will see some values for these elements in the other Periodic Trends below). Nh through Og are the newest members of the Periodic Table; they are intensely radioactive and a limited number of their atoms have been made. Despite all of these issues, those elements with blanks are expected to follow the general trends as described here. For example, other methods of measurement of atomic size do include some elements of Group 18 and, overall, He is the smallest of all atoms.

Let's now focus on the general trend itself. The relationship between size and position in the Periodic Table has two parts, one vertical and one horizontal: atoms get larger going down a Group and atoms get smaller to the right in a 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 shells 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. 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 $Z_{\rm eff}$) has an increasing pull on all electrons. This greater electron-nuclear attraction dominates over the small increase in electron-electron repulsion. Thus, 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 in the gas phase. Technically, IE is for one electron at a time.

Unlike atomic size above, which has different systems of measurement, this is a specific process with a specific energy. We can write this process for an atom as an equation.

neutral atom(g)
$$\rightarrow$$
 cation⁺(g) + e⁻ ΔE = ionization energy = IE

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", sometimes written as $\rm IE_1$. The numbering of ionizations begins with the neutral atom and proceeds from there. The "second ionization" is the next step.

$$cation^+(g) \rightarrow cation^{2+}(g) + e^- \qquad \Delta E = second ionization energy = IE_2$$

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, and this involves a valence electron. Here are some numbers.

IONIZATION ENERGIES (kJ/mol)	1	1 H 1312	2	13	14	15	16	17	18 He 2372	HIGHEST IEs STRONGEST HOLD
	2	Li 520.	Be 900.	B 801	C 1086	N 1402	0 1314	F 1681	Ne 2081	
	3	Na 496	Mg 738	Al 578	Si 787	P 1012	S 1000.	CI 1251	Ar 1521	
	4	K 419	Ca 590.	Ga 579	Ge 762	As 944	Se 941	Br 1140.	Kr 1351	
	5	Rb 403	Sr 549	In 558	Sn 709	Sb 831	Te 869	I 1008	Xe 1170.	
	6	Cs 376	Ba 503	TI 589	Pb 716	Bi 703	Po 812	At 899	Rn 1037	
lowest IEs weakest hold	7	Fr 393	Ra 509	Nh	Fl	Мс	Lv	Ts	Og	

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 (valence) 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 a higher IE as you go left-to-right. That is true in general, but there are two types of inconsistencies to note.

Firstly, on going from Group 2 to Group 13 in the Second, Third and Fourth Periods, there is actually a decrease in IE, contrary to the overall left-to-right pattern. Electron-nuclear attraction is still increasing for Group 13, but you are now pulling an electron from a p orbital instead of from an s orbital, and electrons in p orbitals are not held as tightly as electrons in an s orbital in the same shell. So there's a bit of a drop going from Group 2 to Group 13, although the normal trend resumes in Group 14. But note that the IEs of elements in the Fifth and Sixth Periods do increase from Group 2 to Group 13, so this inconsistency is not consistent.

Secondly, there is a decrease in IE from Group 15 to Group 16, again in the Second, Third and Fourth Periods. Again, electron-nuclear attraction is still increasing left-to-right, but now a fourth electron is being added to the valence p subshell, which means the electrons start pairing up. Pairing electrons in the same orbital is always a detraction, and so it is not as difficult to remove one of those paired electrons. But then the IEs of elements in the Fifth and Sixth Periods do increase from Group 13 to Group 14, so, again, this inconsistency is not consistent.

Despite these variations, the general trend remains as an increase, left-to-right, within a Period.

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 of 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 those 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 $Mg(g) \rightarrow Mg^+(g) + e^ IE_1 = 738 \text{ kJ}$ ► Second ionization $Mg^+(g) \rightarrow Mg^{2+}(g) + e^ IE_2 = 1,451 \text{ kJ}$
- 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 $[Ne]3s^2(1s^22s^22p^63s^2)$; there are two valence electrons.

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

$$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$$
 IE₁ = 738 kJ

▶ Second ionization --This removes the second valence electron from 3s.

$$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$$
 IE₂ = 1,451 kJ

► Third ionization --This removes a core electron from 2p.

$$Mg^{2+}(q) \rightarrow Mg^{3+}(q) + e^{-}$$
 IE₃ = 7,733 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. EA, like IE, involves a specific reaction in the gas phase, for which the energy can be measured. We can write it as follows.

neutral atom(
$$g$$
) + $e^- \rightarrow anion^-(g)$ ΔE

For most Main Group elements, this process is favorable, and those elements have a negative ΔE . The actual term "electron affinity", however, was set to equal the negative of ΔE

electron affinity = EA =
$$-\Delta E$$

so that a liking or desire for another electron was reflected in a positive number. Accordingly, a stronger affinity is reflected in a more positive EA.

On the other hand, some Main Group elements cannot handle an extra electron; technically, they would have a negative EA, but those cases are very difficult to measure quantitatively.

Here are some numbers.

ELECTRON AFFINITIES		1	2	13	14	15	16	17	
(kJ/mol)	1	H 73							L
	2	Li 60.	Be (-)	B 27	C 122	N (-)	0 141	F 328	MORE AFFINITY GREATER DESIRE
	3	Na 53	Mg (-)	 Al 42	Si 134	P 72	S 200.	Cl 349	(excludes Group 18)
	4	K 48	Ca 2	Ga 41	Ge 119	As 78	Se 195	Br 325	
	5	Rb 47	Sr 5	In 37	Sn 107	Sb 101	Te 190.	I 295	
	6	Cs 46	Ba 14	TI 36	Pb 35	Bi 91	Ро	At 233	
less affinity weaker desire	7	Fr	Ra	Nh	FI	Мс	Lv	Ts	

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 positive) to the right of the Periodic Table. EA is also a bit better for elements higher in the Table, although the p-block elements of the Second Period have less electron affinity than the p-block elements of the Third Period. For example, note that F has a lower EA than Cl (and, actually, Cl has the highest EA of all elements). While the small size of F gives it a very high EA (second highest of all), it carries a slight disadvantage, relative to Cl, in accommodating an added electron in a small volume. Besides this comparison, there are other idiosyncrasies involved with EA, moreso than with the prior Periodic Trends of atomic size and ionization energy. We'll just keep it in general terms here without getting more specific.

Notice that the values for Be, N and Mg are simply given as (–), indicating that they can't even hold onto one more electron. A bigger point to note is that I left Group 18 completely out of the picture. 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 be negative if measurable. Thus, the left-to-right increase for EA stops with Group 17. 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. Although most values for first EA have a positive EA, all second (and later) EAs would be negative; thus, no atom can hold two or more extra electrons in the gas phase. Each time you add an electron, the total electron-electron repulsion increases and the size increases, and there is simply not enough electron-nuclear attraction to keep things together, beyond adding one electron. For example, you can add one electron to an O atom to generate O^- but you cannot add another electron to form O^{2-} . This sharply contrasts with the plethora of O^{2-} ionic solids which, however, are stabilized by ionic bonding. Keep in mind that EA (like IE) involves gas phase. The gas phase shows an ion's true colors, by itself, without interaction with anything else.

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 <u>want to keep their own</u> electrons (high IE, strong hold) and they even <u>want another</u> 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 <u>do not hold their own</u> very strongly (low IE, weak hold) and they <u>do not want more</u> 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 which are available 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

- 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. Be has a greater IE₂ than Li.
 - e. The electron affinity is greater for tin than for sulfur.
 - f. 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 S²⁻.
- 3. Give the full configuration for Ca and Ca²⁺.

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. Rg c. Bi d. Ge
6.	Using noble gas abbreviation, give the configuration of each of the following. a. K^+ b. Se^{2-} c. Fe^{3+} d. Ra^{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 $\underline{\text{box}}$ notation, show the configuration of the $\underline{\text{valence}}$ electrons for Al.
9.	Using \underline{box} notation, show the configuration of the $\underline{valence}$ 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 4 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 4d⁶?
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 5p⁵? c. What element forms a 2+ cation whose configuration ends in 4d⁸?
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? $P \qquad S \qquad S^{2-} \qquad CI \qquad CI^- \qquad Br$
17.	Which one of the following has the strongest hold on all of its electrons? Na $^+$ Na Mg K K $^+$ Ca