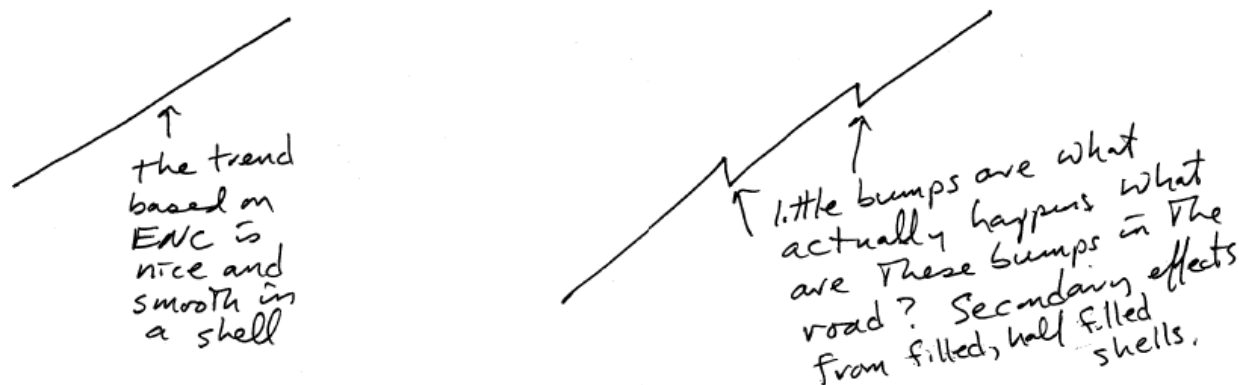


LECTURE 6. THE FINE POINTS IN PERIODICITY: FILLED AND HALF-FILLED SHELL STABILITY

Summary. If ENC was all we needed to explain trends in the periodic table, then life would be easy. But we all know that life isn't easy. And in fact, if we start to scratch to much at the surface of things, we uncover an underbelly that we probably wish we hadn't seen.

So if we let the surface be the nice smooth trends of ENC and we let the underbelly be filled and half filled shell stability, we are staring at the real data for electronic configurations and for periodic trends. You see, rules like Aufbau and ENC are really pretty and give us very straight lines. But the reality is that most of the data has a bunch of bumps in it that create secondary effects we need to explain.



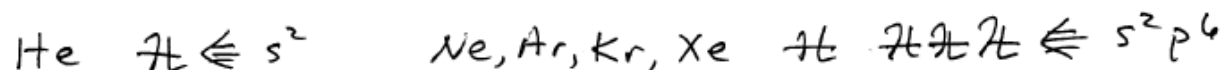
So what are some of these secondary bumps that need to be explained?

- electronic configurations of atom don't always follow Aufbau (example: Cu is s^1d^{10} not s^2d^9)
- electronic configurations of ions don't always follow Aufbau (example: Tl^{3+} is d^{10} not s^2d^8)
- ionization energy trends are not smooth across a row of the periodic table (example: I.E. for O is less than I.E. for N)
- electron affinity trends not smooth across a row of the periodic table (example: I.E. for C is greater than I.E. for N)

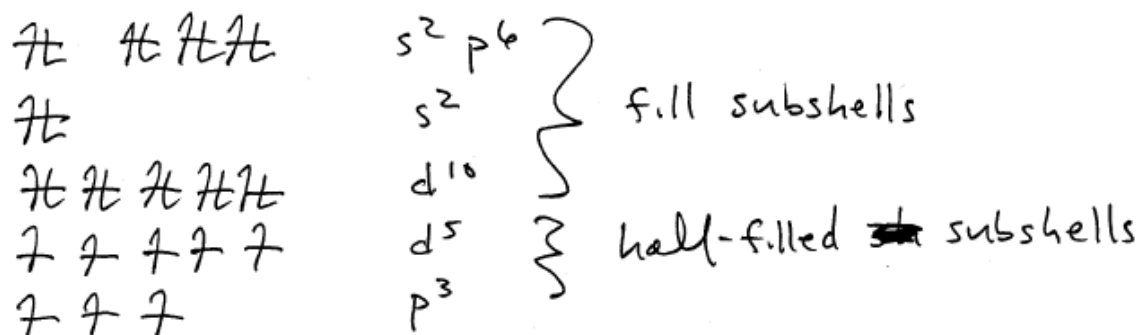
The good news is that once we understand the concept behind filled and half filled shell stability, we can rationalize away the examples above and others like them, with confidence.

Stable filled and half-filled shells

We all know the noble gas elements He, Ne, Ar, Kr, Xe are “stable.” They are unreactive. They are low energy orbitals. They don’t like to change. What they have in common is filled s or p subshells to complete a row.



What is interesting is that there are other “islands of stability” in the periodic table. Groups of elements for which it is also true that other electronic configurations share similar enhanced stability. And they all share in common being filled or half filled.



Hint: During your examination of the periodic table, you should start to see certain groups or columns as just being special. In the same way you will learn to look at the last column of the periodic table, the $s^2 p^6$ group we call the noble gases, as “special, you will learn to look at

s^2 and p^3 and p^6 and d^5 and d^{10}

as special too. Not as special as p^6 , but more special than the other columns. It is these “special” or stable columns in which the glitches in the ENC argument will be found. So if you are working a problem and find yourself in the vicinity of one of these groups, pay attention!!.

Shell stability messes with Electronic Configuration.

Example 1—the d^4 and d^9 cases. Certainly the most famous example of increased shell stability messing up an argument is when we are using the Aufbau principle to fill an electronic configuration. For example, electronic configurations that change because of filled/half-filled shells are all the d^4 and d^9 electron configurations. In each case, a single electron in the s^2 orbital is relocated to the d^5 or d^{10} orbit because of the increased stability in filling or half filling a large d subshell.



Examples of this exception, which applies to not only atoms but also ions with the same number of electrons:

- Cr, Mo, W and ions like Fe^{2+} , Ru^{2+} , Ir^{3+} all provide an electron from s^2 to create a $s^1 d^5$ electronic configuration.
- Cu, Ag, Au and ions like Tl^{2+} , Au^- , all provide an electron from s^2 to create a $s^1 d^{10}$ electronic configuration

Example 2—the large metals with valence p^1 to p^4 electrons.

You may not have noticed that there are a collection of metals at the bottom right of the periodic table. They aren't the famous transition metals like iron or copper. But they are pretty important and actually possess some pretty remarkable properties. This includes some of the “softer metals” like tin, indium, and lead among others.

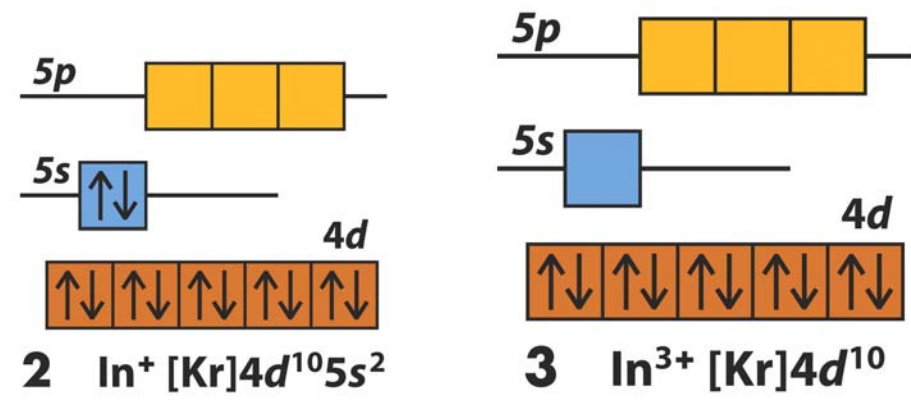
The cations of these soft metals need to lose electrons, and the question is, from what subshell are they lost? According to Aufbau, they should come from the valence p orbitals. But actually the subshells for these larger ions are so far from the nucleus, that the simple Aufbau energy rules fall apart. And instead the question is? Should they come from an s or a p or a d subshell?

The answer? Remove them so that a filled d^{10} can be created as soon as possible.

So the rule is: electrons lost from large ions come off in the following order: p first, s second, d last

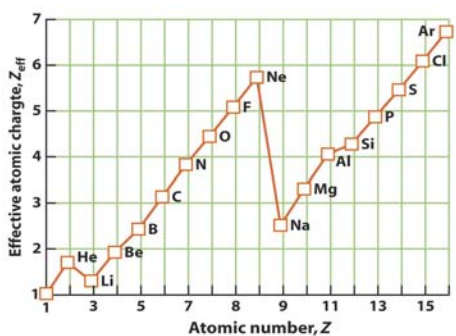
Example: In^+ loses its electron from p orbit, e- configuration to make a $d^{10}s^2$
 In^{3+} loses its electrons from p first and then the s orbitals to make a d^{10}

The pictures below show off the electronic configurations for these exceptions. Remember, all this because we love d^{10} !!



Shell stability messes with Periodic Trends

Recall the phrase: to the right and up. It suggested that we should see beautifully smooth trends that followed ENC.



The reality is that except for atomic radii, this kind of smoothness in the trends just doesn't happen. And instead we see a lot of jaggedness in the pictures of ionization energy or electron affinity. Can we explain this jaggedness? Well since we are in the section on shell stability, this had better be the reason.

So here is something exciting to do. Try staring really closely at the wiggles in the IE and EA data.

Period	Group	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1		H 1 1.01	He 2 2.00						
2		Li 3 519	Be 4 900	B 5 799	C 6 1090	N 7 1400	O 8 1310	F 9 1680	Ne 10 2080
3		Na 11 494	Mg 12 736	Al 13 577	Si 14 786	P 15 1011	S 16 1000	Cl 17 1255	Ar 18 1520
4		K 19 418	Ca 20 590	Ga 31 577	Ge 32 764	As 33 947	Se 34 941	Br 35 1140	Kr 36 1550
5		Rb 37 402	Sr 38 548	In 49 556	Sn 50 707	Sb 51 834	Te 52 870	I 53 1008	Xe 54 1170
6		Cs 55 376	Ba 56 502	Tl 81 590	Pb 82 716	Bi 83 703	Po 84 812	At 85 1037	Rn 86 1036

Ionization energy (kJ·mol⁻¹)

- 2001-2500
- 1501-2000
- 1001-1500
- 501-1000
- 1-500

Period	Group	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1		H 1 -73	He 2 0						
2		Li 3 -60	Be 4 0	B 5 -27	C 6 -122	N 7 -7	O 8 -141	F 9 -328	Ne 10 0
3		Na 11 -53	Mg 12 0	Al 13 -43	Si 14 -134	P 15 -72	S 16 -200	Cl 17 -349	Ar 18 0
4		K 19 -48	Ca 20 2	Ga 31 -29	Ge 32 -116	As 33 -78	Se 34 -195	Br 35 -325	Kr 36 0
5		Rb 37 -47	Sr 38 -5	In 49 -29	Sn 50 -116	Sb 51 -103	Te 52 -190	I 53 -295	Xe 54 0
6		Cs 55 -46	Ba 56 -14	Tl 81 -19	Pb 82 -35	Bi 83 -91	Po 84 -174	At 85 -270	Rn 86 0

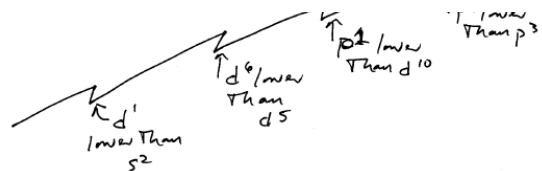
Electron affinity (kJ·mol⁻¹)

- >300
- 200-300
- 100-200
- 0-100
- <0

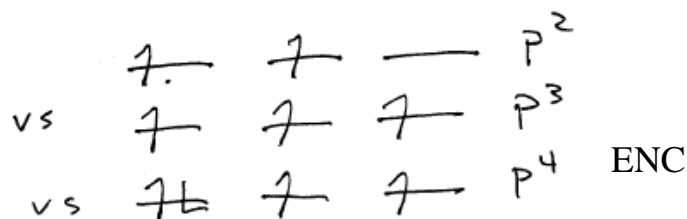
What you should notice is that the seemingly random up and down actually occurs around the islands of stability—the filled and half filled shells and subshells.

In the blow up below of IE data, notice that the group to the right of a stable group is higher in energy (less stable.)

you know

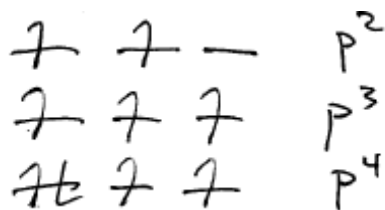


Ranking IE for C, N and O. The famous examples of this phenomenon, often found on exams, occurs for the stable half filled p^3 subshell. Consider what is going on with electron configuration around p^2 , p^3 and p^4 , and ask, how would you rank IE for C, N and O? The answer is $C < O < N$ NOT $C < N < O$. Why? Look at which configurations are most stable.



C is lower than N because N has higher ENC
 N is *higher* than O because p^3 doesn't want to lose electron
 O is *lower* than N because p^4 likes to become p^3 offsetting ENC

Ranking EA for C, N and O. Another famous examples of this phenomenon, also found on exams, occurs for the stable half filled p^3 subshell. Consider what is going on with electron configuration around p^2 , p^3 and p^4 , and ask, how would you rank EA for C, N and O? The answer is $N < C < O$ NOT $C < N < O$. Why? Look at which configurations that are most stable



C has a more positive EA because adding e^- makes p^3
 N has a more negative EA because adding e^- makes p^4
 O has the most positive EA due to higher ENC

And if you want to see the numerical proof of these examples, it is presented below.

	C	N	O	F
IE	1090	1400	1310	1680
EA	+122	-7	+141	+328

The hiccup in the smooth trend suggested by ENC is directly attributed to the islands of stability around p^3 .

Ranking the islands of stability

No doubt you will wonder some times just whether to look for exceptions and the magnitude of the stability increase is going to matter. Is there a way to quantify how much extra stability is realized? Sure, program a computer with the Schrodinger equation. But barring that, can we come up with a ball park idea of how important the added stability is? Sure. Obviously the noble gas configuration is way more stable than anything else. And based on the examples we have seen:

$$p^6 \gggggggg > d^{10} >ggg > d^5 > p^3 >> s^2$$

Relative extent of stability from filled and half filled shells.

