'4s' before '3d', Really? A First Year Blog: 6th December 2019

(This is merely a *summary* of some of the things that you need to know. *Everything in this blog, and much more, can be found in the First Year, Foundation Chemistry Book*.)

- The best way to do what you have to do is to understand why you are doing what you are doing. Let me therefore, in this Blog, talk in general about the configuration of electrons around the nucleus of an atom (from the Chemist's point of view rather than the Physicist's point of view).

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- My granddaughter has just got her Degree and has secured a job which pays well and she is thinking of buying an apartment for herself. She therefore asked me to go along with her to look at an apartment that she had seen on the web.

- When we arrived at the block of flats, I was intrigued. There were no apartments on the ground floor,
  GROUND FLOOR **no apartments**

  so we entered the lift and presssed the button for the 1st floor, and here there were just two apartments, and the doors were labelled
  FIRST FLOOR $\mathbf{1s^1}$ and $\mathbf{1s^2}$

- We therefore got into the lift and pressed the button for the second floor, and on the second floor there were just eight apartments. On the *left of the lift* there were two apartments and their front doors were marked
  SECOND FLOOR (a) $\mathbf{2s^1}$ and $\mathbf{2s^2}$
  and then on the *right of the lift* there were six apartments and they were marked
  SECOND FLOOR (b) $\mathbf{2p^1}$/ $\mathbf{2p^2}$/ $\mathbf{2p^3}$/ $\mathbf{2p^4}$/ $\mathbf{2p^5}$/ $\mathbf{2p^6}$

- We therefore got back in the lift and went up to the third floor and it was similar to the second floor but this time there were **twelve** apartments and they were marked

  $\mathbf{3s^1}$, $\mathbf{3s^2}$ and $\mathbf{3p^1}$, $\mathbf{3p^2}$, $\mathbf{3p^3}$, $\mathbf{3p^4}$, $\mathbf{3p^5}$, $\mathbf{3p^6}$, $\mathbf{3p^7}$, $\mathbf{3p^8}$, $\mathbf{3p^9}$, $\mathbf{3p^{10}}$

  and then we noticed a strange thing.

- There was a mezzanine floor between the **third** and **fourth** floor, and strangely enough, there were only 2 apartments on the whole mezzanine floor – and they were marked

  $\mathbf{4s^1}$ and $\mathbf{4s^2}$

  but the mezzanine floor had a big notice that said "These apartments are actually physically located **HIGHER UP** the building, but it takes **less energy** to climb up to these apartments than it does to get to the **3d** apartments" – and I found this statement intriguing and puzzling. How could it take less energy to get to $\mathbf{4s^1}$ and $\mathbf{4s^2}$ than to get to the higher up $\mathbf{3d^1}$-$\mathbf{3d^{10}}$ apartments?

- Being a scientist, I was deeply curious about the way the apartment block had been built, so I got into the lift and went down to the Receptionist and said "I'm awfully sorry to trouble you Sir, but I am curious about the way that this building has been built. Why are there only two apartments on the 1st floor, then eight on the 2nd and twelve on the 3rd floor, and then a mezzanine floor between the 3rd and 4th floors with only 2 apartments on the whole mezzanine floor?", and at that very moment my mobile phone rang and I saw that it was my granddaughter calling so I said "Excuse me Sir" to the Receptionist and took the call from my granddaughter: "Grandpa, grandpa, she cried. I am now on the 4th floor and it is totally different. This really is a very strange numbering system, because there is a notice that says "for apartments

  $\mathbf{4s^1}$ and $\mathbf{4s^2}$

please look below apartments

$3d^1$, $3d^2$, $3d^3$, $3d^4$, $3d^5$, $3d^6$, $3d^7$, $3d^8$, $3d^9$, and **$3d^{10}$**

- In the Middle Ages, in Classical Literature, *allegories* were very popular – but I am going to stop this allegory/this analogy and get back to Chemistry because you will already have realised that I am not talking about grandchildren and apartment blocks at all, but talking about the way that shells and sub-shells are configured around nuclei.

- With regard to how electrons are configured around the nucleus of an atom, you should know that

a)
- **SHELLS are made up of sub-shells , and**
- **SUB-SHELLS are made up of orbitals, and**
- **an orbital is a volume of space in which an electron is most likely to be found, and one or two (but never more than two) electrons may occupy an ORBITAL.**

b)
- **Shell** n=1 contains **1 sub-shell** viz.[1] 1s
- **Shell** n=2 contains the **2 sub-shells** viz. 2s 2p
- **Shell** n=3 contains the **3 sub-shells** viz. 3s 3p 3d
- **Shell** n=4 contains the **4 sub-shells** viz. 4s 4p 4d 4f

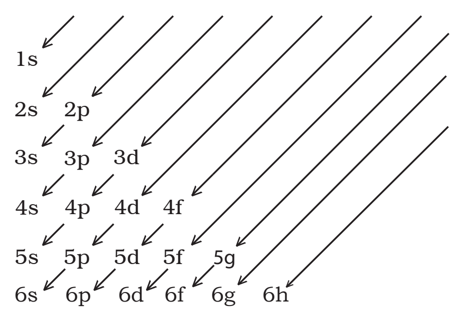
.... and so on.

c)
- every ‘s’ sub-shell contains only ONE orbital, and
- every ‘p’ sub-shell contains THREE orbitals, and
- every ‘d’ sub-shell contains FIVE orbitals, and
- every *‘f’* sub-shell contains SEVEN orbitals.

[*NB Please note the progression 1, 3, 5, 7, ... etc. You do not need to know about ‘g’ sub-shells for ‘A’ Level, but I am sure that you can work out how many orbitals they have!*]

d) There is a specific order in which electrons go into orbitals, and the order in which the orbitals are filled is given by the grid below

e) **The orbitals in a <u>SUB-SHELL</u> are always filled singly until ALL the orbitals have <u>one electron in them</u>, *and then only are the second electrons added in until the appropriate number of electrons has been achieved*** and **it is very important that this rule MUST always be obeyed (other than for the exceptions that are discussed in Chapter 3 of my First Year book on “Foundation Chemistry” viz. Chromium and Copper)!**



- *If you did electron configurations at GCSE Level, then you may have been taught something that will be very **unhelpful** to you at ‘A’ Level, so please now watch carefully and **UNLEARN** what you may have learnt at GCSE Level.*

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[1] The abbreviation “*viz.*” stands for “*namely*” or “that is to say”.

REMOVING electrons rather than ADDING electrons

- When starting with an atom, a positively charged "ion" (a cation) is created by removing electrons from a neutrally charges species and a negatively charged species (an anion) will be the result of adding an electron onto a neutrally charged species – and now I want to look very briefly at the electron configuration of *ions*.

- If you look at the little grid on page 2, you will see that the order of filling the orbitals 1s, 2s, 2p, 3s and 3p is very straightforward. It is only after 3p that you have to start being careful. After 3p you do NOT go on and start filling 3d – **instead you go to 4s and start filling that orbital**! Let us do the electron configuration of the first element where 3d starts to be filled i.e. the electron configuration for Scandium, Sc (cf. footnote[2]) viz

  $_{21}$Sc $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^1$, $4s^2$ [NB 2 + 2 + 6 + 2 + 6 + 1 + 2 = 21]

- If you did electron configurations at GCSE Level, then could you please note very carefully that
  I did NOT write $_{21}$Sc $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
  but instead I wrote $_{21}$Sc $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^1$, $4s^2$

- There are two differences in the two configurations above viz. my configuration has commas at the end of each completed shell (*and this is a trivial thing that I do in order to differentiate one shell from another*), but the second difference is not trivial. I did **NOT** write the sub-shells in the order that I was putting the electrons into them. The reason for this is that when you come to do the electron configurations for **IONS**, then **you must remove electrons <u>NOT</u> in the order in which orbitals are filled, but instead you must remove them first of all from an orbital IN THE OUTERMOST SUB-SHELL CONTAINED IN THE OUTERMOST SHELL** – therefore if you use the GCSE notation, when you come to create the electron configuration for an ion, you could get it wrong. As it happens, the *natural* ion of Scandium is Sc^{3+}, therefore you cannot get the electron configuration for the *natural* ion of Scandium wrong, but if you wanted to write the electron configuration for the first (*artificial*) ion of Scandium (i.e. the ion that would be created if you removed just *one* electron from an atom of Scandium), then if you used the GCSE notation for the atom and knocked off one electron, you would first have written $_{21}$Sc $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
  and then **INCORRECTLY** have written $_{21}Sc^+$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ *(<—* **THIS IS WRONG**)
  instead of correctly writing the $_{21}Sc^+$ ion of Scandium as

  $_{21}Sc^+$ $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^1$, $4s^1$ **<— THIS IS CORRECT**
  or as [Ar] **$3d^1$** , **$4s^1$** **<— this is another way of writing it**

- The ending for the artificial ion $_{21}Sc^+$ is ..... **$3d^1$, $4s^1$** (and NOT .... $3p^6\ 4s^2$)!

- Let me therefore repeat my advice – do NOT write electron configurations according to the order in which orbitals are filled (even though you may have been taught to do so when you were learning GCSE Chemistry); but, instead, write your electron configurations in the SHELL order, **and then you will never get your electron configurations for <u>IONS</u> wrong**.

- When you hear someone say something, you may think that you have understood what was said – but, in truth, you will not understand it until you have bashed the concepts around in your head and got to grips with them for yourself. Could I therefore urge you now to practise writing out lots and lots of electron configurations for atoms and ions.

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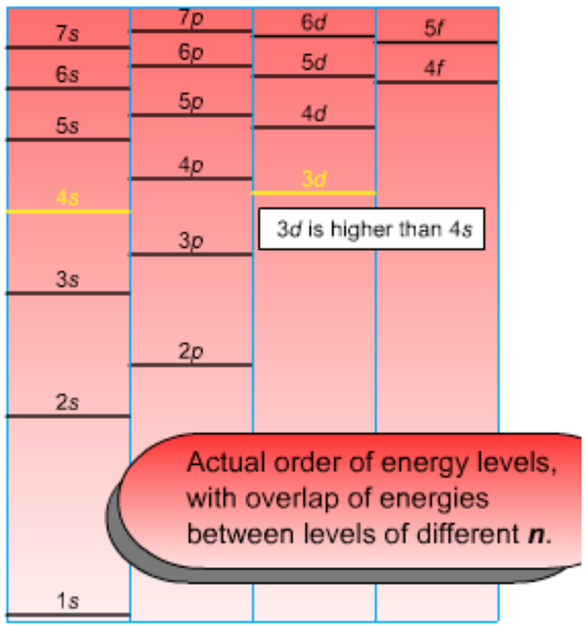
[2] You must familiarise yourself with the symbols for the names of all the different elements (or at very least for the first 36 elements in the Periodic Table – because that is what the 'A' Level syllabus requires you to know).

APPENDIX

1) The factors that underlie electron configuration are the physical distance of an electron from a nucleus/the energy level that it occupies/and the mutual repulsion between entities that possess a similar electrostatic charge.

2) The grid with the arrows on page 1 of this Chapter follows from the energy levels of the different sub-shells



Source : Professor Stephen Lower, Simon Fraser University

- The reason that (to create an ion) you remove electrons from '4s' before '3d' is because (with regard to distance) an empty '4s' is farther away from the nucleus than '3d', and an empty '4s' has less energy than an empty '3d'. However, **when '3d' starts having electrons put into it**, then (since electrons repel each other) the electrons that are now in '3d' are repelled by the electrons that have **already** been put in '4s', and **the '4s' electrons are now pushed farther away from the nucleus and go to a higher energy level than '3d'.** Once the '4s' sub-shell starts to have electrons in it, **the '4s' sub-shell is pushed physically further away from the nucleus than the '3d' sub-shell, and up above '3d' in ENERGY terms also.**

- **When creating an ion, the outermost electrons/the highest energy electrons must be removed FIRST, and THAT is why when you start taking electrons away to form an ion, the electrons in '4s' MUST be removed before the electrons in '3d'. They are both farther away from the nucleus than '3d' electrons, AND they have more energy than '3d' electrons.**

- **Isn't it just lovely when you start to see how things work in Chemistry!**