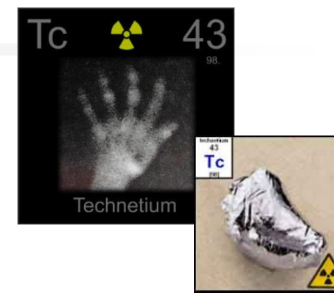
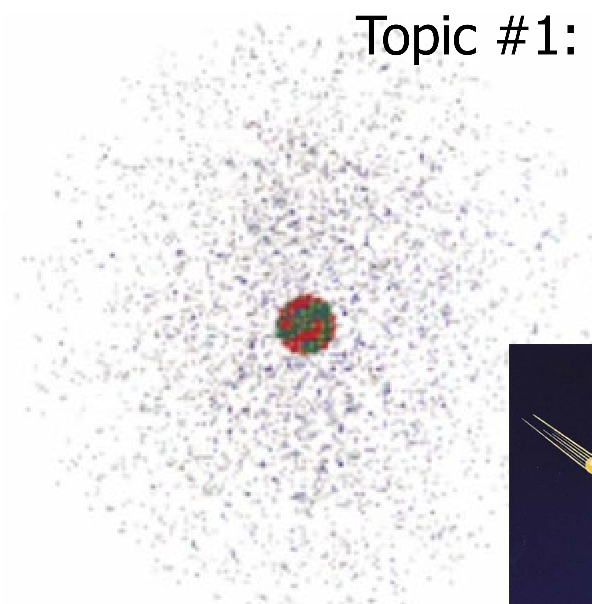
CHEMISTRY 1000



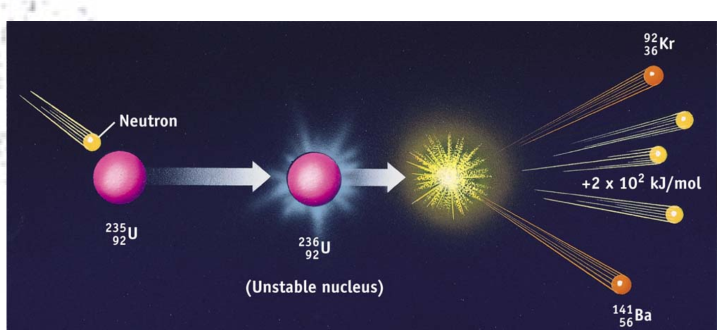


Topic #1: Atomic Structure and Nuclear Chemistry

Fall 2020

Dr. Susan Findlay

See Exercises 5.1 to 5.2



Electron Spin and Magnetism

- We have seen that an atomic orbital is described by three quantum numbers: n, l, and m_l

- An electron in the atomic orbital is also described by these three quantum numbers as well as a fourth, the **spin magnetic quantum number, m_s**

- Electrons behave as if they spin on their axes. Because they are charged, this generates a ______________________________ around the electron (giving the electron a magnetic dipole).

- When an electron is exposed to a magnetic field, its dipole can take on one of two possible orientations. It can line up with or be opposed to the dipole of the external magnetic field:

Electron Spin and Magnetism

- How can we show that electrons have only two possible spins?
  - When a beam of hydrogen <u>atoms</u> is passed through a magnetic field, it will split into two beams – one of atoms in which the electron has m_s = +½ and one of atoms in which the electron has m_s = -½.
  - When a beam of helium atoms is passed through the same magnetic field, it does not split. This is because every helium atom contains two electrons, one with m_s = +½ and one with m_s = -½. We say that the two electrons in the helium atom are **spin-paired**. Effectively, their spins cancel each other out.

Electron Spin and Magnetism

- How can we classify substances based on magnetic behaviour?
  - Those (like helium) in which all of the electrons are paired are called __________________________. When exposed to a magnetic field, they are weakly repelled by it.
  - Those (like hydrogen) in which one or more electron is unpaired are called __________________________. When exposed to a magnetic field, they are attracted to it.
  - Those which have many unpaired electrons that have all had their spins aligned are called ____________________________. They can be used to make magnets since they do not require an external magnetic field to keep the electron spins aligned.

Assigning Electrons to Atomic Orbitals

- In 1925, Wolfgang Pauli stated the **Pauli exclusion principle**:

- Because electrons in the same atomic orbital have the same values for *n, l* and m_l *and* because there are only two possible values for m_s (____ and ____), each atomic orbital can contain a maximum of ____ electrons.

- In order for an atom to be in its ground state, each electron must have the lowest energy wavefunction permitted by the Pauli exclusion principle. In other words, electrons fill the lowest energy orbitals first. *(Orbitals are not actually 'boxes' to be filled but it's often easiest to think of them as such.)*

Assigning Electrons to Atomic Orbitals

- We can draw **orbital occupancy diagrams** for the first four elements:

	1*s*	2*s*	2*p*		
H *(1e$^-$)*					
He *(2e$^-$)*					
Li *(3e$^-$)*					
Be *(4e$^-$)*					

  - The orbitals are listed in order of increasing energy (left to right).
  - Electrons are filled in from left to right, completely filling one type of orbital before moving to the next.
  - Arrows show the electrons' relative spin ('up' or 'down').

Assigning Electrons to Atomic Orbitals

- **Electron configurations** can also be written using **line notation** which lists how many electrons are in each subshell. e.g. Be = $1s^2\,2s^2$

- Write electron configurations in line notation for H, He and Li.

- Recall that the number of orbitals in a subshell is $2l+1$. Since only two electrons fill each orbital, $2(2l+1)$ electrons fill each subshell. You may find it easier to just remember:
  - *s* subshells can have up to ____ electrons each ($l=0$),
  - *p* subshells can have up to ____ electrons each ($l=1$),
  - *d* subshells can have up to ____ electrons each ($l=2$),
  - *f* subshells can have up to ____ electrons each ($l=3$).

Assigning Electrons to Atomic Orbitals

- When we assign electrons to orbitals in a *p*, *d* or *f* subshell, we can imagine three options:
  - Fill one orbital at a time then move to the next:

C *(6e$^-$)* 

  - Assign one electron to each orbital then go back and add a second electron once all orbitals are half full. Keep spins aligned.

C *(6e$^-$)* 

  - Assign one electron to each orbital then go back and add a second electron once all orbitals are half full. Keep spins “paired”.

C *(6e$^-$)* 

Assigning Electrons to Atomic Orbitals

- Unpaired electrons have lower energy if their spins are aligned so we use the second option **(Hund's rule)**. Knowing this, we can draw **orbital occupancy diagrams** for elements 5-10:

B	*($5e^-$)*					
C	*($6e^-$)*					
N	*($7e^-$)*					
O	*($8e^-$)*					
F	*($9e^-$)*					
Ne	*($10e^-$)*					
		1*s*	**2*s***		**2*p***	

Assigning Electrons to Atomic Orbitals

- So far, we have filled orbitals starting at the lowest shell and working up. This order breaks down when we get up to $n = 3$. This is because the energy of an orbital is determined by both n and l. As a general rule, orbitals with more nodes are higher energy (# nodes = $n - 1$) – but planar nodes raise the energy more than radial nodes.

- Instead of filling orbitals in order of increasing n, we should really be filling them in order of increasing $n + l$ (using n as a 'tiebreaker').

- Use quantum numbers to compare the energies of:

  3*s* 3*p* 3*d* 4*s* 4*p* 4*d* 5*s*

Assigning Electrons to Atomic Orbitals

- This order (used to fill orbitals in *most* atoms) is referred to as the **aufbau order**. A common trick to remember the aufbau order is to draw the diagram below.

- Write electron configurations in line notation for:

  Ti

  Pb

Assigning Electrons to Atomic Orbitals

- Electron configurations for the larger elements are lengthy to write out. Because of this, chemists have adopted a short cut called **noble gas notation** in which the symbol for a noble gas is used as an abbreviation for its electrons.
  - e.g. Neon has an electron configuration of $1s^2 2s^2 2p^6$.

    The electron configuration for sodium can be written as <u>either</u> $1s^2 2s^2 2p^6 3s^1$ <u>or</u> [Ne] $3s^1$.
  - In this way, some or all of the **core electrons** are represented by the noble gas while the configuration of all **valence electrons** is still listed.

- Write electron configurations in noble gas notation for:

  Ti

  Pb

Assigning Electrons to Atomic Orbitals

- Conveniently, it turns out that the periodic table is arranged according to electron configuration. ***The properties which were used to group the elements together into columns were caused by those elements having similar electron configurations!***

  Now that we know how to write electron configurations, we can build the periodic table ourselves by writing the last orbital filled (and how many electrons went in it):

$1s^1$											$1s^2$
$2s^1$	$2s^2$					$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$3s^1$	$3s^2$					$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	etc…	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
$5s^1$	$5s^2$	$4d^1$	$4d^2$	$4d^3$	etc…	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$

Assigning Electrons to Atomic Orbitals

- Thus, we can also determine electron configurations using the periodic table to tell us what order to fill the subshells.

- What neutral elements have each electron configuration below?
  - $1s^2 2s^2 2p^3$
  - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
  - [Ne] $3s^2 3p^3$
  - [Kr] $5s^2 4d^5$

  How many core and valence electrons are in each atom above?

- Valence electrons are particularly important because they are the electrons that 'do the chemistry'. *(Electrons in a d or f subshell are only valence electrons if it was the last subshell filled. As such, a* ***valence electron*** *is* ***"any electron in the highest energy shell containing electrons <u>or</u> in the highest energy subshell".)***

Exceptions to the (Aufbau) Rule!

- There are a few exceptions to the aufbau order, most of which stem from the fact that full and half-full subshells are most stable. As such, if an atom gains a full or half-full subshell by breaking from the aufbau order, it often will.
  - Cr is not [Ar] $4s^2 3d^4$; it is [Ar] $4s^1 3d^5$
  - Cu is not [Ar] $4s^2 3d^9$; it is [Ar] $4s^1 3d^{10}$
- Why do you think it is more stable (lower energy) for Cr to have six orbitals with one electron each rather than one orbital with two electrons and four orbitals with one electron each?

Exceptions to the (Aufbau) Rule!

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
$1s^1$ 1																	$1s^2$ 2
$2s^1$ 3	$2s^2$ 4											$2p^1$ 5	$2p^2$ 6	$2p^3$ 7	$2p^4$ 8	$2p^5$ 9	$2p^6$ 10
$3s^1$ 11	$3s^2$ 12											$3p^1$ 13	$3p^2$ 14	$3p^3$ 15	$3p^4$ 16	$3p^5$ 17	$3p^6$ 18
$4s^1$ 19	$4s^2$ 20	$3d^1$ 21	$3d^2$ 22	$3d^3$ 23	$4s^1 3d^5$ 24	$3d^5$ 25	$3d^6$ 26	$3d^7$ 27	$3d^8$ 28	$4s^1 3d^{10}$ 29	$3d^{10}$ 30	$4p^1$ 31	$4p^2$ 32	$4p^3$ 33	$4p^4$ 34	$4p^5$ 35	$4p^6$ 36
$5s^1$ 37	$5s^2$ 38	$4d^1$ 39	$4d^2$ 40	$5s^1 4d^4$ 41	$5s^1 4d^5$ 42	$4d^5$ 43	$5s^1 4d^7$ 44	$5s^1 4d^8$ 45	$5s^0 4d^{10}$ 46	$5s^1 4d^{10}$ 47	$4d^{10}$ 48	$5p^1$ 49	$5p^2$ 50	$5p^3$ 51	$5p^4$ 52	$5p^5$ 53	$5p^6$ 54
$6s^1$ 55	$6s^2$ 56	La-Lu	$5d^2$ 72	$5d^3$ 73	$5d^4$ 74	$5d^5$ 75	$5d^6$ 76	$5d^7$ 77	$6s^1 5d^9$ 78	$6s^1 5d^{10}$ 79	$5d^{10}$ 80	$6p^1$ 81	$6p^2$ 82	$6p^3$ 83	$6p^4$ 84	$6p^5$ 85	$6p^6$ 86
$7s^1$ 87	$7s^2$ 88	Ac-Lr	$6d^2$ 104	$6d^3$ 105	$6d^4$ 106	$6d^5$ 107	$6d^6$ 108	$6d^7$ 109	110	111							

Developed by Prof. R. T. Boeré (updated January, 1999)

$4f^0 5d^1$ 57	$4f^1 5d^1$ 58	$4f^3$ 59	$4f^4$ 60	$4f^5$ 61	$4f^6$ 62	$4f^7$ 63	$4f^7 5d^1$ 64	$4f^9$ 65	$4f^{10}$ 66	$4f^{11}$ 67	$4f^{12}$ 68	$4f^{13}$ 69	$4f^{14}$ 70	$5d^1$ 71
$5f^0 6d^1$ 89	$5f^0 6d^2$ 90	$5f^2 6d^1$ 91	$5f^3 6d^1$ 92	$5f^4 6d^1$ 93	$5f^6$ 94	$5f^7$ 95	$5f^7 6d^1$ 96	$5f^9$ 97	$5f^{10}$ 98	$5f^{11}$ 99	$5f^{12}$ 100	$5f^{13}$ 101	$5f^{14}$ 102	$6d^1$ 103

- All of these exceptions are elements from either the '*d*-block' or the '*f*-block', so they are either transition metals (Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt, Au), lanthanides (Ce, Pr, Gd), or actinides (Th, Pa, U, Np, Pu, Cm).

Electron Configurations of Ions

- We use the periodic table to determine how many electrons reside in each atom. If an atom is neutral, this will be the ________ number *(Z)*. For an ion, **# electrons = *Z* − charge**. Thus, an **anion** will have ______ electrons than the neutral atom while a **cation** will have ______ electrons than the neutral atom.

- Subshells in anions are filled using the ________________________.

- Subshells in most cations are filled by writing the electron configuration for the neutral atom then ***removing valence electrons*** starting with the outermost shell (highest '*n*') until the correct charge is reached. *If this leaves two partially filled orbitals (e.g. 4s & 3d), drop the **'s'** electron into the lower shell.*

Electron Configurations of Ions

- Write electron configurations for the following:

corresponding neutral atom | ion listed

Li^{+}

P^{3-}

Cr^{2+}

Sn^{2+}

Sn^{4+}

Electron Configurations of Ions

- We can use electron configurations to predict which ions are likely to form. As a general rule, ions may form if they have:
  - The same electron configuration as the closest noble gas,
  - A *pseudo* noble gas configuration (noble gas configuration plus a full *d* or *f* subshell), or
  - A noble gas configuration for everything but *d* or *f* electrons.

Electron Configurations of Ions

- Which of the following ions are likely to form? For those which are not, what ion would you expect to form from that element?
  - O^{2-} Cl^{+}
  - Mg^{6-} Ca^{+}
  - Pb^{4+} Ga^{3+}