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This class closely follows the second chapter of Callister

Atomic structure

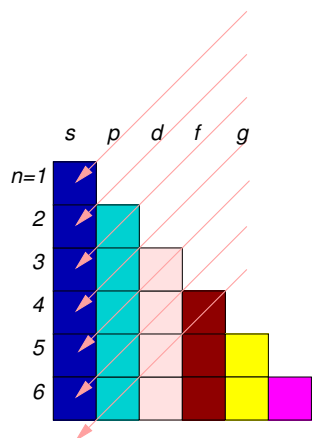
Atoms are composed of protons (positively charged), neutrons (no charge) and electrons (negatively charged). The number of electrons in an atom (which is equal to the number of protons) is called the atomic number. The number of electrons (or protons) + the number of neutrons is called the mass number. The atomic mass (which is numerically, a value close to the mass number) is the weighted average mass of a number of *isotopes* of the element, expressed in a system of units where the common isotope of carbon ^{12}C has an atomic mass of precisely 12.00000. The unit of atomic mass in g is equal to $1.00000/(\text{Avogadro Number}) = 1.00000/6.0221367 \times 10^{23} = 1.66054 \times 10^{-24}$ g. This is sometimes called the Lochschmidt number. One atom of ^{12}C weighs 12 times this, 1.99265×10^{23} g. If instead of counting atom by atom, we count in bunches corresponding to the Avogadro number, we have *moles* of something, and 1 mole of ^{12}C weights *precisely* 12.00000 g. One mole of a normal carbon sample (which is a mixture of isotopes with different mass numbers) actually weighs 12.011 g.

Atoms have protons and neutrons in the core, in a nucleus. The electrons whiz around the nucleus according to two models, a simple one called the **Bohr** model, and a more complicated one called the atomic orbital model.

In the Bohr model, electrons whiz around in different shells, the K shell, the L, shell, the M shell, the N shell, and so on. The K shell can accommodate 2 electrons, M can accommodate 8, M can accommodate 18 and N 32. The more sophisticated atomic orbital model has four kinds of orbitals, *s*, *p*, *d* and *f* (and for extremely heavy elements, a *g* orbital), that arise as solutions of the Schrödinger equation for atoms. This equations forms the basis of quantum mechanics. One of the outcomes of the solving the Schrödinger equation is that every electron in an atom is associated with a set of 4 numbers called the *quantum* numbers. The first number, the principle quantum number *n* takes on values as shown below and these correspond to the different shells of the Bohr atom.

n	Shell	Subshells	States	Electrons
1	K	s	1	2
2	L	s	1	2
		p	3	6
3	M	s	1	2
		p	3	6
		d	5	10
4	N	s	1	2
		p	3	6
		d	5	10
		f	7	14

In an atom, the electrons will always attempt to go to states with the lowest energy. This is the *aufbau* (or building-up) principle. However, you cannot fill states beyond a certain point. For example, if you finish filling $3d$ states with 10 electrons, you have to move on to $4s$. This is a consequence of the *Pauli exclusion principle* which states that no two electrons in an atom can share identical sets of the four quantum numbers. The scheme below shows the rules for filling up electrons in an atom. First all the “core” electrons fill up. Towards the end, the “valence” electrons start filling up. It is the valence electrons that usually decide the properties of the atom, such as its reactivity towards other elements.



The periodic table:

The rules for filling up electrons in an atom result in the periodic table. Note that elements in the periodic table are separated into various categories. You must learn to understand these different categories: Alkali metals, alkaline earth metals, transition metals,

main group elements (consisting of metalloids and non-metals) and the noble gases. Also, there are the lanthanide and actinide elements.

PERIODIC TABLE OF THE ELEMENTS

<http://www.kf-split.hr/periodni/en/>

Legend:

- Metal Metal
- Semimetal Semimetal
- Nonmetal Nonmetal
- Alkali metal Alkali metal
- Alkaline earth metal Alkaline earth metal
- Transition metals Transition metals
- Lanthanide Lanthanide
- Actinide Actinide
- Chalcogens element Chalcogens element
- Halogens element Halogens element
- Noble gas Noble gas

Standard State (100 °C, 101 kPa):
Ne - gas Fe - solid
Ga - liquid Tc - synthetic

Groups: IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA
Periods: 1, 2, 3, 4, 5, 6, 7

LANTHANIDE

57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.04	71 174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERIUM	LUTETIUM

ACTINIDE

89 (227)	90 232.04	91 231.04	92 238.03	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (259)	103 (262)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM

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Count the electrons in the noble gases. Note that they correspond to filled K shells (He), filled L shells (Ne), filled M shells (Ar) ... These are stable configurations and the noble gases are rather unreactive. It is always useful to know how far an element is from the nearest noble gas. For instance, Br is just one electron away from Kr, and as a result, will grab an electron whenever it gets the chance. K has just one electron more than Ar and is always trying to get rid of it (the one electron). Another way of stating this is that Br has 7 valence electrons (and tries to get one more to reach 8) while K has 1 valence electron and tries to get rid of it to reach zero.

In general, atoms that can adopt the configuration of the nearest noble gas by gaining electrons, have a tendency to grab electrons from other atoms. This tendency is called electronegativity, and Pauling introduced a scale to describe this tendency. The scale runs to 4 (corresponding to F) which is an atom that always tries very hard to grab electrons. Atoms that have can gain a noble gas configuration by giving up electrons are electropositive, and their electronegativity values are small (usually below 1.5).

Bonding:

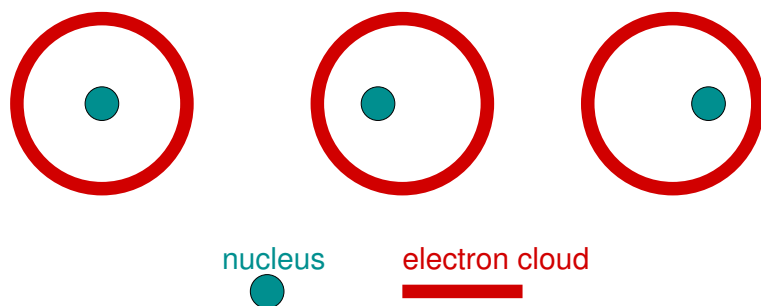
- There are four forces in nature. The *strong* and the *weak* interactions act between electrons, protons, neutrons and other elementary particles and do not concern us. We do not know of any normal material whose properties (melting point, for example) depend on the magnitude of these forces. The two other forces are *gravitational* and *electromagnetic*.
- Gravitational forces account for large scale phenomena such as tides, and seasons, and together with intermolecular forces, decide the length of a giraffe's neck. We shall not discuss gravitation.
- All interactions that are important for solids, should in principle, come out as solutions of the Schrödinger equation (SE). Unfortunately, solutions of the SE are hard to come by for many real systems, and even if they were available, their utility would not be assured. We therefore continue to propagate the useful fiction that cohesive interactions in materials can be classified as belonging to one of four categories – van der Waals, ionic, covalent or metallic.¹ We keep in mind that these are not very easily distinguished from one-another in many solids.

For a delightfully readable text on the nature of cohesion between molecules, and between molecules and surfaces, look at J. N. Israelachvili, *Intermolecular and Surface Forces*.

van der Waals

- The simplest solids are perhaps those obtained on cooling down a noble gas – He, Ne, Ar, Kr or Xe. He does not form a solid at ambient pressure. All the other noble gases do.
- The interactions between noble gas atoms (which have closed shells of electrons) is of the van der Waals type (note: van der Waals, not van der Waal's !) which means that the interaction is between instantaneous dipoles formed because the atoms “breathe” and this breathing causes the centers of positive and negative charges to, from time to time, not coincide. The forces are therefore also referred to as induced dipole-induced dipole interactions, or London dispersion forces (after F. W. London).

¹Hydrogen bonds are somewhere between being ionic and covalent and we do not see a good reason to place them in a class by themselves.



- If we were to believe the above scheme, it should come as no surprise that the largest noble gas atom should be the most *polarisable* and therefore the most cohesive. The boiling points (often better indicators of cohesion than melting points) testify to this:

Atom	T_M (K)	T_B (K)
Ne	24	27
Ar	84	87
Kr	116	120
Xe	161	165

- Other columns of elements in the periodic table don't follow this simple trend. For example:

Atom	T_M (K)	T_B (K)
Cu	1353	2833
Ag	1235	2433
Au	1333	3133

Ionic

- As a good thumb rule, atoms at the two ends of the electronegativity scale either give up their valence electrons very easily to form stable cations (ions with small values of electronegativity) or take up electrons very easily to form anions (ions with large electronegativities).

H		...					
2.2		...					
Li	Be	...	B	C	N	O	F
1.0	1.6	...	2.0	2.6	3.0	3.4	4.0
Na	Mg	...	Al	Si	P	S	Cl
0.9	1.3	...	1.6	1.9	2.2	2.6	3.2
K	Ca	...	Ga	Ge	As	Se	Br
0.8	1.0	...	1.8	2.0	2.2	2.6	3.0
Rb	Sr	...	In	Sn	Sb	Te	I
0.8	0.9	...	1.8	1.9	2.1	2.1	2.7
Cs	Ba	...	Tl	Pb	Bi	Po	At
0.8	0.9	...	1.8	2.1	2.0	2.0	2.2

- The process of giving up electrons (in the case of cations) and of taking electrons (anions) permits the ion to achieve a stable electronic configuration such as that of
 - a noble gas: For example, Na^+ and F^- have the Ne configuration
 - the d^{10} configuration: Ga^{3+} takes this up
 - the s^2 configuration: Pb^{2+} and Bi^{3+} take this up
- Once they have done this, they can pair up suitably to form *ionic* solids that are held together by Coulombic interactions
- For any ionic crystal, the attractive Coulombic part (per mole) is:

$$\Delta U_{\text{Att.}} = - \left(\frac{LA|z_+||z_-|e^2}{4\pi\epsilon_0 r} \right)$$

L is the Avogadro number.

- The repulsive part arises because atoms and ions behave nearly like hard spheres. This is a consequence of the *Pauli exclusion principle* which says that no two electrons in a system can have all four quantum numbers the same.
- The repulsion can be approximated by the expression:

$$\Delta U_{\text{Rep.}} = \frac{LB}{r^n}$$

where B is called the repulsion coefficient and n is the Born exponent. n is normally around 8 or 9.

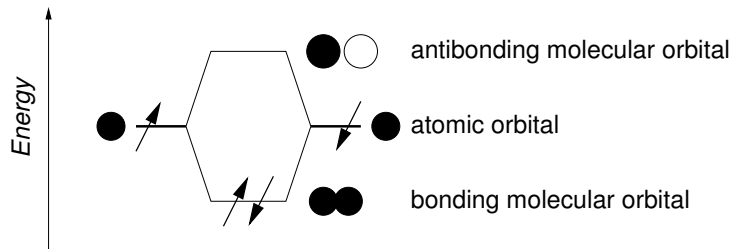
The two terms add:

$$\Delta U(0 \text{ K}) = -\frac{LA|z_+||z_-|e^2}{4\pi\epsilon_0 r} + \frac{LB}{r^n}$$

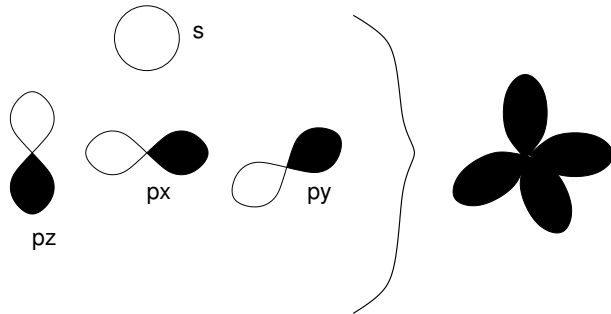
Covalent bonding

- Covalent bonds are formed between non-metallic (usually) atoms of similar electronegativity. s or p orbitals are used.

For example, the $1s$ orbitals on two hydrogen atoms combine to form the molecular orbitals $\sigma(1s)$ which is bonding and $\sigma^*(1s)$, which is antibonding. The two electrons occupy the bonding level and leave the antibonding level empty. In the following depiction, the circles are the $1s$ orbitals:



- Why is covalent bonding *strongly directional* ? The example of sp^3 hybrids in diamond and Si:



Hybrid orbitals are obtained from linear combinations of atomic orbitals on the *same* atom. These hybrid orbitals can then overlap with similar hybrid orbitals on neighboring atoms, just as the $1s$ orbitals do in the hydrogen chain.

Metallic bonding

This is a special case of covalent bonding where all the states are not filled up, and the electrons float around fixed nuclei in the solid.