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ENR116 Engineering Materials

Module 1 Introduction to Materials

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Chemical bonding

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Intended Learning Outcomes

At the end of this section, students will be able to:-

- Plot the attractive, repulsive and net forces between two atoms or ions.
- Describe primary and secondary bonding types.
- Note which materials exhibit which types of bonding

The intended learning outcomes from this presentation are for students to understand the types of forces between atoms and ions; describe primary and secondary bonding and identify which materials exhibit these.

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The Periodic Table

Group VIIA and VIA elements are, respectively, *one and two electrons deficient* from having stable structures.

Key: 29 ← Atomic number; Cu ← Symbol; 63.54 ← Atomic weight

Nonmetal

Intermediate

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

Adapted from Fig. 2.06, *Callister & Rethwisch 8e.*

In the previous presentation I introduced the concepts of atomic structure, electron orbitals and valence electrons. I would like to begin this lecture summary by looking at the periodic table which was developed by the Russian scientist Dmitri Mendeleev. The periodic table is composed of periods and groups, so the elements are placed in order of increasing atomic number from left to right and top to bottom. What is common to the elements is the groups, columns of elements, which have similar electron configurations and so similar chemical properties. So the VIIA and VIA groups outlined here are respectively one and two electrons in the outer electronic orbital short of a stable filled shell.

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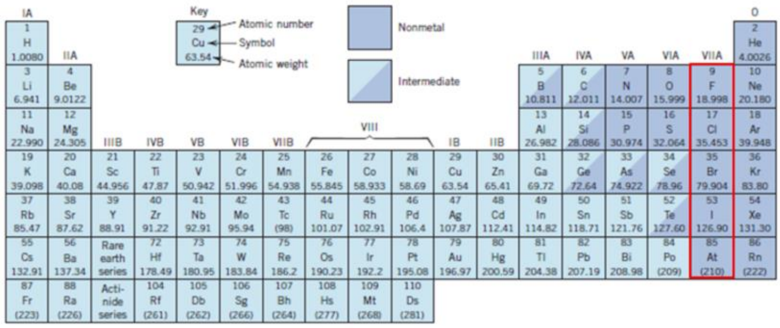
The Periodic Table

The Group VIIA elements (F, Cl, Br, I, and At) are sometimes termed the *halogens*.



Adapted from Fig. 2.06, *Callister & Rethwisch 8e.*

The group VIIA elements are sometimes referred to as the halogens and they are all relatively reactive non-metals.

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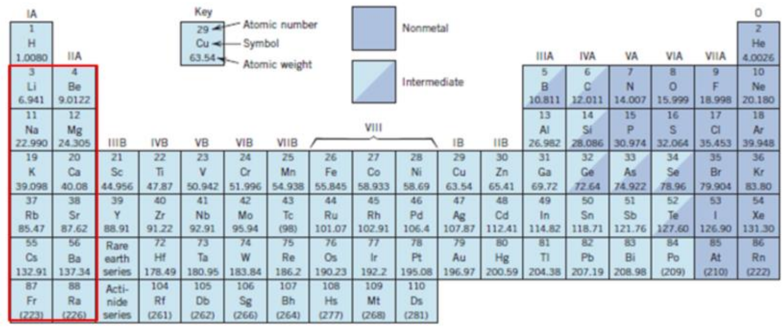
The Periodic Table

The *alkali* and the *alkaline earth metals* (Li, Na, K, Be, Mg, Ca, etc.) are labelled as Groups IA and IIA, having, respectively, one and two electrons in excess of stable structures.



Adapted from Fig. 2.06, *Callister & Rethwisch 8e.*

At the other side of the periodic table we have the groups labelled IA and IIA and these are characterised by having just 1 or 2 electrons in the outermost shell.

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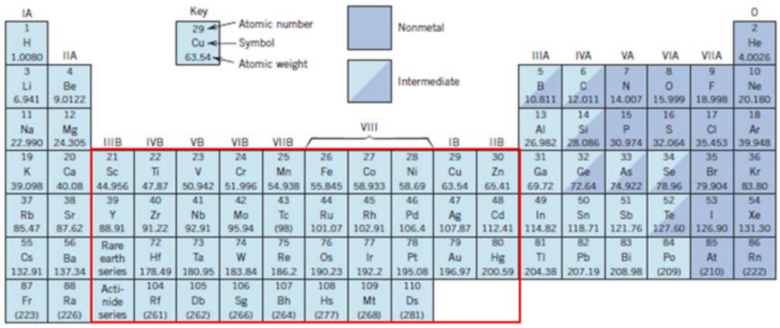
The Periodic Table

The elements in the three long periods, Groups IIIB through IIB, are termed the *transition metals*, which have partially filled *d electron states* and in some cases one or two electrons in the next higher energy shell.



Adapted from Fig. 2.06, *Callister & Rethwisch 8e.*

This section of the periodic table are known as the transition metals. They are characherised by their partially filled d electron states.

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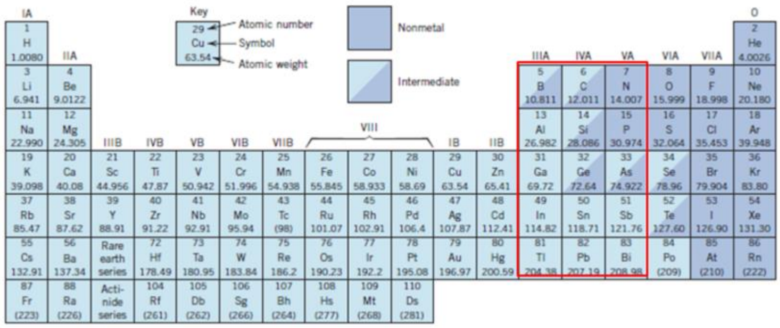
The Periodic Table

Groups IIIA, IVA, and VA (B, Si, Ge, As, etc.) display characteristics that are intermediate between the metals and non-metals by virtue of their valence electron structures.



Adapted from Fig. 2.06, *Callister & Rethwisch 8e.*

The three groups outlied here have characteristics which are imtermediate between metals and non-metals.

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Electronegativity

Ranges from 0.7 to 4.0

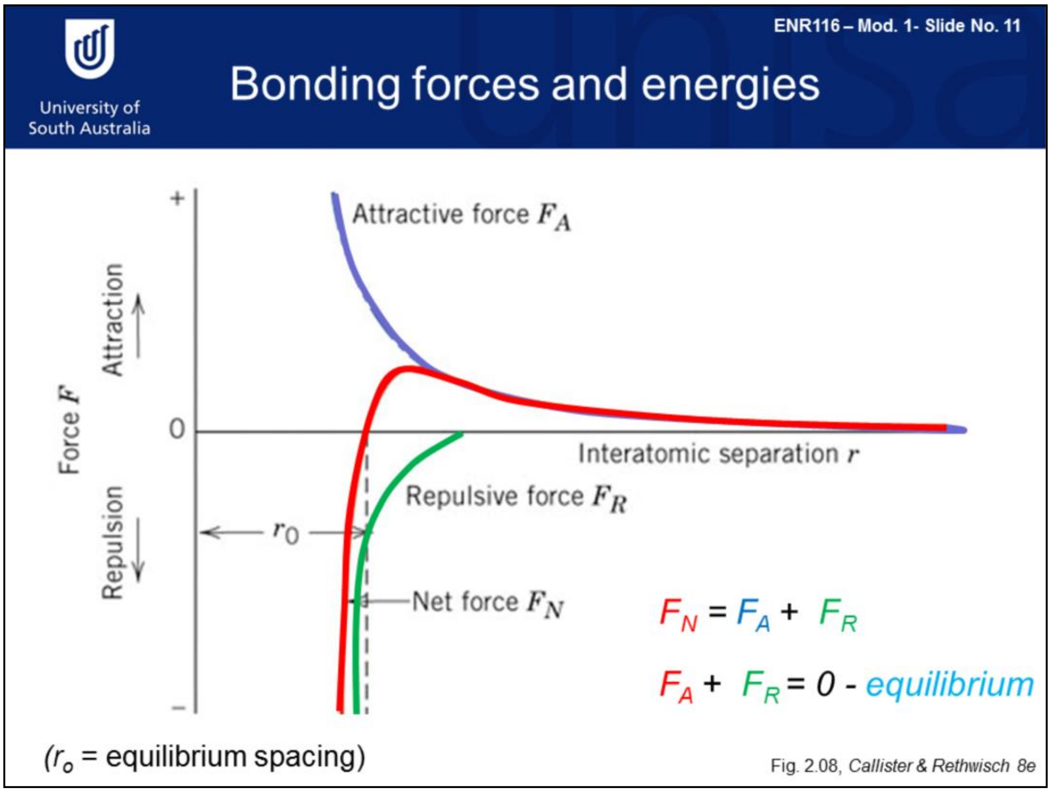
Large values: tendency to acquire electrons.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Smaller electronegativity

Larger electronegativity

Another important property of elements is that of electronegativity. This is the ability of one specific element to acquire electrons. In considering the periodic table the electronegativity increases from the bottom left corner to the top left corner. On the left are elements with low electronegativity and on the right are elements with high electronegativity, so the alkali earth metals and the alkali metals have low electronegativities and the non-metals such as oxygen and fluorine have high electronegativities. The exception is the inert gas group which, because of their filled outer shells, do not have any electronegativity.



The forces and energies binding the atoms of a material dictate many of it's properties and this can be seen schematically. The overall force between two atoms, the red line, is the sum of the attractive force see as the blue line and the repulsive force, the green line. In a similar manner we can plot the potential energies between the atoms from which we can determine the bonding energy.

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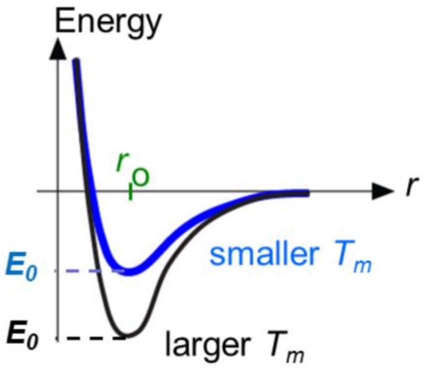
Properties From Bonding: T_m

Melting Temperature, T_m



T_m is larger if E_o is larger.

Whilst these plots of energy against the separation between two atoms can be considered as the ideal situation they can tell us a great deal about the material as a whole. As seen here the greater the value for bonding energy the higher the materials melting temperature and in later lectures the influence of this interatomic bonding on a materials mechanical properties will be explored.

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Interatomic Bonding

Primary bonds:

The bonding necessarily involves the valence electrons.
The nature of the bond depends on the electron structures of the constituent atoms.
Bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert gases, by completely filling the outermost electron shell.

Ionic Covalent Metallic

Secondary (Physical) bonds:

These bonds are weaker than the primary ones, but nonetheless influence the physical properties of some materials.

The final part of this week's lectures will discuss bonds and atomic bonding. These are generally described as primary bonds and secondary bonds. The primary bonds will involve the valence electrons; the nature of the bond depends on the electron structure of the constituent atoms, and the bonding will arise from the tendency of the atoms to assume stable electron structures - which we have already discussed like the inert gases, by completely filling the outermost electron shell. The primary bonds are the ionic bond, the covalent bond and the metallic bond. There are also secondary bonds and these are much weaker bonds than primary bonds but they are still very important in defining the properties of materials.

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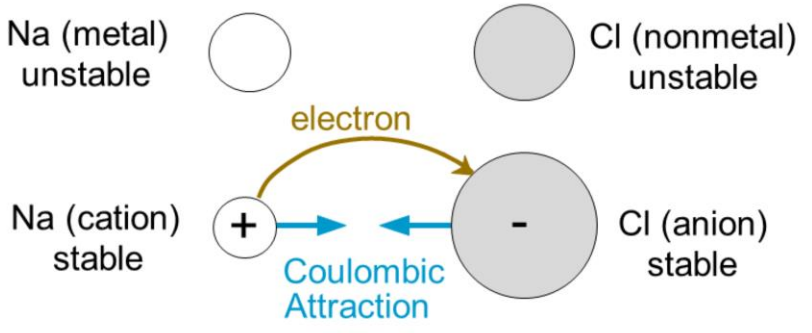
Ionic Bonding

Occurs between (+) and (–) ions

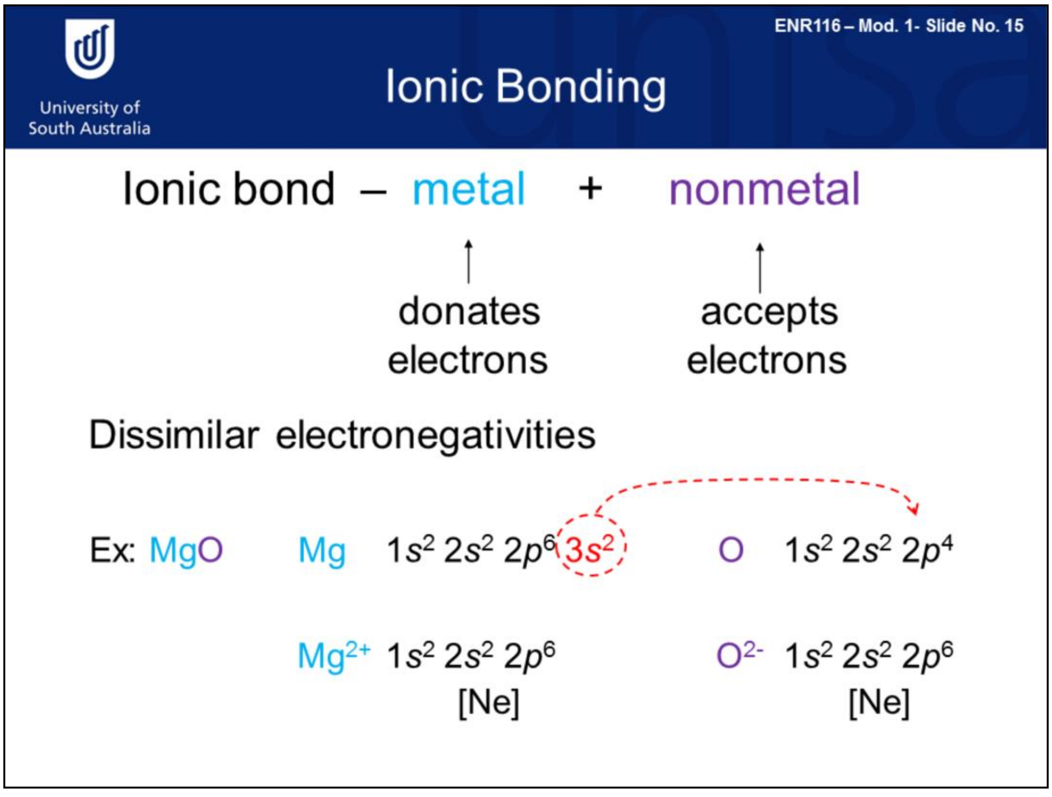
Requires electron transfer

Large difference in electronegativity required

Example: NaCl

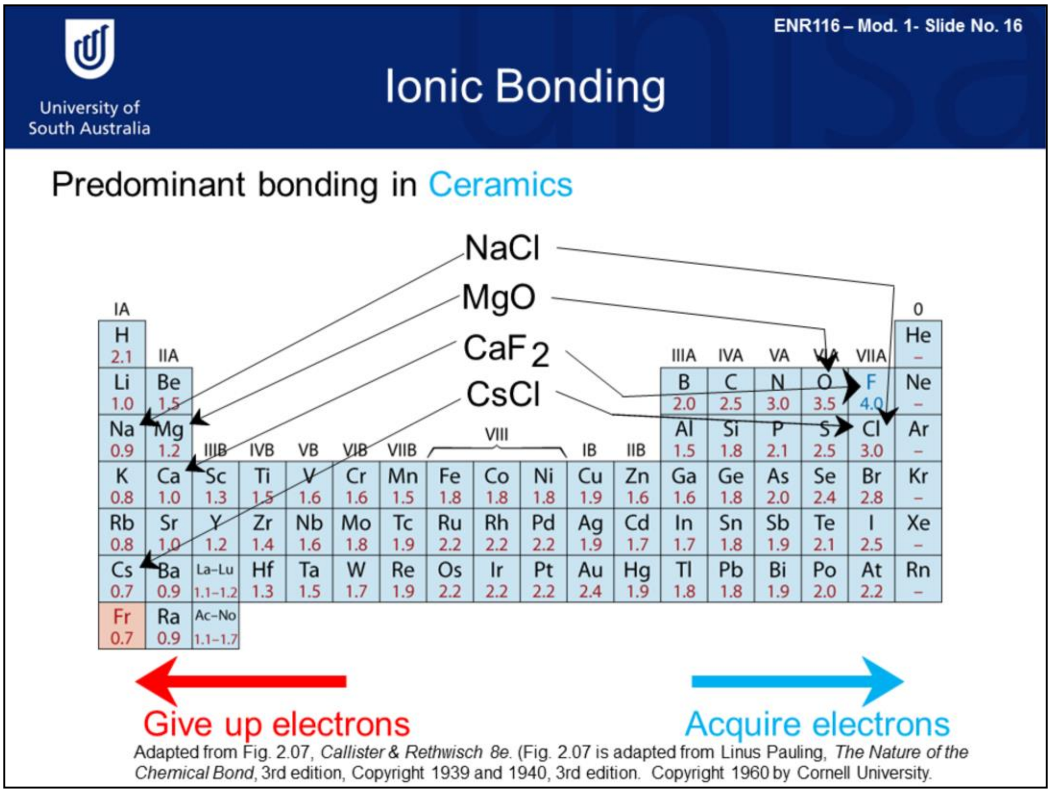


Ionic bonding occurs between ions. If you have two atoms with very different electro-negativities, such as sodium, which is on the left of the periodic table, and chlorine, which is on the right - they have very different electronic activities and they will form sodium chloride, table salt. So how does this happen? Chlorine is very much electronegative and so it has a strong tendency to acquire electrons, so pulling away the valence electrons of the sodium. Thus the sodium atom will become deficient of one electron and so become an ion of one positive charge. Chlorine on the other side will acquire one electron, so it become an ion of one negative charge. Then the plus and minus charged ions will attract each other forming an ionic bond.



So again, ionic bonding will happen between metals and non-metals, involving elements of lower and higher electronegativities; between elements with very different electronegativities. The metal will tend to donate electrons and is so known as the electron donor, and the non-metal, accepting the donated electrons, will be electron acceptors.

Another example of ionic bond will be magnesium oxide. Magnesium has two extra electrons compared to the stable configuration of neon whilst oxygen has two electrons less. The magnesium donates its extra two electrons and the oxygen accepts them to form the ionic bonds present in magnesium oxide.



Ionic bonds will occur between elements of very different electronic activities, such as the sodium on the left and chlorine on the right, the magnesium on the left and oxygen on the right. Another example would be calcium fluoride or caesium chloride and there are many other combinations which we will see throughout the unit.

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Ionic Bonding

Sodium chloride (NaCl)

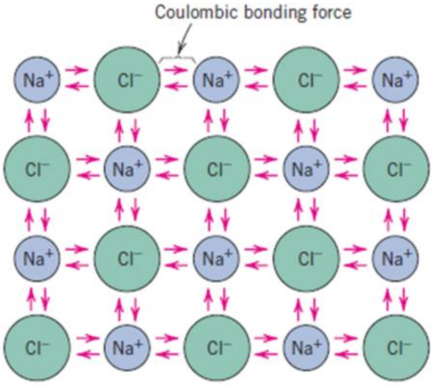


Fig. 2.09, *Callister & Rethwisch 8e.*

The bond is generally non-directional.

Bonding energies generally range between 600 and 1500 kJ/mol.

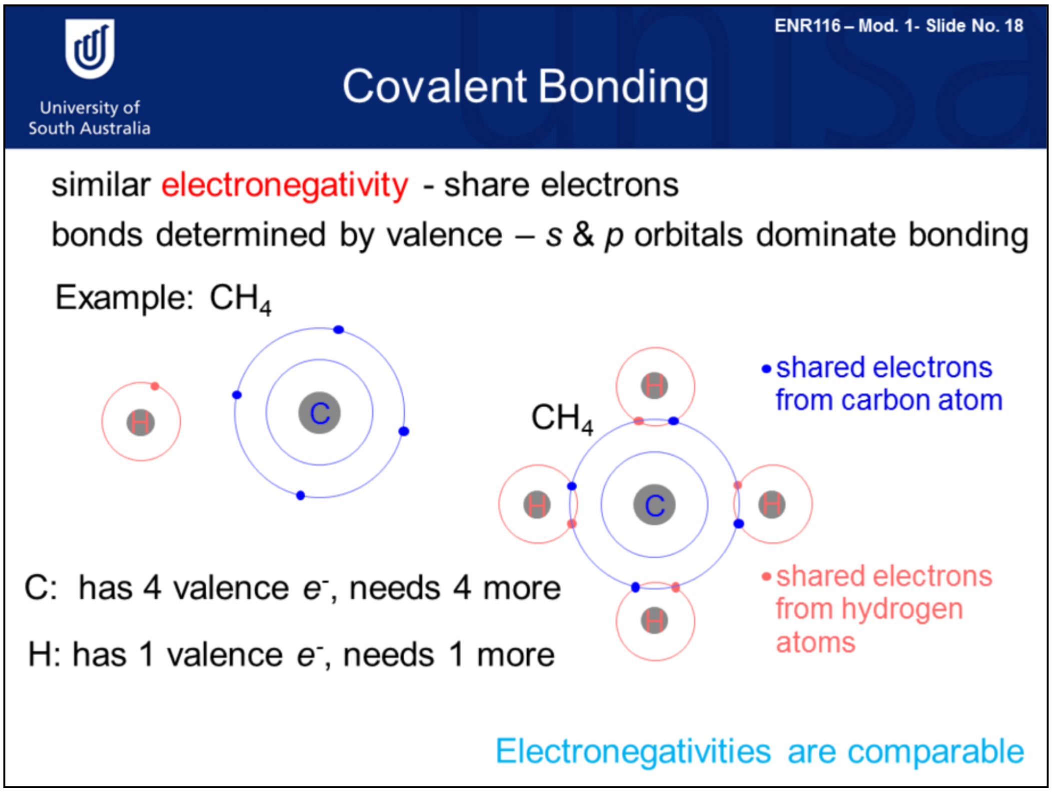
Ionic compounds have high melting temperatures.

They are hard and brittle and, furthermore, electrically and thermally insulative.

Predominant bonding in ceramic materials.

This is an example of the ionic bonding. This is the structure of the sodium chloride. You will see that each atom, either negative or positive, is surrounded by oppositely charged ions, so each sodium atom has four neighbours. These bonds are generally non-directional, the bonding energies will be between 600 and 1500 kJ/mol which means that they are strong bonds. The ionic compounds, because of these strong bonds, in general will have high melting temperatures.

They are hard and brittle and will be electrically and thermally insulated because of the alternation of positive-negative, positive-negative, and this is the predominant bonding in ceramic materials.



The next type of bonding is covalent bonding. Here again the atoms will acquire stable electron configurations but in another manner. This bonding usually happens between elements of similar electronegativity and typically between the non-metals.

Let's see an example here with methane which is formed with one carbon and four hydrogen atoms. Carbon, has four valence electrons, four electrons in one shell. Hydrogen has one electron, so it's one electron deficient of a filled shell and carbon is four electrons deficient. Both want extra electrons and so they share their electrons.

The four hydrogen's each share their four single electrons with the four electrons in the outer orbital of the carbon; each hydrogen will have two electrons and become like helium whilst the carbon will have eight electrons in the outer shell.

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Covalent Bonding

Many nonmetallic elemental molecules (H_2, Cl_2, F_2, etc).

Molecules containing dissimilar atoms (CH_4, H_2O, HNO_3, HF).

Solids such as diamond, silicon, germanium and other solid compounds of elements located on the right-hand side of the periodic table, such as gallium arsenide (GaAs), and silicon carbide (SiC).

The covalent bond is typical for many non-metallic elements such as hydrogen, chlorine, fluorine etcetera. They can be molecules that contain dissimilar atoms such as water, nitric acid and hydrogen fluoride; they can be solids such as diamond or silicon.

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Covalent Bonding

Polymeric materials:

Bonding energies and melting points are variable.

T_m diamond > 3550°C

T_m bismuth = 270°C

Number of covalent bonds for a particular compound = 8 - *N'*

N' – number of valence electrons

Examples: *Cl – 7 valence electrons – one covalent bond*

C – 4 valence electron – 4 covalent bonds

Covalent bonding is also present in polymeric materials.

The bonding energies of covalent bonds can be very different; they can be very strong such as in diamond, the hardest material with a very high melting temperature. Alternatively they can be very weak such as those in bismuth which is seen by it's low melting temperature.

We can determine the number of covalent bonds which an element can form using a simple expression 8 - N' where N' is the number of the valence electrons.

An example would be chlorine which has 7 valence electrons - 8 minus 7 is 1 so it can form one covalent bond. Carbon has 4 valence electrons, and so can form 4 covalent bonds.

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Mixed covalent and ionic bonds

Very few compounds exhibit pure ionic or covalent bonding.

For a compound, the degree of either bond type depends on the relative positions of the constituent atoms in the periodic table.

The greater the difference in electronegativity – the more ionic character.

The percentage ionic character of a bond between elements A and B (A being the more electronegative) may be approximated by the expression:

$$\% \text{ ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$$

where X_A and X_B are the electronegativities for the respective elements.

However, very few compounds are formed with purely covalent or purely ionic bonds. In most of the cases the bond type will be a mixture of both covalent and ionic bonds. The greater the difference in the electronegativities of the constituent elements the more ionic character.

The percentage ionic character may be determined by this simple expression: where X subscript A and X subscript B are the electronegativities of the respective elements. We will look more closely at this calculation in the first tutorial session.

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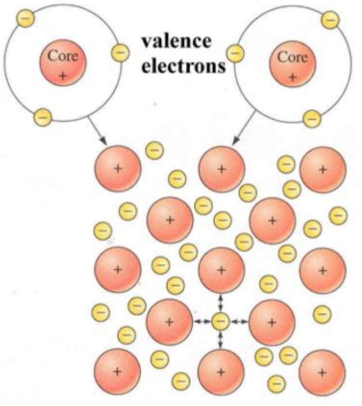
Metallic Bonding

This bond is found in metals and their alloys.

The valence electrons are not shared between any specific or particular atoms in the solid.

The electrons are free to move throughout the entire metal.

Electrons may be thought of as belonging to the metal as a whole forming a “sea of electrons” or an “electron cloud.”



The metallic bond is a bond found in metals and their alloys. What is different in metallic bonding is the fact that the electrons are not shared between any specific or particular atoms; they are shared between all the atoms in the metallic material. As such the valence electrons are free to travel across the material and thus they form an electron cloud and this will determine the properties of the material. It is this aspect of metals which makes them good conductors of electricity.

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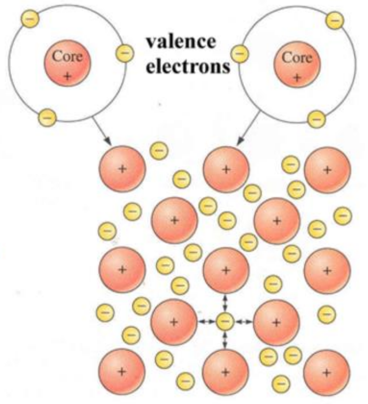
Metallic Bonding

The remaining non-valence electrons and atomic nuclei form ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom.



The free electrons shield the ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another.

The free electrons act as a “glue” to hold the ion cores together.

The non-valence electrons are not free to move and will stay around the nucleus. But, since the valence electrons are moving the ion cores assume a net positive charge. The atoms are closely packed together and the free electrons do not belong to any particular number of atoms but to the whole material.

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Metallic Bonding

Bonding energies may be weak or strong

E_o W (tungsten) = 850 kJ/mol; T_m = 3410°C
E_o Hg (mercury) = 68 kJ/mol; T_m = -39°C

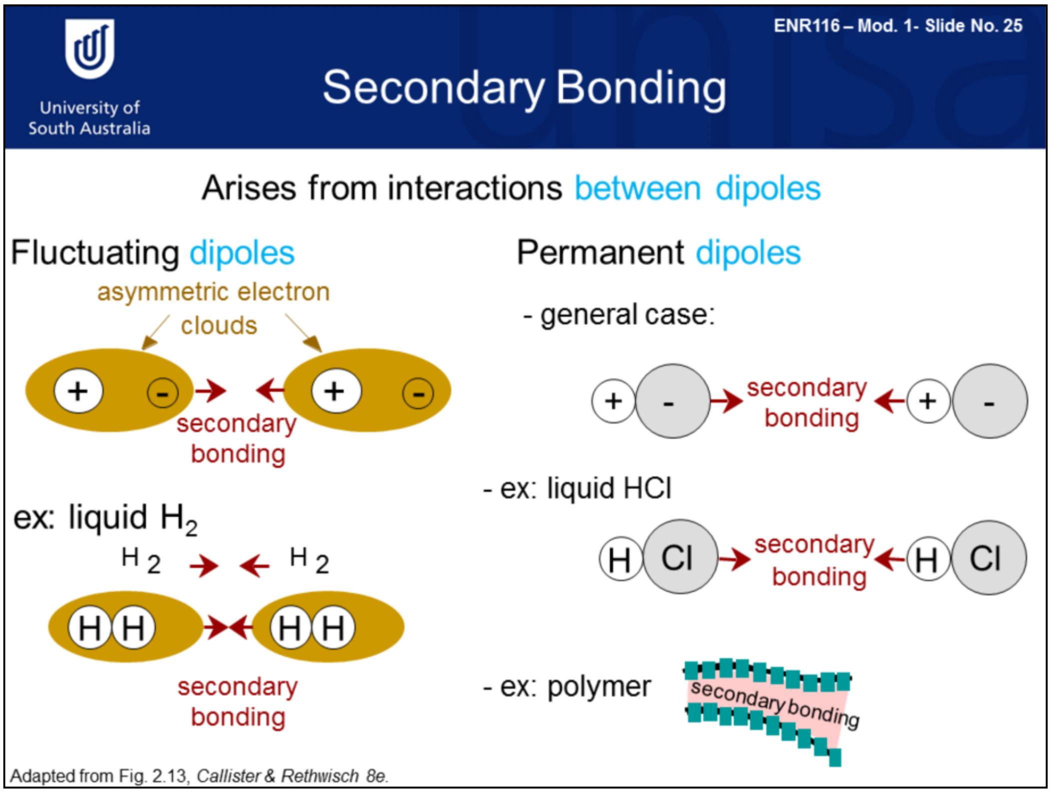
Metals are good conductors of both electricity and heat, as a consequence of their free electrons.

Metals and their alloys are usually ductile (capacity for plastic deformation), opaque, shiny and lustrous.

The majority of metals have higher densities than the majority of non-metals, except the alkali and alkaline earth metals.

The metallic bond can be very strong such as in tungsten with it’s very high melting temperature, or they can be very weak such as in mercury.

Metals, because of the free electron cloud are good conductors of electricity and heat; they are usually ductile because of the electron structure, opaque and the majority, excepting the alkali or alkali earth metals, have higher densities than most of the other elements.



There is another class of bonding known as secondary bonding or van der Waals bonding. Secondary bonding is much weaker than primary bonding but it's still very important. It has a value of about 10 kJ/mol and occurs between dipoles.

A dipole can be considered as the attraction between unlike charges in a similar manner to opposite poles of a magnet. Wherever there is an atom or molecule with a positively charged region and a negatively charged region then the possibility of secondary bonding between adjacent atoms and molecules will exist. The strength of these bonds will depend on the atoms involved and their relative electronegativities.

This slide illustrates some of the instances where secondary bonding occurs; for example between simple molecules and polymer chains.

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Hydrogen bond

It is strongest of the secondary bonds (as high as 51 kJ/mol).

It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H_2O) and nitrogen (as in NH_3).

For each H—F, H—O, or H—N bond, the single hydrogen electron is shared with the other atom.

HF

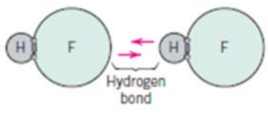

Fig. 2.15, *Callister & Rethwisch 8e.*

H_2O

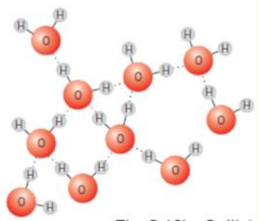

Fig. 2.16b, *Callister & Rethwisch 8e.*

The hydrogen bond is another example of secondary bonding however it has a strength of 51 kJ/mol and is typical found between molecules in which hydrogen is covalently bound to fluorine, oxygen or nitrogen.

With hydrogen bonding the electron of the hydrogen is strongly attracted towards the other element such that the hydrogen atom is left with a bare nucleus and so has a much stronger positive charge than normal. The result is a dipole forming a strong attraction between the hydrogen of the one molecule and the corresponding element of an adjacent molecule.

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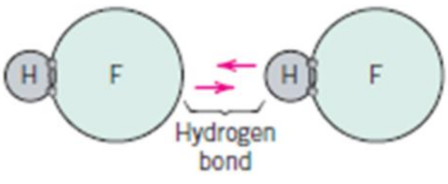
Hydrogen bond

Melting and boiling temperatures for hydrogen fluoride and water are abnormally high in light of their low molecular weights, as a consequence of hydrogen bonding.



HF

Fig. 2.15, *Callister & Rethwisch 8e.*

H_2O

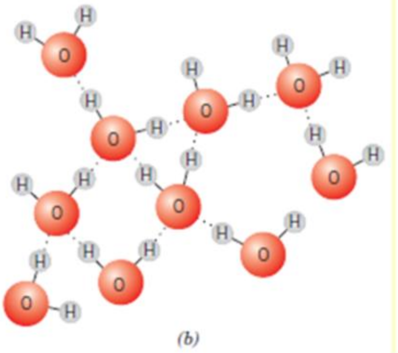
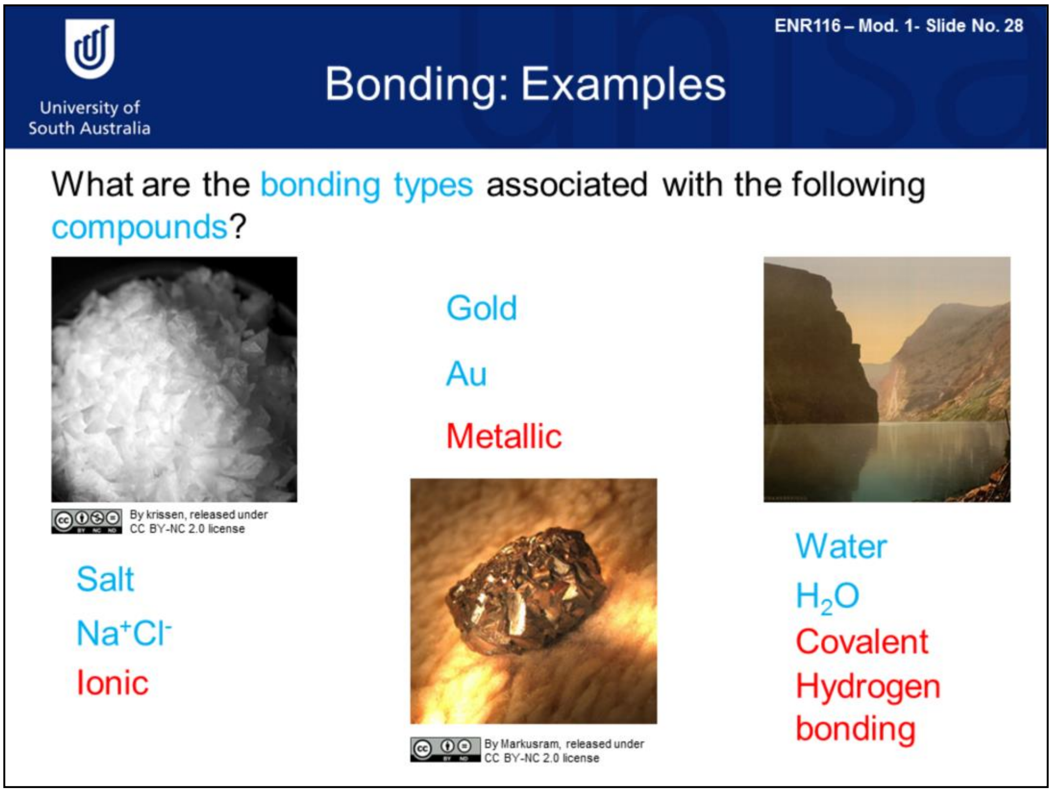


Fig. 2.16b, *Callister & Rethwisch 8e.*

The abnormally high melting point and boiling point of water, relative to it’s molecular weight, is due to the hydrogen bonds that occur between the water molecules.



So materials are formed with a range of bonds between the constituent atoms and molecules. For example common salt comprises of ionic bonds between the sodium and chlorine atoms. Another example is gold whose atoms form dense metallic bonds between each other and finally water; covalent bonds between the two hydrogen atoms and one oxygen atom are accompanied by hydrogen bonds between the adjacent water molecules.

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Summary

- The forces between two atoms or ions depend on their interatomic spacing.
- The primary bonding types are covalent, ionic and metallic.
- Secondary bonding types include van der Waals and hydrogen bonding.

In summary, there are a number of primary and secondary bonding types between elements forming compounds. The primary bonds are stronger than the secondary however the secondary bonds can still be an influence on a compound and it's material properties.

Thank you

If you have any questions or desire further clarification please post a question or comment on the Engineering Materials Discussion Forum.