Crystal Chemistry

A mineral is a solid with a highly ordered ***atomic*** arrangement and a definite, but not fixed, ***chemical*** composition.

1. What is an atom?
2. What are the common atoms/elements in common geological minerals?
3. How are the atoms arranged?
4. How do the atoms interact with one another?
5. How does the nature and arrangement of elements in a mineral vary, both the chemical and physical properties, of minerals?

What is an atom?

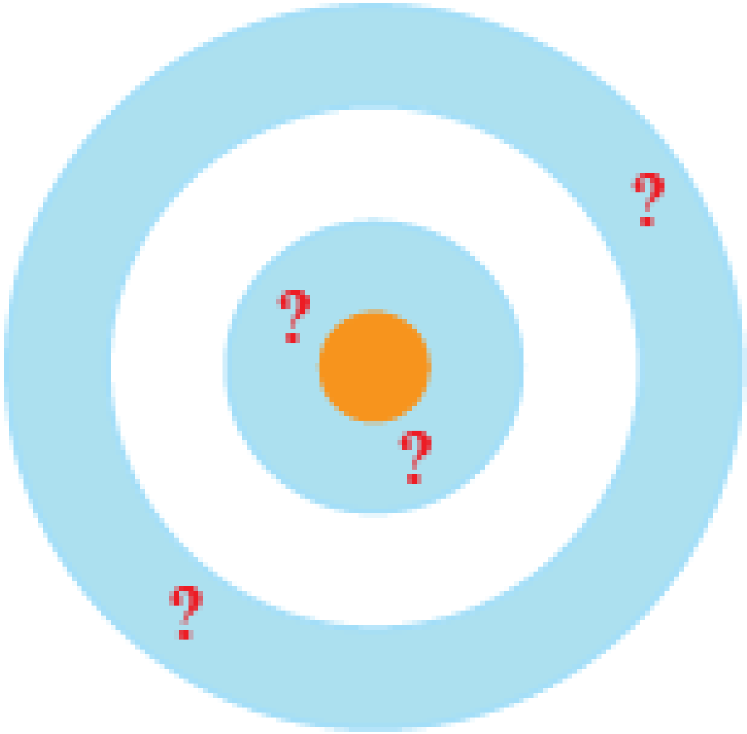
The smallest subdivision of matter that retains the characteristics of the element.

Models for the atom have evolved with greater understanding of particle physics.

Early models, such as that of Rutherford, predicted that an atom was just like the solar system.

Bohr refined the model quantifying the orbits.

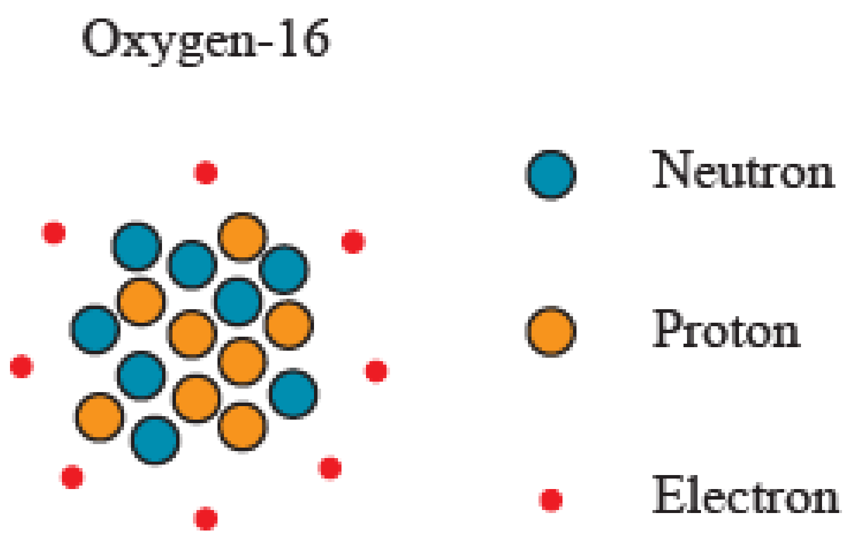
The work of Schrödinger and Heisenberg refined the model further, rejecting precise orbits, and promoting regions of electron occurrence – *orbitals*.



Structure of an atom

The fundamental difference between atoms of different elements is the electrical charge of the nucleus.

The nucleus of an atom consists of two sub-atomic particles: **protons** and **neutrons** (of essentially equal mass = 1amu), with the former defining the atomic number (Z).



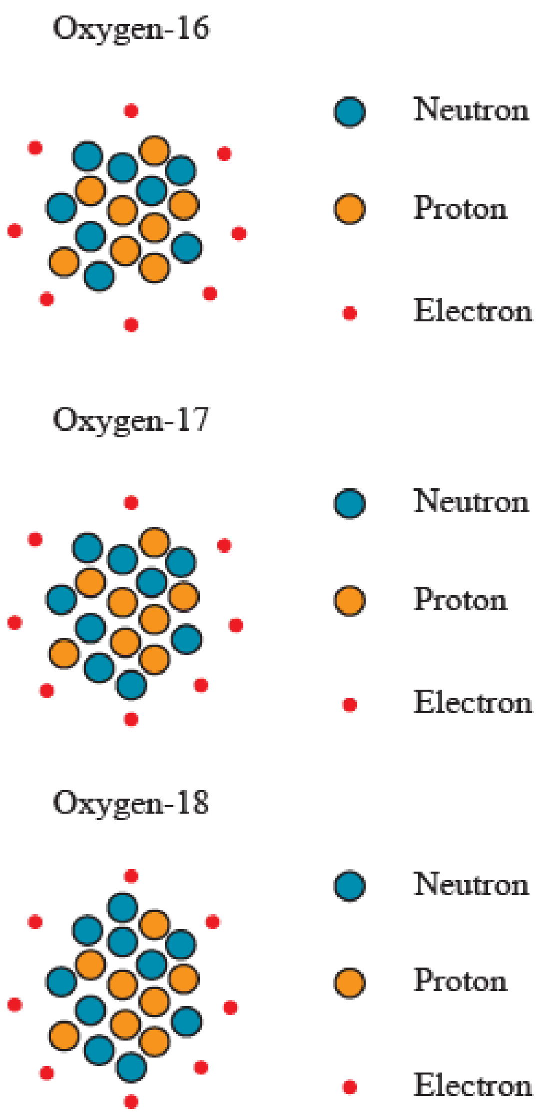
All atoms are electrically neutral.

The number of protons is balanced by the same numbers of electrons.

In the case of ^{16}O, there are 8 of each, plus 8 neutrons.

This gives an atomic weight of 16.

Isotopes



The properties of an atom are defined by the number of protons and electrons, so in the case of oxygen (Z = 8), the atomic weight is almost 16 (15.9994).

Many elements have alternative mass configurations, but retain the same Z; these are called isotopes.

Stable isotopes (C, O, N ….), retain the same properties and position in the periodic table, but have a higher mass due to a higher number of neutrons.

Oxygen has three stable isotopes. The mass of stable isotopes does not change.

Rules for e^- occupying space around the nucleus

1) Orbitals s, p, d, f are predicted using the Schrödinger equation:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Orbital shapes become increasingly complex with increasing numbers of electrons

2) Size of orbitals increase as they get farther from the nucleus – the smallest lowest energy orbitals are closest to the nucleus (ground state)

3) With the different orbital shapes there are associated different numbers of orbitals – the result is a specific number of electrons per shaped orbital s, p, d, f

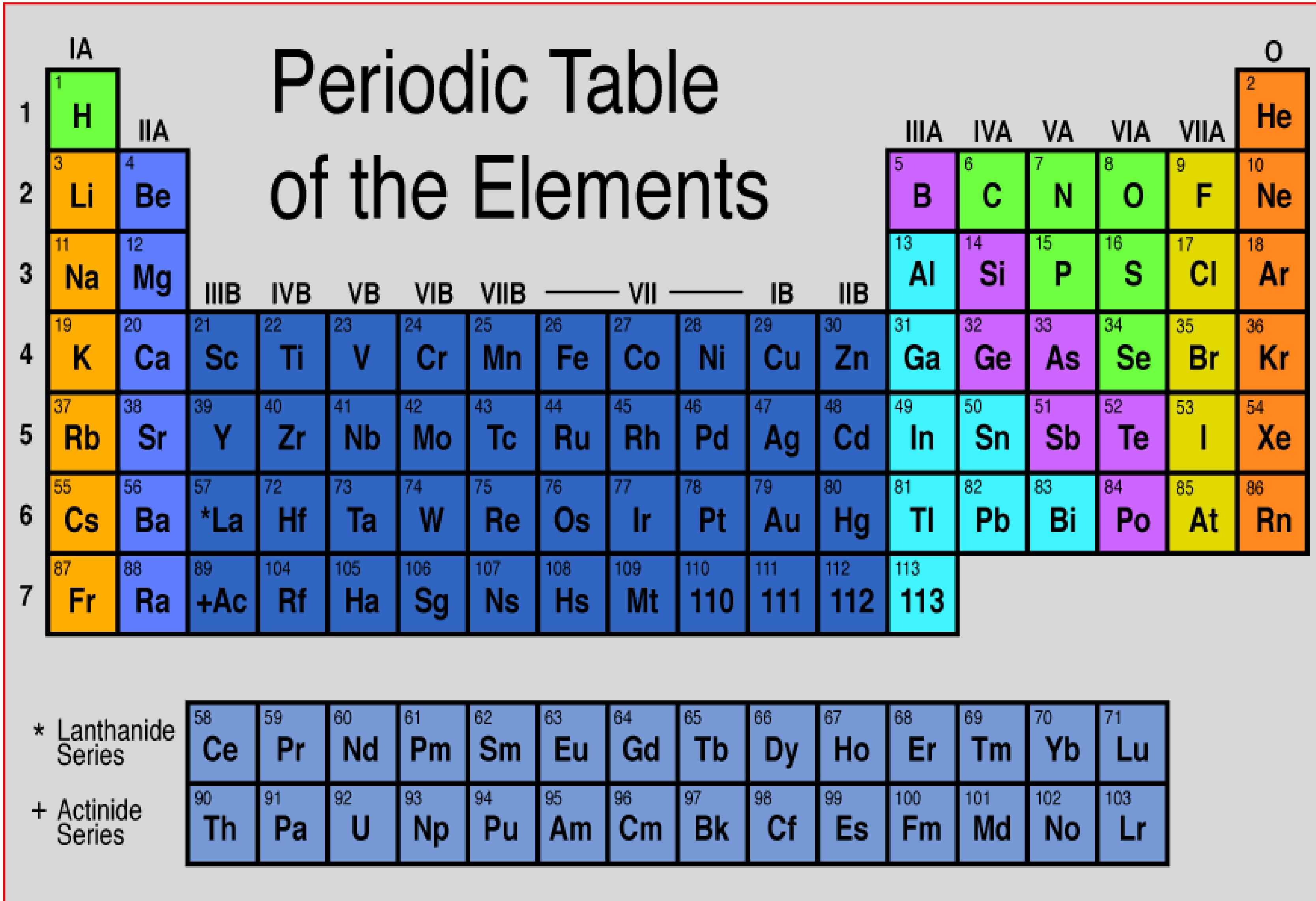
Type of orbital	# of orbitals	total # electrons
s	1	2
p	3	6
d	5	10
f	7	14

4) Each orbital can only accommodate 2 e^- spinning in opposite directions

5) For most neutral atoms the filling order is:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*/5*d*, 6*p*, 7*s*, 5*f*/6*d*

2. What are the common elements in geological minerals?

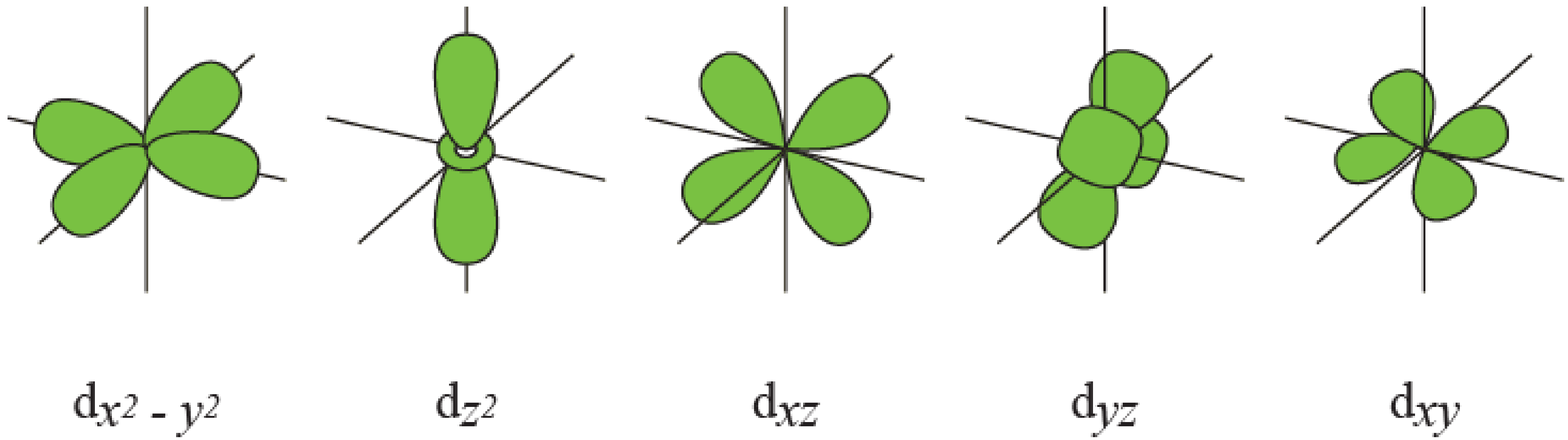


Making atoms into ions

- converting an atom from a neutral state via the gain or loss of an electron will create a charged particle
- whenever there are an unequal number of protons and electrons, an ion is created
- when it is easier for an atom to gain electron(s) the ion generated has a net negative charge (with outer shells being filled with electrons first) = *anion*
- *cations* are generated by the net loss of electron(s)

- with the gain of electrons, the electron cloud becomes larger = increased total size, with the loss of electrons, the cloud contracts

Electronic Configuration across the Periodic Table

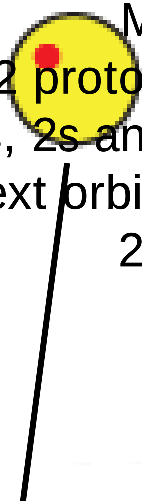


Principle Quantum No. n	Subshell Designation	No. of orbital shell	Maximum No. of e^-	
1 (K)	1s	1	2	**2**
2 (L)	2s	1	2	**8**
	2p	3	6	
3 (M)	3s	1	2	**18**
	3p	3	6	
	3d	5	10	
4(N)	4s	1	2	**32**
	4p	3	6	
	4d	5	10	
	4f	7	14	

Each orbital can accommodate a maximum of 2 electrons.
The orbitals must be filled in a specific order

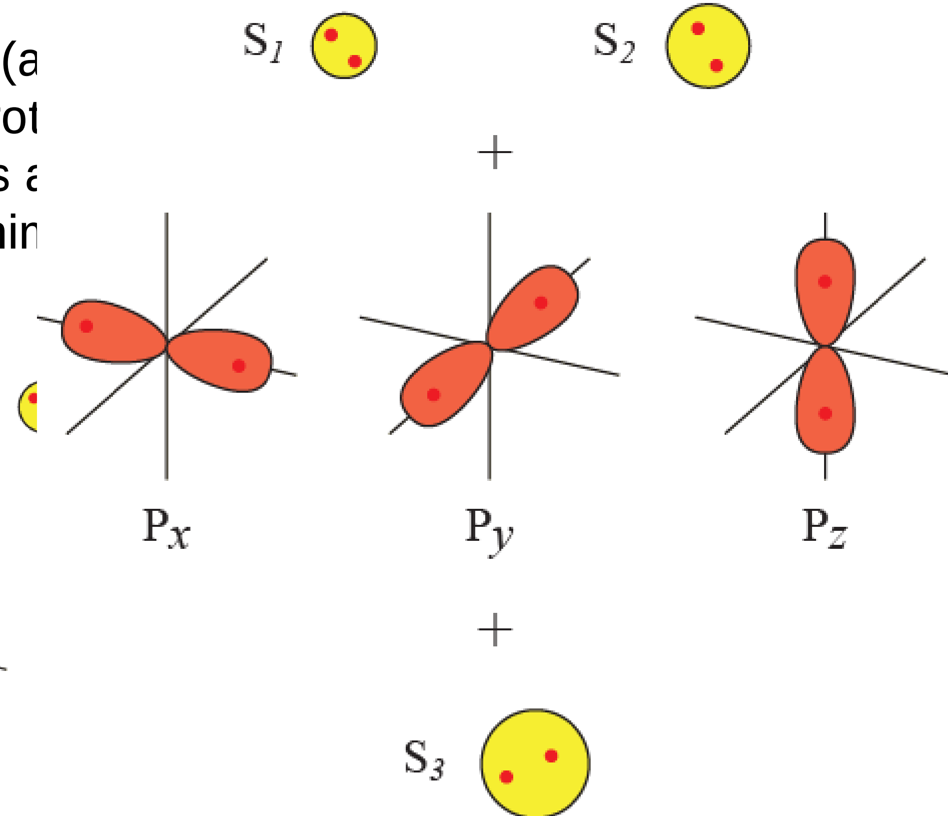
Oxygen (a
8 prot
Electrons a
minin

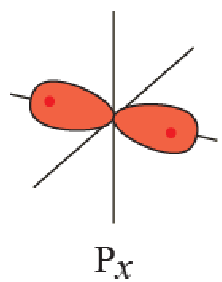
Hydrogen
1 proton + 1 electron

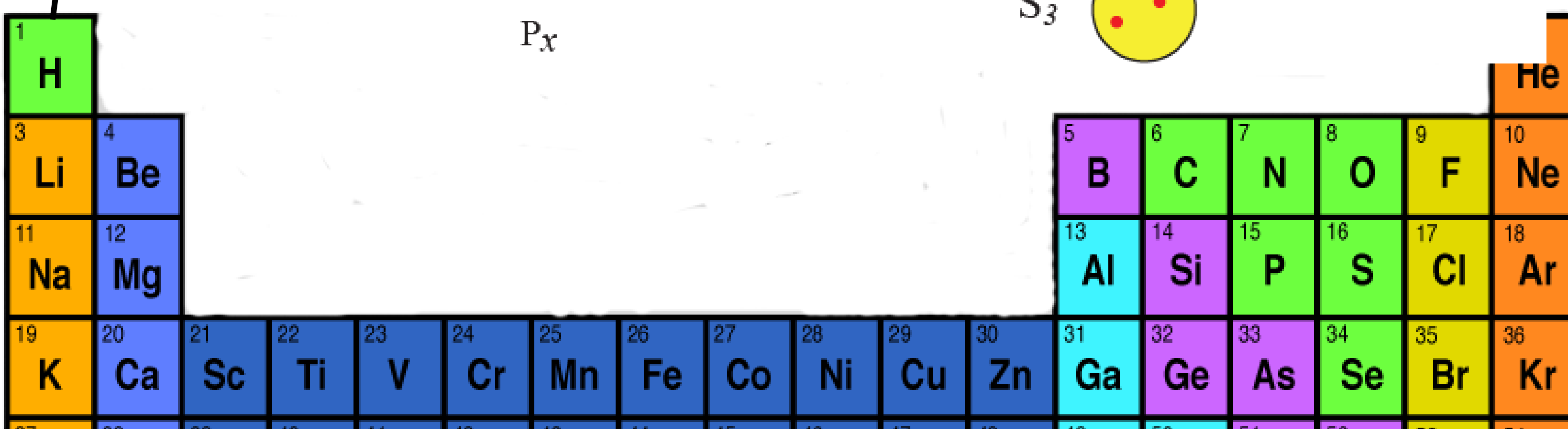


Magnesium
12 protons + 12 electrons
The 1s, 2s and 2p orbitals are filled,
The next orbital tier, the 3s also has
2 electrons.

ectrons







atoms = no. of protons = no. of electrons

but atoms can be sub-divided into those that tend to ***give up*** electrons, and those that ***accept*** electrons.

Those that give up electrons lie to the left-hand side (metals).

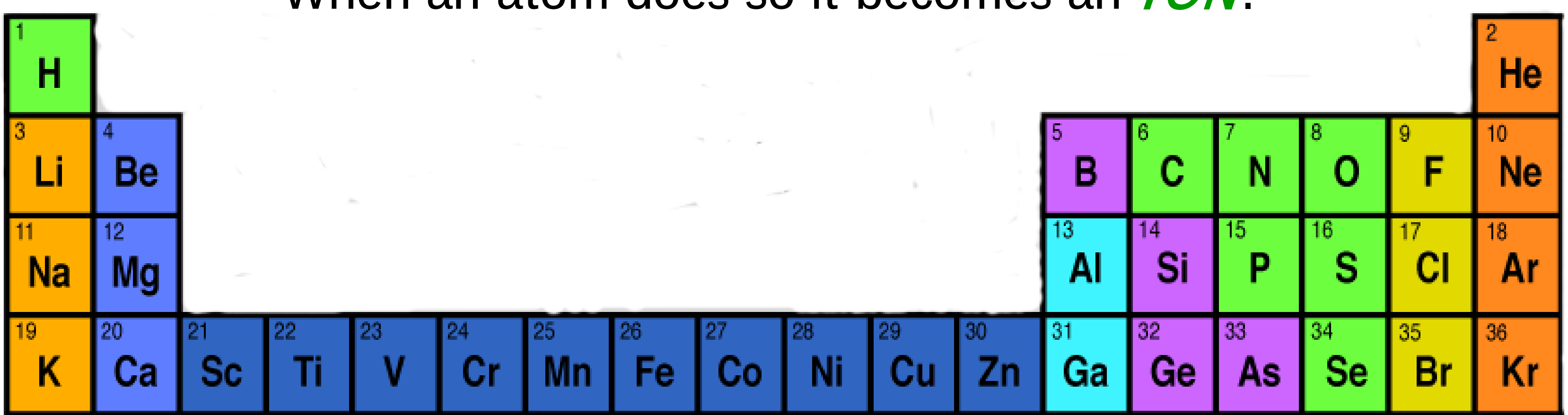
Those that accept electrons lie to the right-hand side (non-metals).

There are exceptions....

Some elements ***give up*** AND ***accept*** electrons.

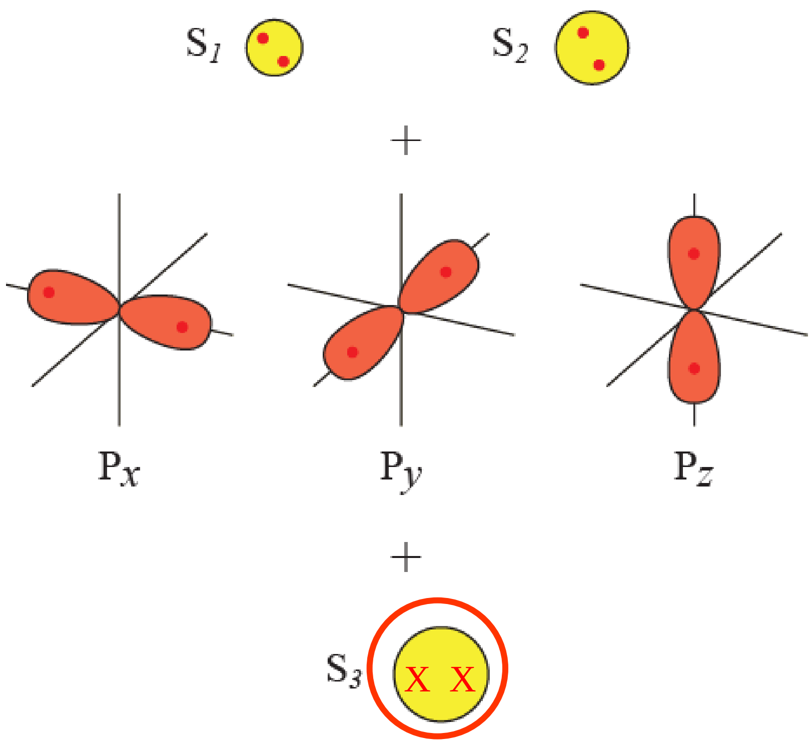
Some elements do neither.

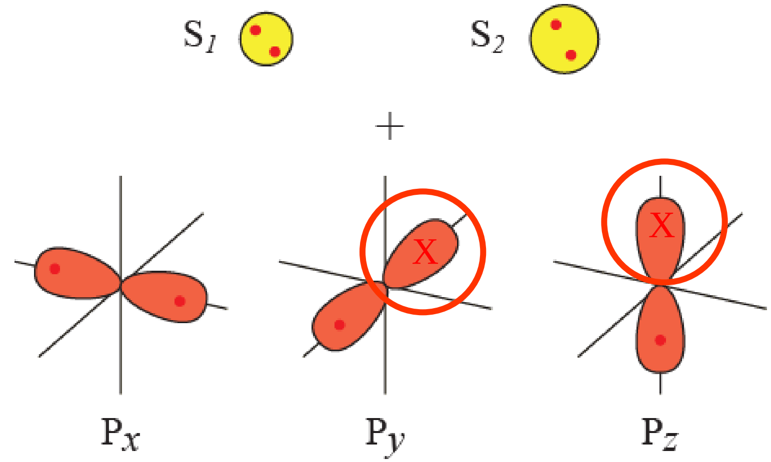
When an atom does so it becomes an ***ION***.



Ionisation

In the case of oxygen, the 2p orbital ***accepts*** 2 e^- and the orbital is filled, creating an oxygen ***anion*** with a 2-negative charge (O^{2-})





While in magnesium, the outermost 3s orbital ***gives up*** 2 e^- and the orbital is empty, creating an oxygen ***cation*** with a 2-positive charge (Mg^{2+})

The energy required to remove the most weakly held electron from a neutral atom is the ***first ionisation potential***. The energy requires to remove the next electron is the ***second ionisation potential*** and so on.

An ion forms by gaining or loosing its ***valence*** electrons and taking on the orbital electron configuration of a noble-gas.

Radiogenic Isotopes

There are some elements, with perhaps the geologically important being Th and U (Z = 90 and 92), which have isotopes that are unstable.

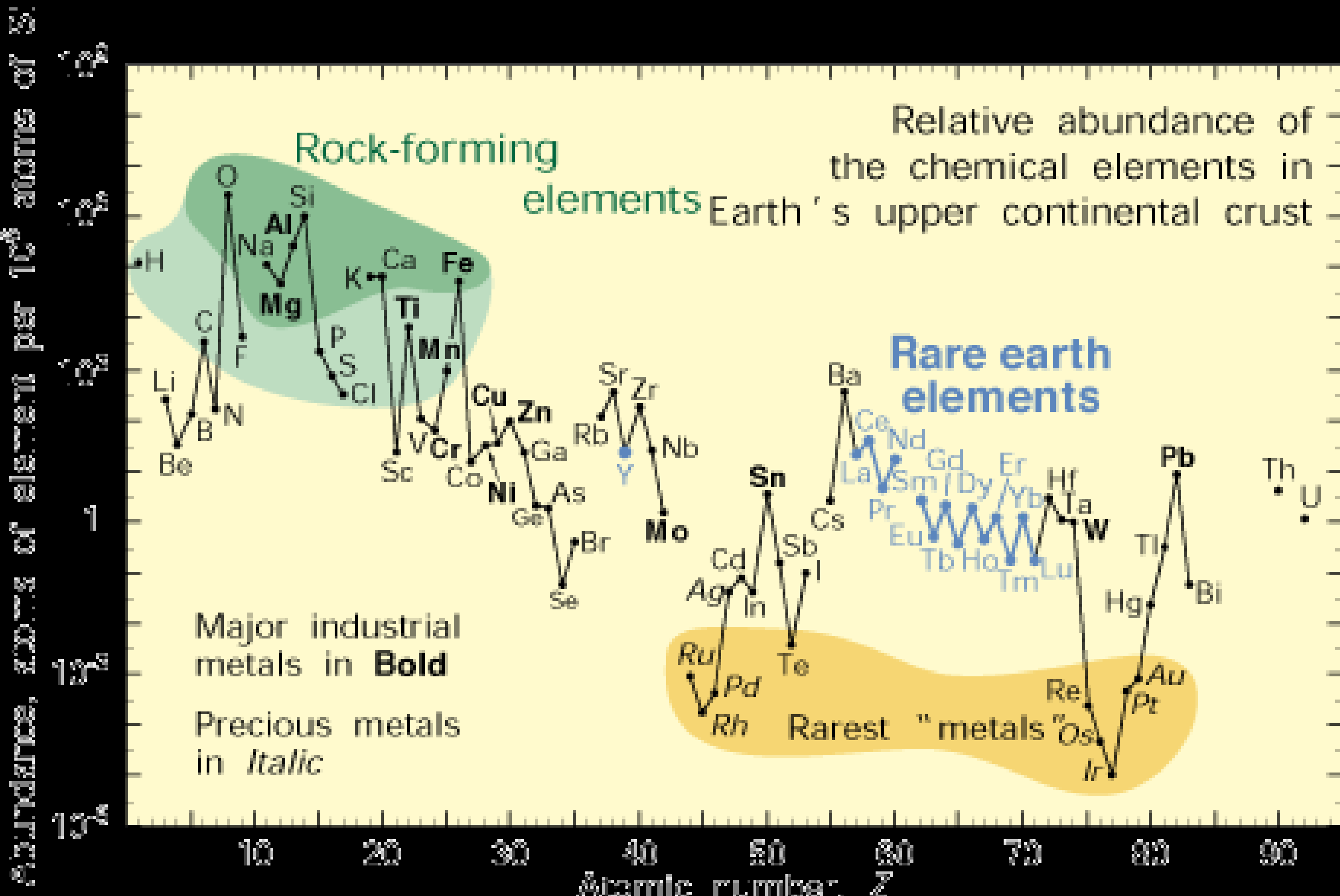
^{232}Th, has 142 neutrons and 90 protons. ^{238}U has 146 neutrons and 92 protons.

The electronic configuration of unstable atoms changes by radioactive decay.

This involves the rejection of either as *alpha* particle (^{4}He), or a *beta* particle (e^{-}).

Each new atomic arrangement created by decay is a new element, and is a daughter product of the original parent element.
The rate of radiogenic decay is called the half-life.

The end product of ^{232}Th and ^{238}U radioactive decay are ^{208}Pb and ^{206}Pb.



Relative abundance of the chemical elements in Earth's upper continental crust
Rock-forming elements
Rare earth elements
Major industrial metals in Bold
Precious metals in Italic
Rarest "metals"
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
1
10
20
30
40
50
60
70
80
90
Atomic number, Z

Multiple atoms are needed to make up a mineral

How do atoms interact (bond) and what are the resultant arrangements?

Bonds are the forces that bind atoms, ions, or ionic group to one another together to form crystalline solids.

Bonds are essentially electrical in nature and their nature and intensity are largely responsible for the physical and chemical properties of minerals.

with increasing bond strength,

→

increase the hardness, the melting point and produce a smaller coefficient of thermal expansion

The 5 principle bond types are:

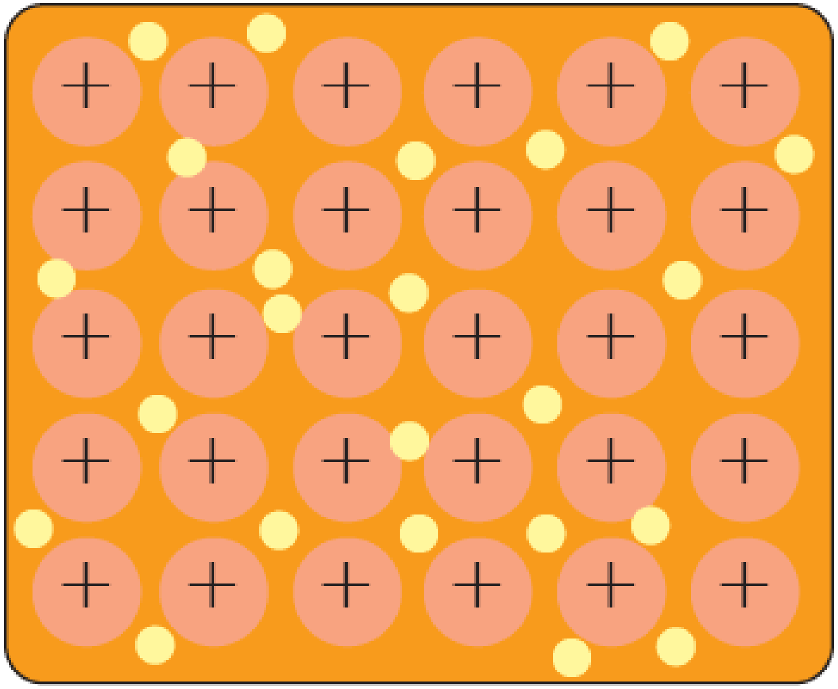
van der WAALS **HYDROGEN** **METALLIC** **IONIC** **COVALENT**

The metallic bond

All true metals are good conductors of heat and electricity, while X-ray diffraction analysis reveals that they have regular repetitive pattern of true crystalline solid.

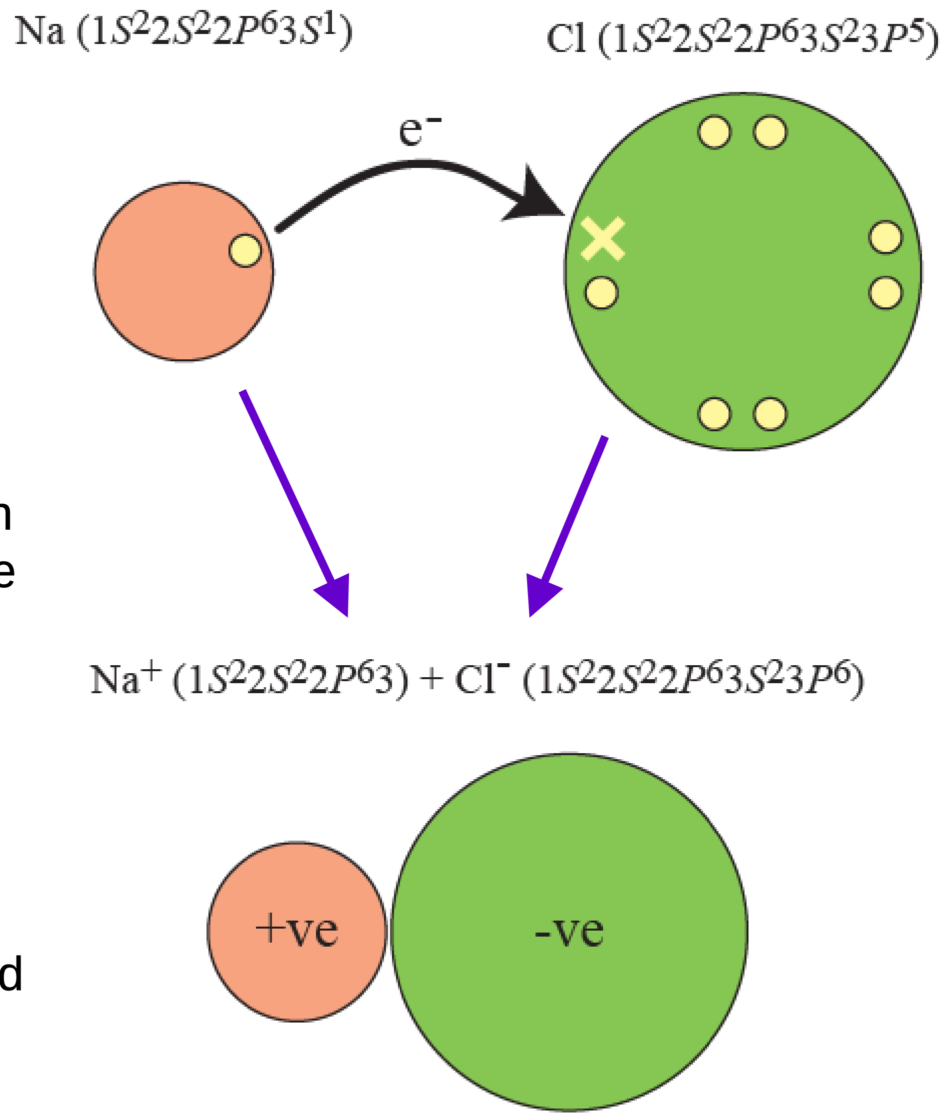
Electrons are very poorly associated with a specific nuclei and are free to move through the structure.

The metal is held together by the combined attractive force between nuclei with their filled electron orbitals and the dense cloud of "free" valence electrons.



The ionic bond

When electron(s) in the valence shell of a metallic atom are transferred to the valence shell of a non-metallic atom, with both achieving inert gas configuration, an ionic bond is formed.



In this example the single outer electron of Na is readily lost, and captured by the Cl atom, resulting in two ions

The new ions are attracted to one another because they are of opposite charge.

The electrostatic charge of the ionic bond is evenly spread.
Ionic bonds are ***non-directional***.

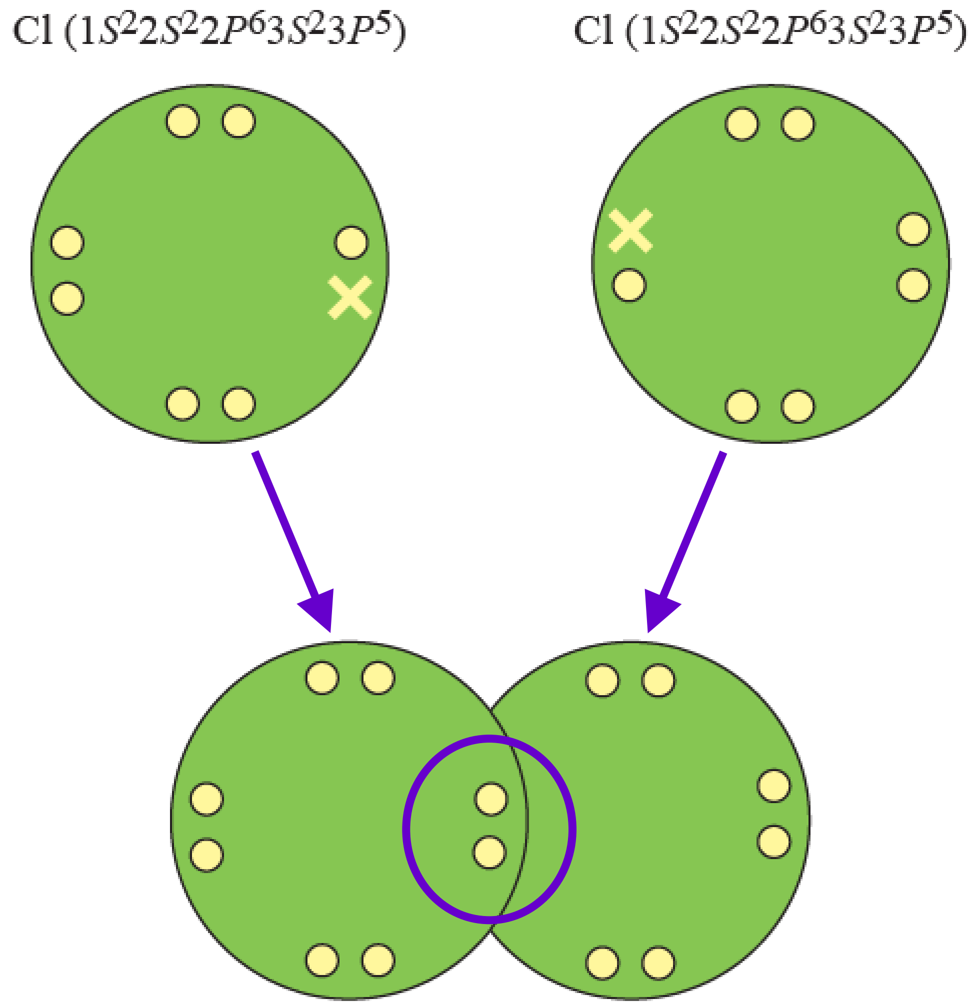
The covalent bond

Non-metallic elements have a strong affinity for electrons, and elements such as Cl have high reactivity.

Cl will seize and combine with anything that can provide the electron required to fill the valence shell.

In a mixture of Cl gas it is a second Cl atom that provides the electron, but not by giving up the electron, but by sharing it.

Covalent bonds are very strong and are characteristic of minerals that are insoluble and generally quite stable.



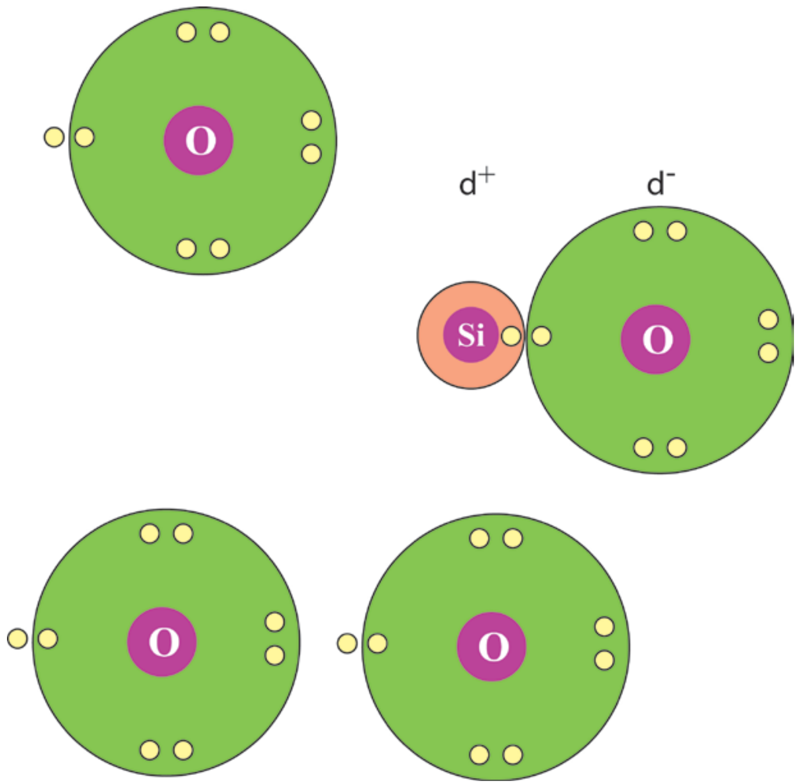
The stable form of chlorine gas is Cl_2.

Ionic + covalent bonding

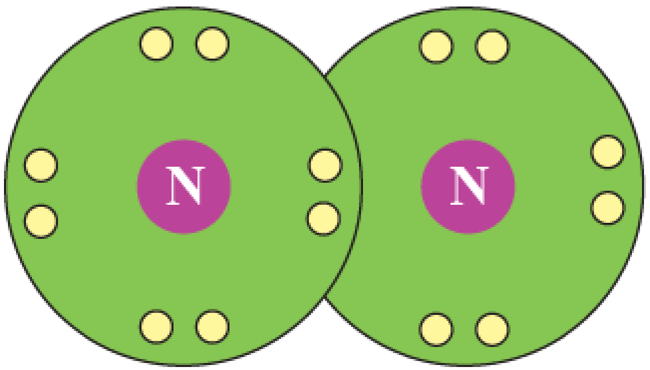
Commonly, multiple bond types coexist to create mineral structures. A good example of this is Si^{4+} and O^{-} to create the silica tetrahedra, one of the fundamental building blocks of many minerals.

In such cases, the association of electrons with one nuclei or another changes depending on the P/T conditions of the situation.

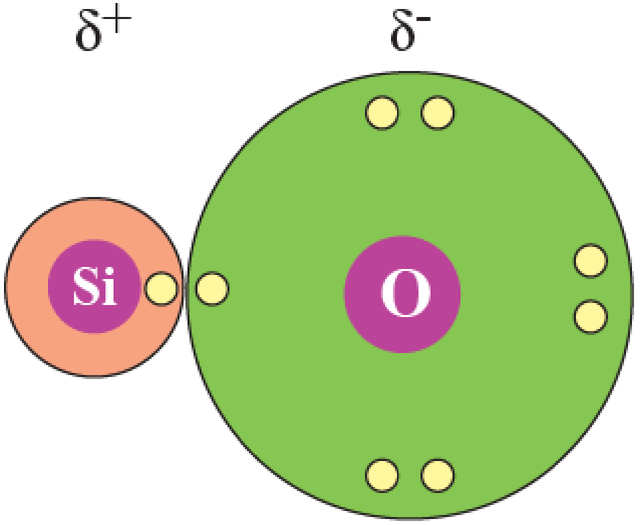
Given a particular set of conditions, it will be more likely to find a majority of either covalent or ionic bonds.



Bond Polarisation



The partial-positive charge of each N nuclei in a N_2 molecule has an equal attraction to the electrons. There is bond is effectively neutral with no polarisation.



In an Si-O bond, the greater concentration of electrons towards oxygen, which has a higher electronegativity, leads towards a partial polarisation of the bond.

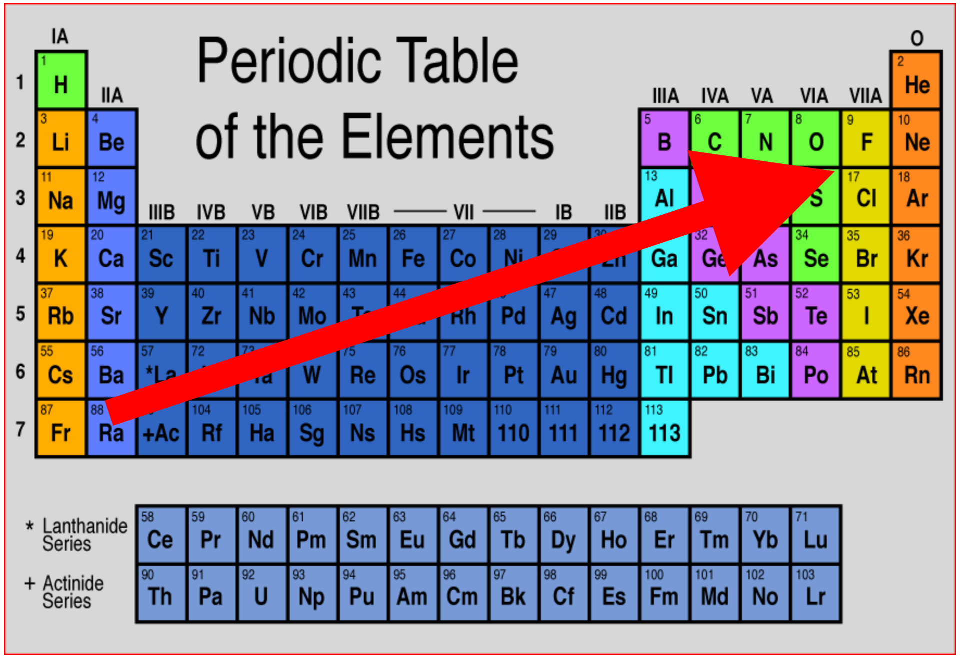
Electronegativity

The ability of an atom to attract electrons toward it in a bond. This pair is shared with another atom in a chemical bond.

The difference in electronegativity between two atoms is an expression of the bond type.

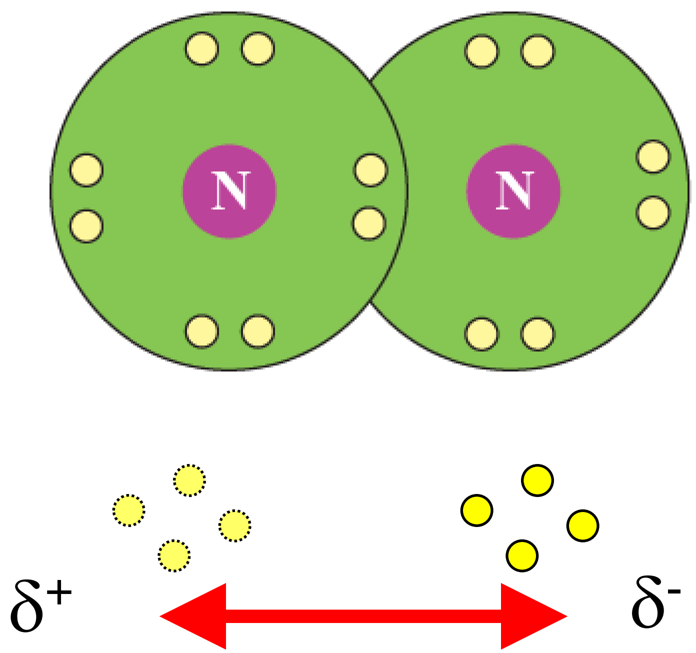
Electronegativity increases towards top-right-hand-side of Periodic Table and is measured on the Pauling scale (relationship of ionization energy and electron affinity).

The greater the difference, the more ionic in nature the bond.



The van der Waals bond

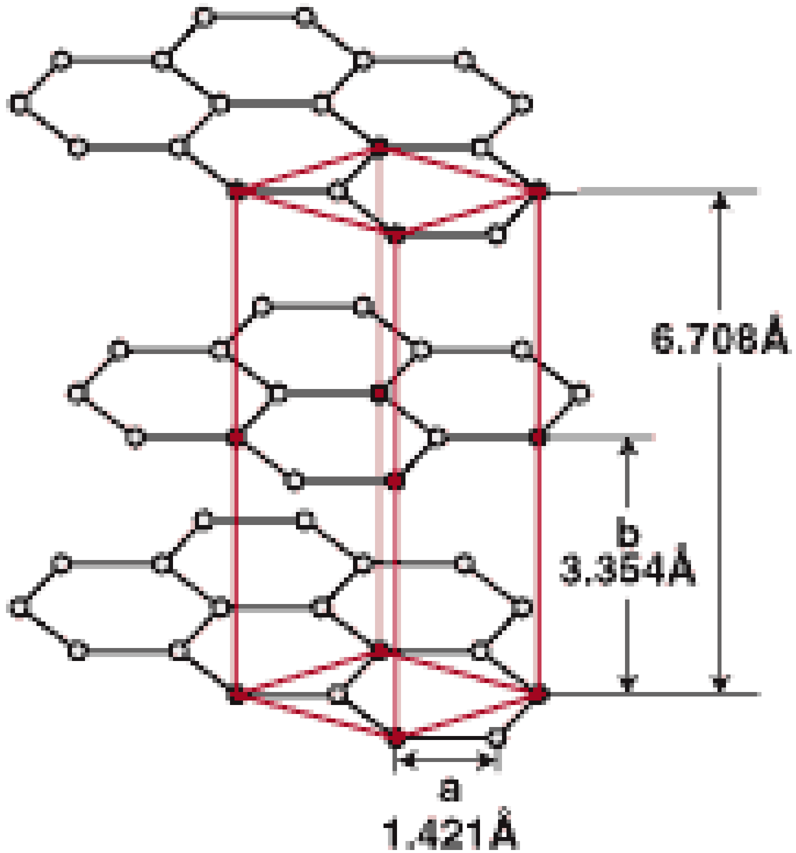
These bonds occur in circumstances where adjacent atoms are unlikely to lose or gain electrons. Attractions in this case are a combination of repulsion of electrons in adjacent orbitals and the attraction of electrons having the same motion.



The electron cloud will still vibrate around the molecule creating transient, short term, polarisation.

Gases (N_2, O_2, Cl_2) will form molecular solids with cooling. Eventually the molecules simply collapse upon themselves, forming a close-packed structure, as the vibrational energy of the bonds is significantly reduced.

Graphite



Carbon (C) occurs in several elemental states with each displaying different bonding properties.

The bonds in graphite take one of two types:

Covalently bonded 2D sheets consisting of 6-member carbon rings. The sheets themselves are held together by the small residual charges of the surface created by spare valence electrons. This is an example of *van der Waals bonding*.

The hydrogen bond

Hydrogen bonds occur in crystalline structures of polar molecules.

Hydrogen moelcules are electrostatic bonds between the partial positively charged end of one molecule and the negatively charged end of another.

Ice is an especially good example of hydrogen bonding in action.