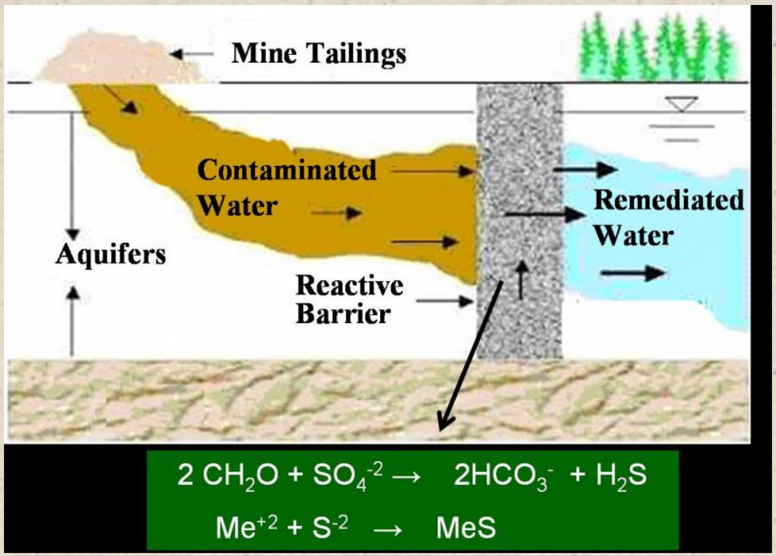
GEOL3150 Environmental Geochemistry

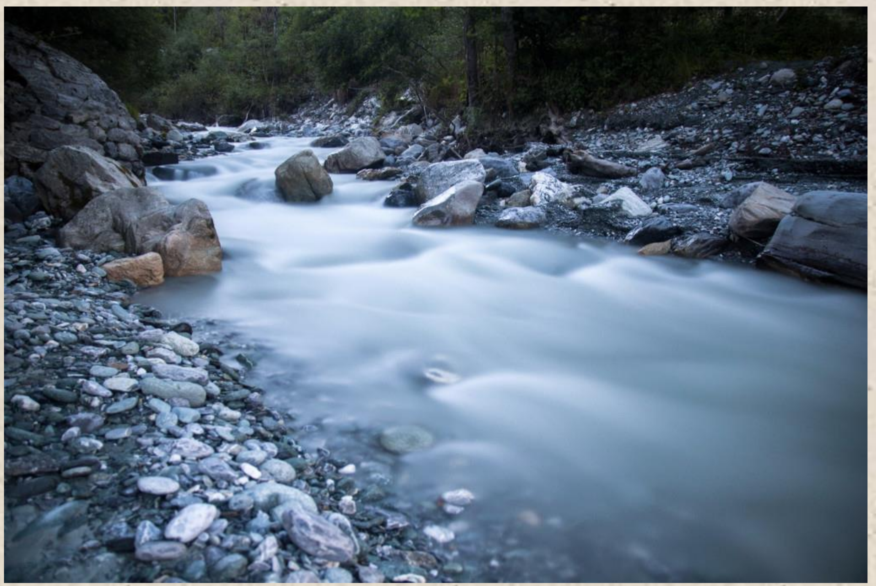
The problem: Acid mine drainage

The solution: a reactive barrier

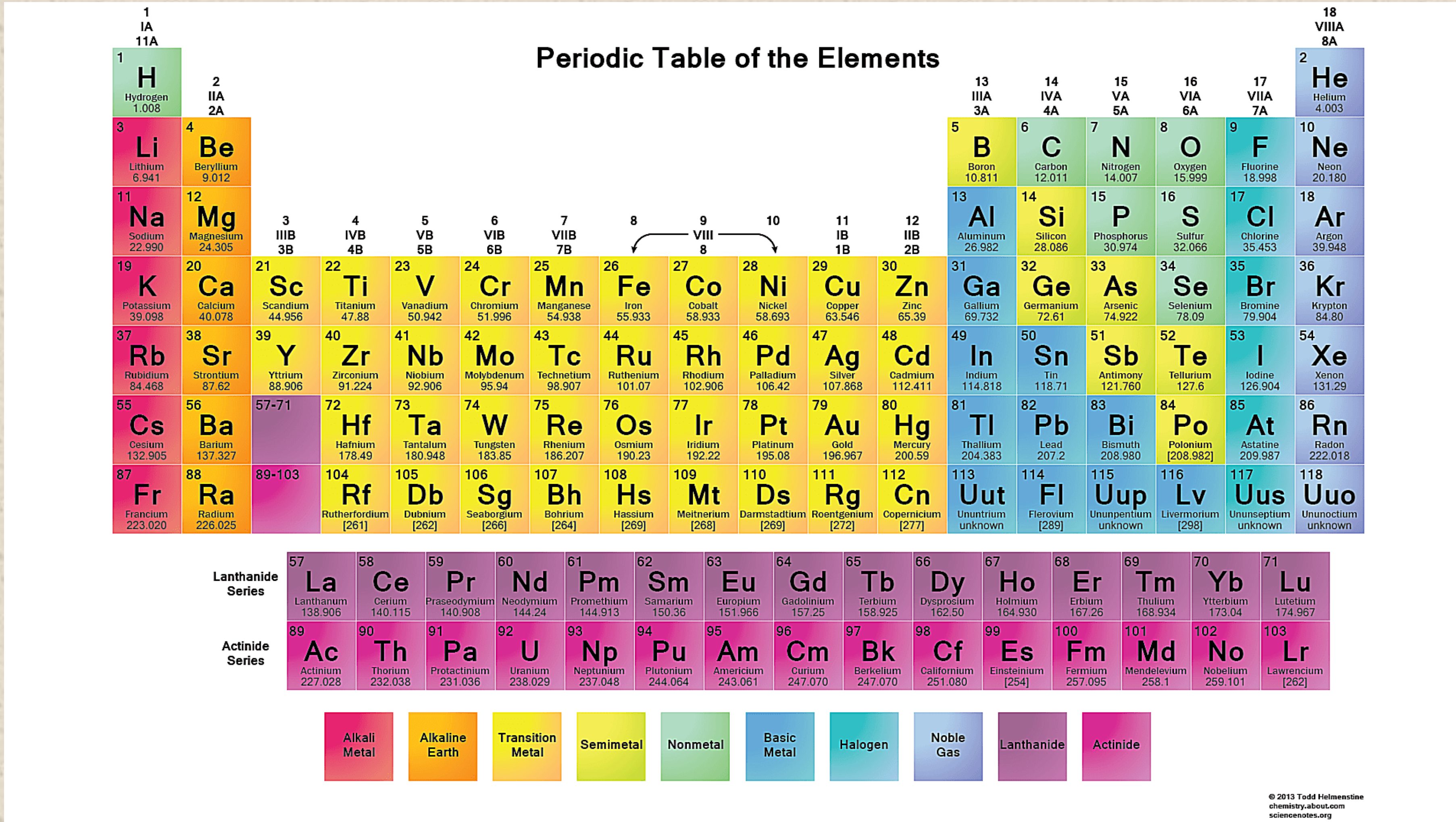
The outcome: clean water

This is Environmental Geochemistry



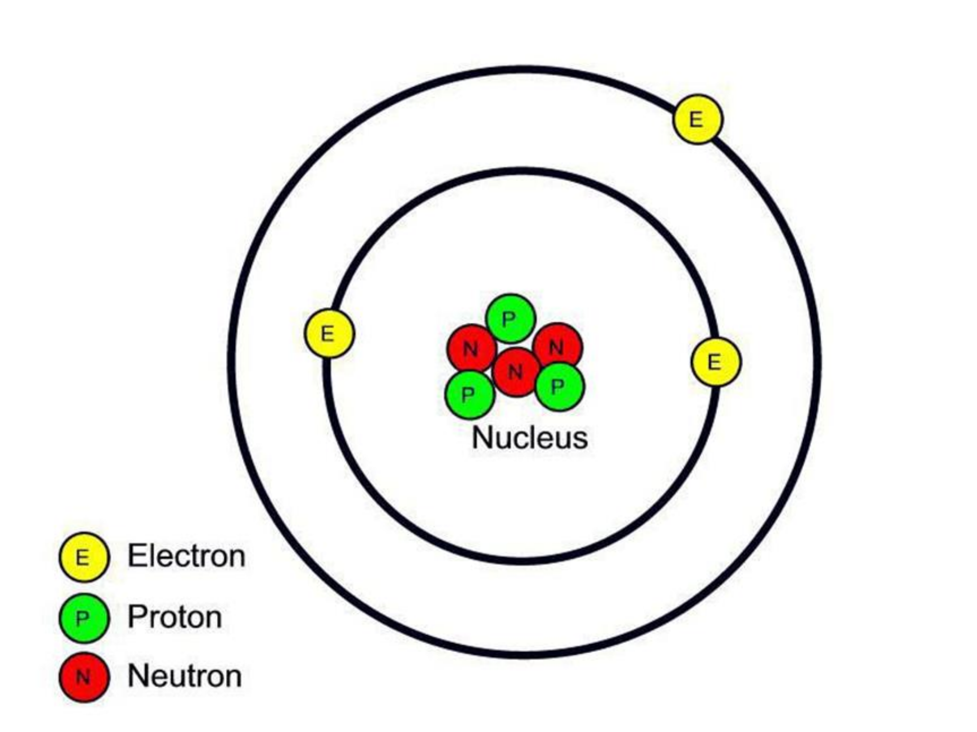


Where It All Begins



The Bohr atom – A simple, but insightful, model

Atoms consist of a nucleus (composed of protons and neutrons) and electrons which revolve around the nucleus at fixed distances.



For a stable atom

Potential Energy = Kinetic Energy

or

Electrostatic Force = Centrifugal Force

Electrons exist in stable orbits at certain discrete distances from the nucleus.

The allowable distances were determined by restricting the angular momentum of the electrons to multiples of:

$h/2\pi$ h=6.62607x10-34Js (Plank's Constant)

The energy (E) of an atom is the sum of the kinetic and potential energies.

The kinetic component = the revolution of the electrons around the nucleus.
The potential component = the electrostatic attraction between positively charged protons and negatively charged electrons.

$$E = \frac{-2\pi^2 m k^2 e^4}{n^2 h^2}$$

E = total energy of an atom (PE + KE)

k = proportionality constant

e = charge of the electron

If an electron moves from one energy level to another it emits or absorbs energy according to the relationship

E = h/v (Planck's constant/frequency)

This emitted energy can appear to behave as a particle (a photon) as first described by Einstein (the photoelectric effect).

Finally we can write $E = hc/\lambda$ where $c = 3.0 \times 10^8$ m/s (speed of light in a vacuum and λ = the wavelength

Example 1 -1: Calculate the energy released when an electron moves from the third allowed orbit to the second allowed orbit.

The mass of the electron **(m) = 9.109 x 10^{-31}kg**, the charge of the electron **(e) = 1.602 x 10^{-19}C**, and **k = 8.98742 x 10^{9}Nm^{2}C^{-2}, h=6.62607x10^{-34}Js** . For **n = 2**,

$$E = \frac{-2\pi^2 m k^2 e^4}{n^2 h^2}$$

$\Delta E = E_3 - E_2$ and ($-2\pi^2 m k^2 e^4 = 9.566 \times 10^{-85}$)

$E_2 = -5.441 \times 10^{-19}$ J and $E_3 = -2.418 \times 10^{-19}$ J

$\Delta E = 3.023 \times 10^{-19}$ J

Quantum Numbers

- **Principal quantum number (*n*)** - describes the **SIZE** of the orbital or **ENERGY LEVEL** of the atom.
- **Angular quantum number (*l*) or sublevels** - describes the **SHAPE** of the orbital.
- **Magnetic quantum number (*m*)** - describes an **orbital**'s **ORIENTATION** in space.
- **Spin quantum number (*s*)** - describes the **SPIN** or direction (clockwise or counter-clockwise) in which an electron spins.

Quantum numbers, primary energy levels, and energy sublevels.

Table 1-1 Summary of Quantum Numbers

Name	Symbol	Values
Principal	n	1, 2, 3, . . . , ∞
Azimuthal	l	n – 1, n – 2, n – 3, . . . , 0
Magnetic	m	0, ±1, ±2, . . . , ±(l – 1), ±1
Spin	s	

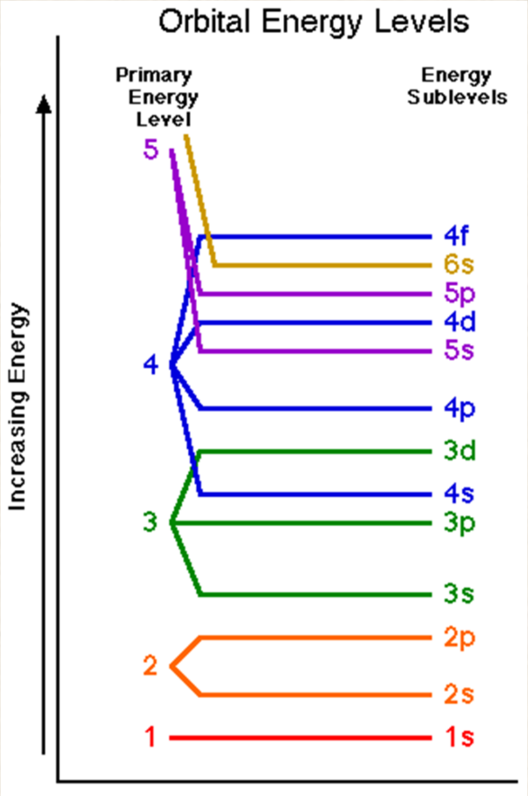
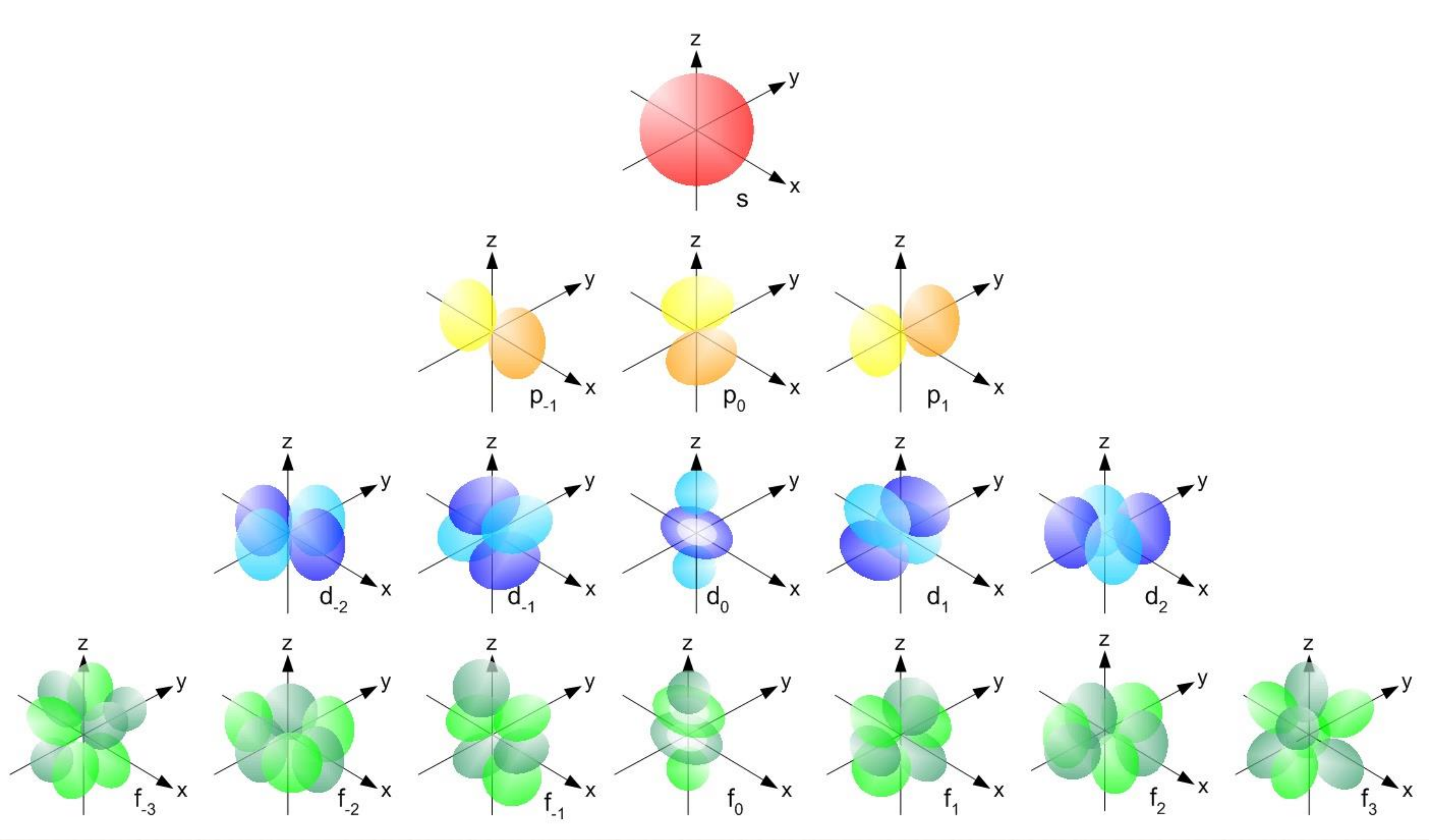


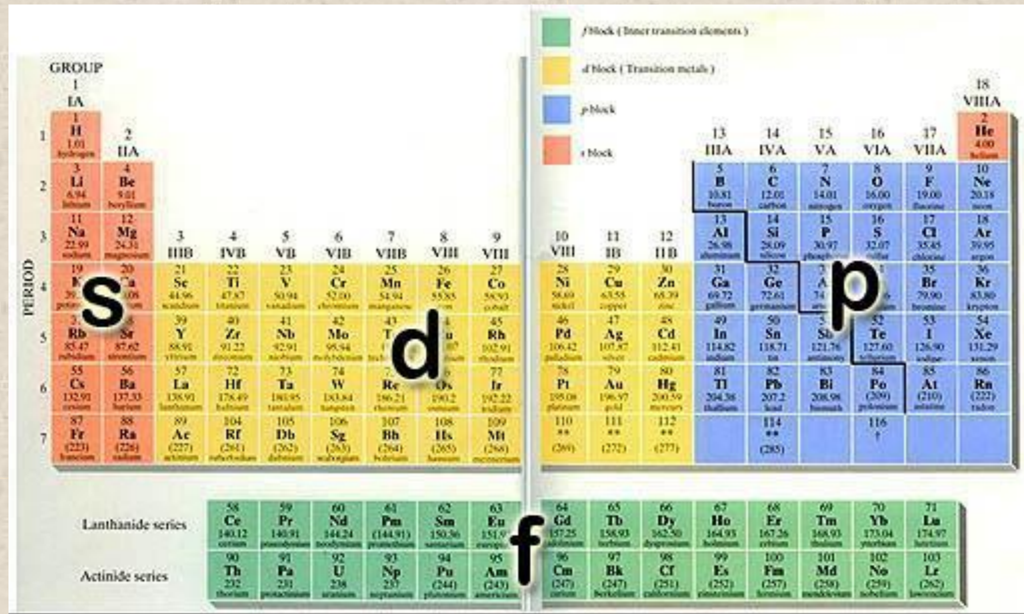
Table 1-2 Relationship between Quantum Numbers and Electron Orbitals

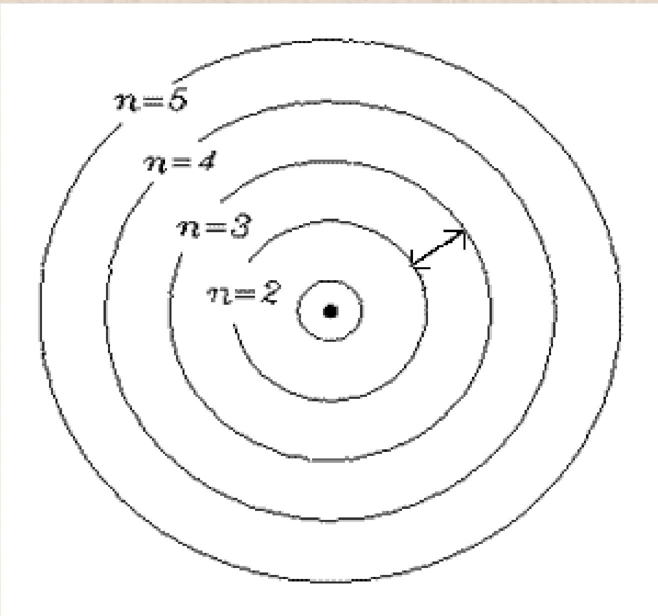
n	L	M	Number of subshells	Number of orbitals	Designation
1	0	0	1	1	1s
2	0	0	2	1	2s
	1	−1, 0, 1		3	2p
3	0	0	3	1	3s
	1	−1, 0, 1		3	3p
	2	−2, −1, 0, 1, 2		5	3d
4	0	0	4	1	4s
	1	−1, 0, −1		3	4p
	2	−2, −1, 0, 1, 2		5	4d
	3	−3, −2, −1, 0, 1, 2, 3		7	4f

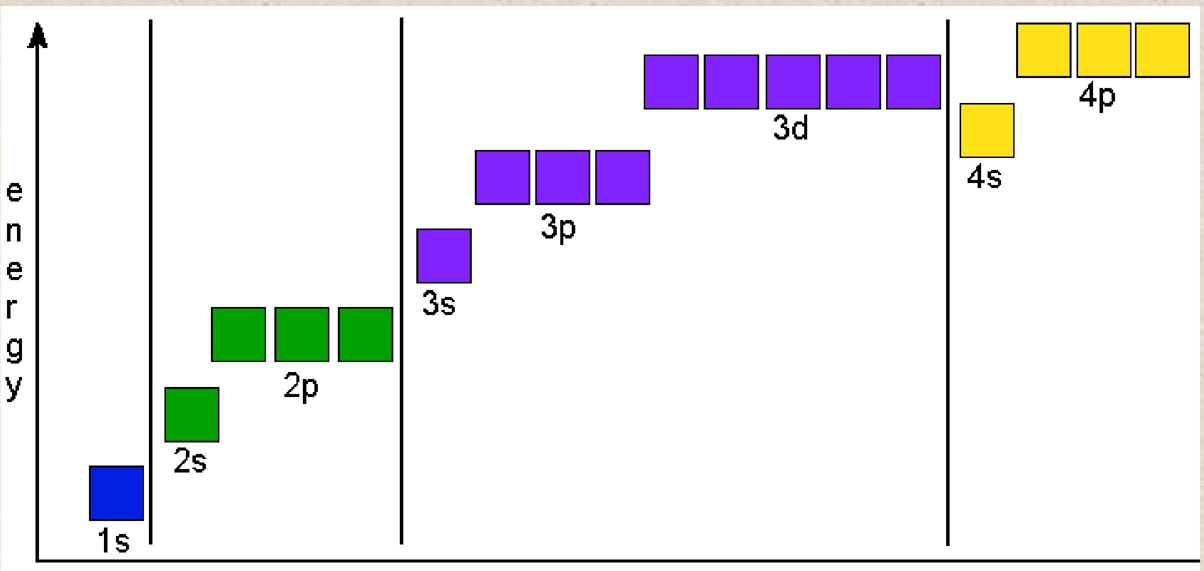
Shape of Orbitals



Relationship between orbitals and the periodic table



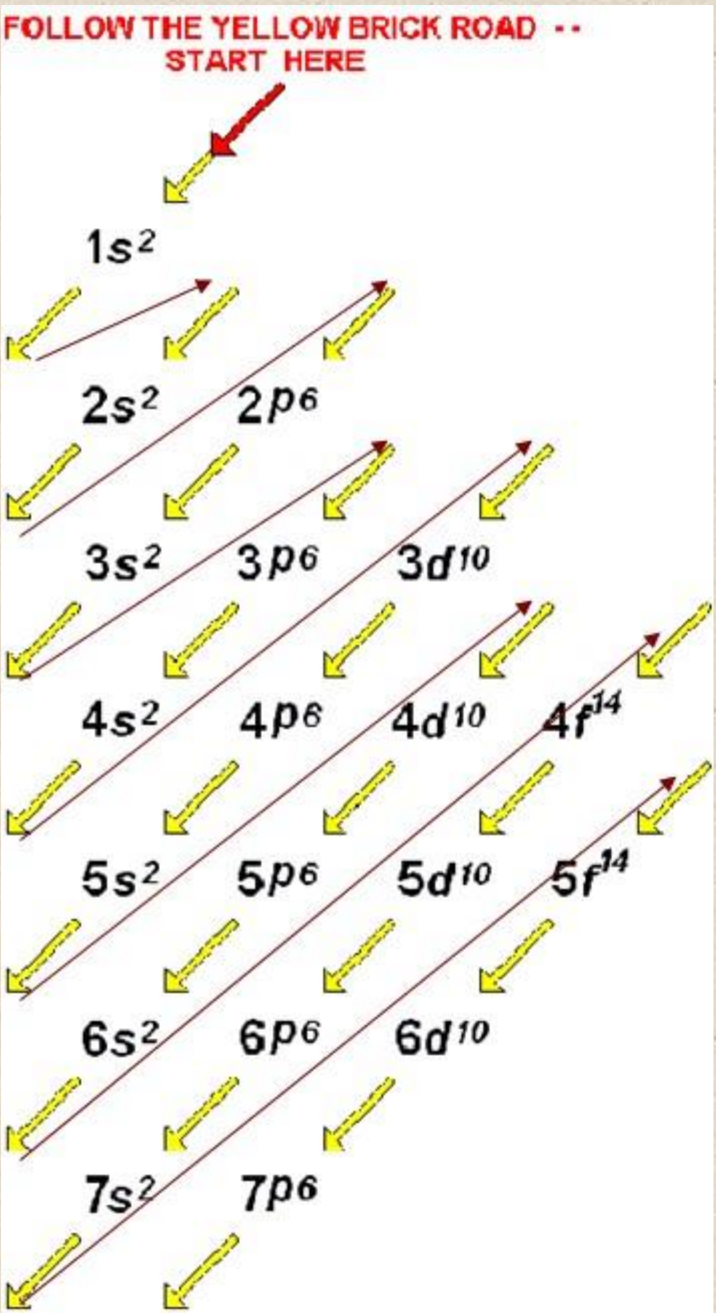




1. An electron will enter the available orbital with the lowest energy. The overall energy of the atom is minimized.

2. For each set of orbitals (s, p, d, f) the electrons will first be added singly to each available orbital. After all the orbitals in a set have a single electron, subsequent electrons can enter these orbitals if they have the opposite spin.

3. Atoms attain their maximum stability when the available orbitals are either completely filled, half-filled or empty.



Let's do a couple of examples…

A neutral Na atom has 11 electrons. What is its configuration?

$1s^2\ 2s^2\ 2p^6\ 3s^1$

A neutral Cl atom has 17 electrons. What is its configuration?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

*Remember: stable atoms may have full, half full or empty orbitals

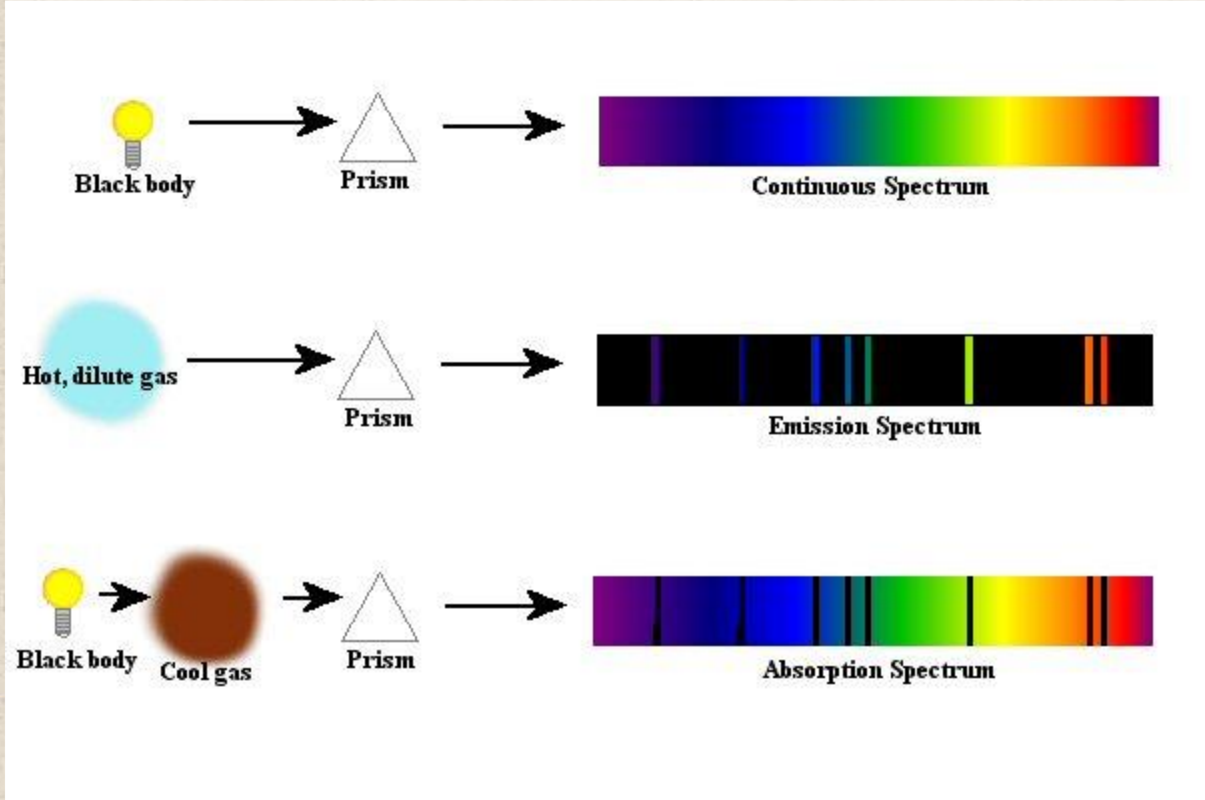
Spectra and Elemental Analysis

For neutral atoms, transitions between orbitals release different amounts of energy, and the resulting emission spectra are different and characteristic for each element.

If the atoms have been ionized, the sequence of emission lines will be slightly shifted because the electrostatic attraction between the nucleus and electrons will have changed.

These transition are the basis for a number of analytical methods used to analyze the elemental composition of solids and liquids.

Types of Spectra: Continuous, Emission, and Absorption



A *continuous spectrum* is produced by a perfect radiator – all wavelengths are emitted.

Stefan-Boltzmann Law

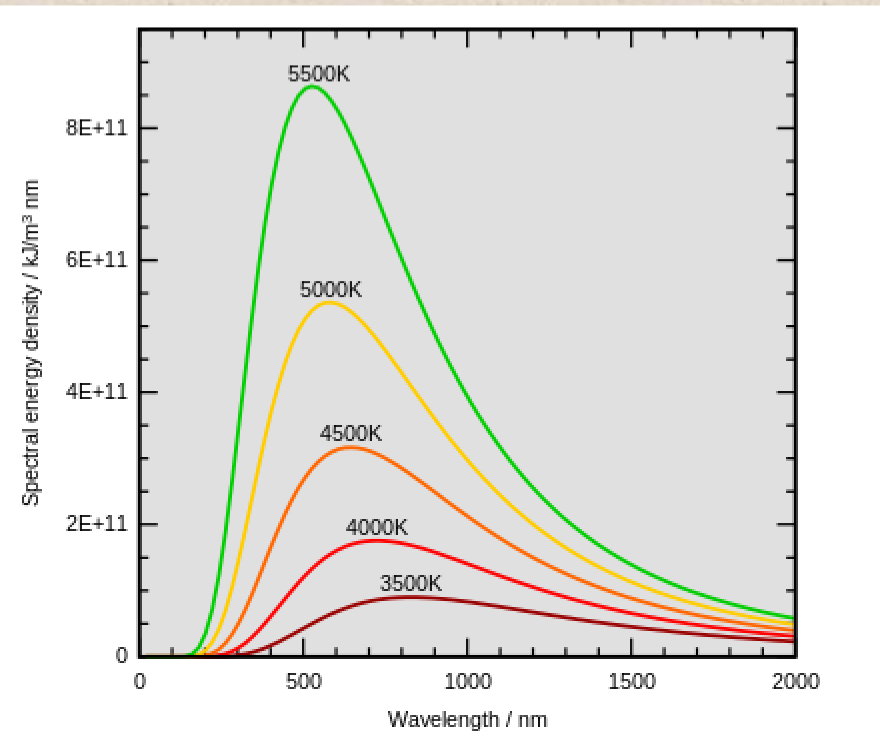
$E = \sigma T^4$

E = energy flux/unit area
σ = Stefan-boltzmann constant
T = absolute temperature

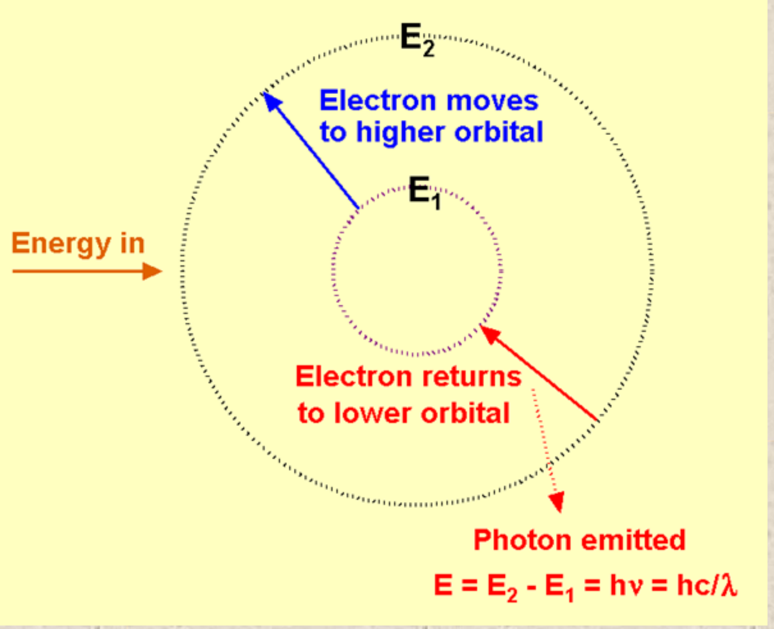
Wien's Displacement Law

$\lambda_{max} = a/T$

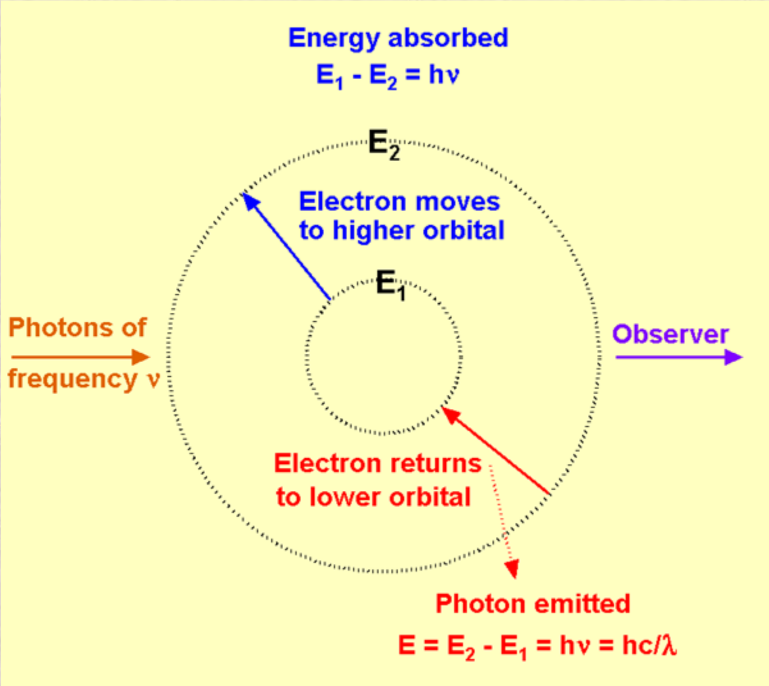
λ_{max} = wavelength of maximum energy
a = Wein Displacement Law constant
T = absolute temperature

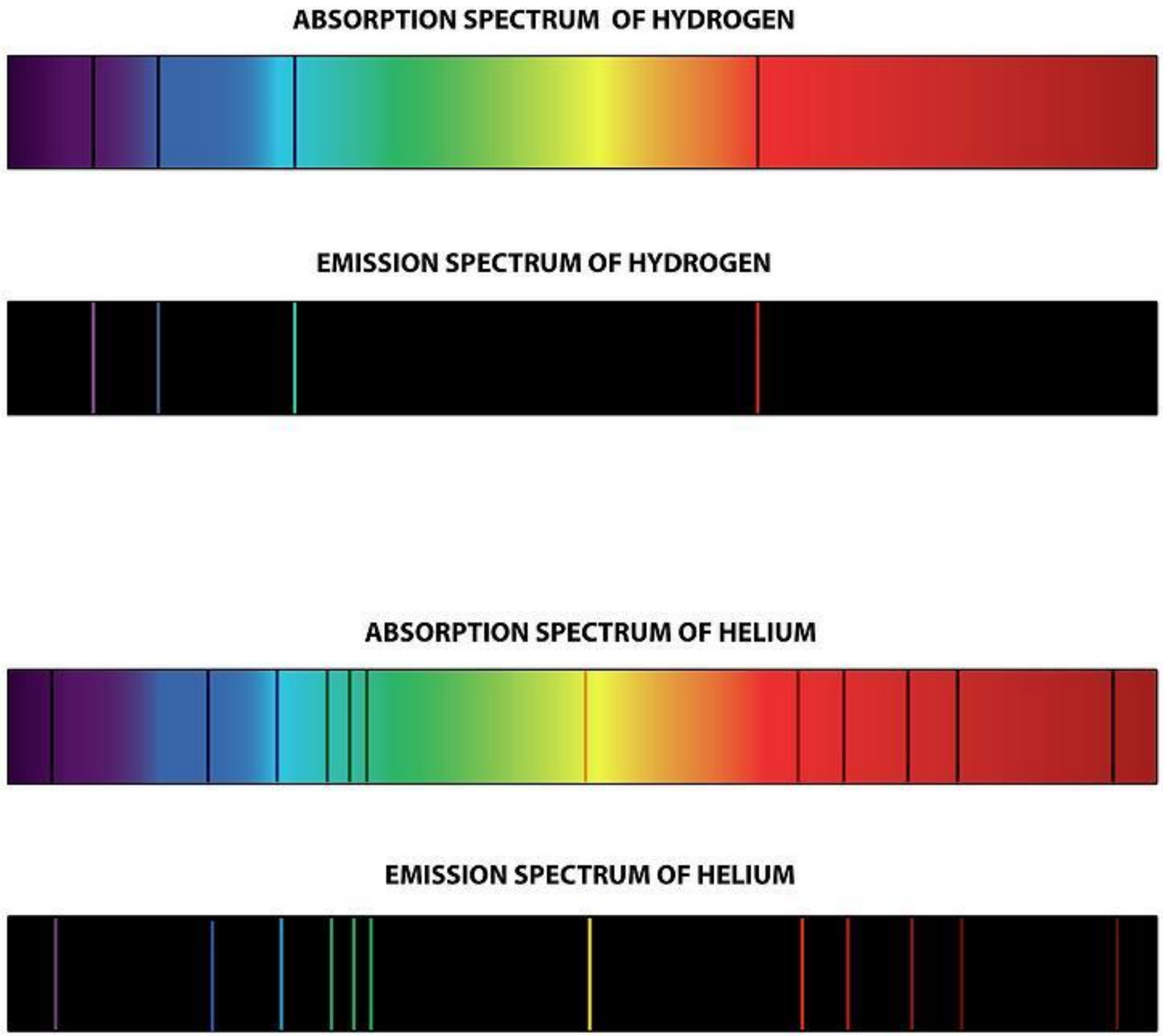


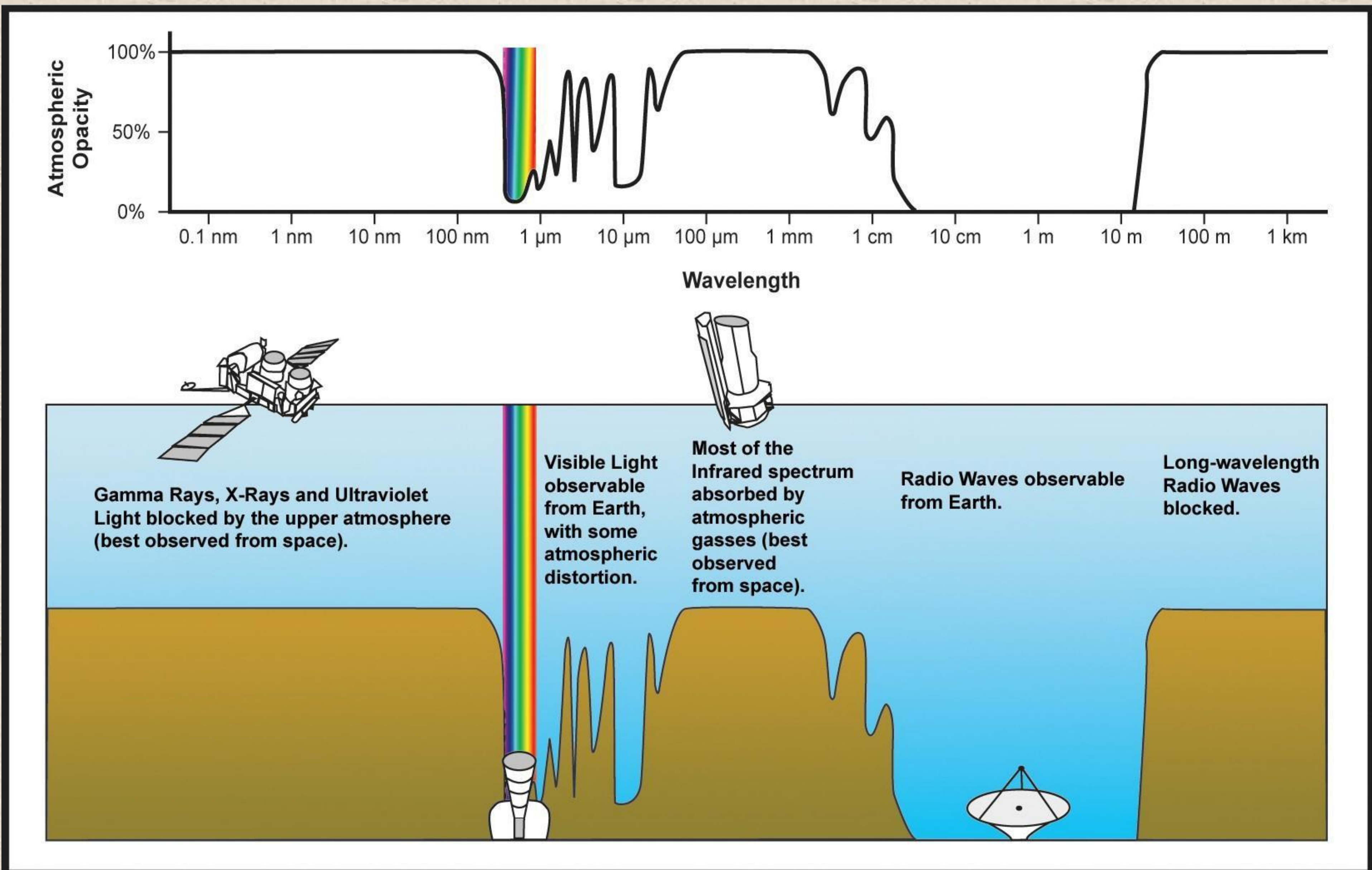
Emission spectrum: the spectrum produced when electrons move from higher orbitals to lower orbitals. This gives rise to light-lines of specific wavelength appearing, and the other wavelengths not characteristic of the specific atoms, remaining dark.



Absorption spectrum: the spectrum produced when white light travels through a cold, dilute gas, and atoms in the gas absorb at characteristic frequencies. This gives rise to dark lines (absence of light) in the otherwise continuous spectrum.




ABSORPTION SPECTRUM OF HYDROGEN
EMISSION SPECTRUM OF HYDROGEN
ABSORPTION SPECTRUM OF HELIUM
EMISSION SPECTRUM OF HELIUM



100%
50%
0%
Atmospheric Opacity
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
10 cm
1 m
10 m
100 m
1 km
Wavelength
Gamma Rays, X-Rays and Ultraviolet Light blocked by the upper atmosphere (best observed from space).
Visible Light observable from Earth, with some atmospheric distortion.
Most of the Infrared spectrum absorbed by atmospheric gasses (best observed from space).
Radio Waves observable from Earth.
Long-wavelength Radio Waves blocked.

Ionization and Valences

Valence: the combining capacity of atoms.

Valence electrons: those electrons occupying the outer-most shell.

Valence charge: the net charge of an atom or oxidation number.

Ions: atoms that have gained or lost electrons.

Anions: an atom that has gained an electron(s) giving the atom a net negative charge.

Cations: an atom that has lost an electron(s) giving the atom a net positive charge.

Ionization potential: the energy required to remove an electron from an atom and place it at an infinite distance.

In any given row of the periodic table, as we move from left to right, the ionization potential tends to increase…

It becomes more difficult to remove electrons from the atom.

Hence, elements on the left-hand side of the periodic table tend to form cations and those on the right-hand side (excluding the noble gases for the moment) tend to form anions.

Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

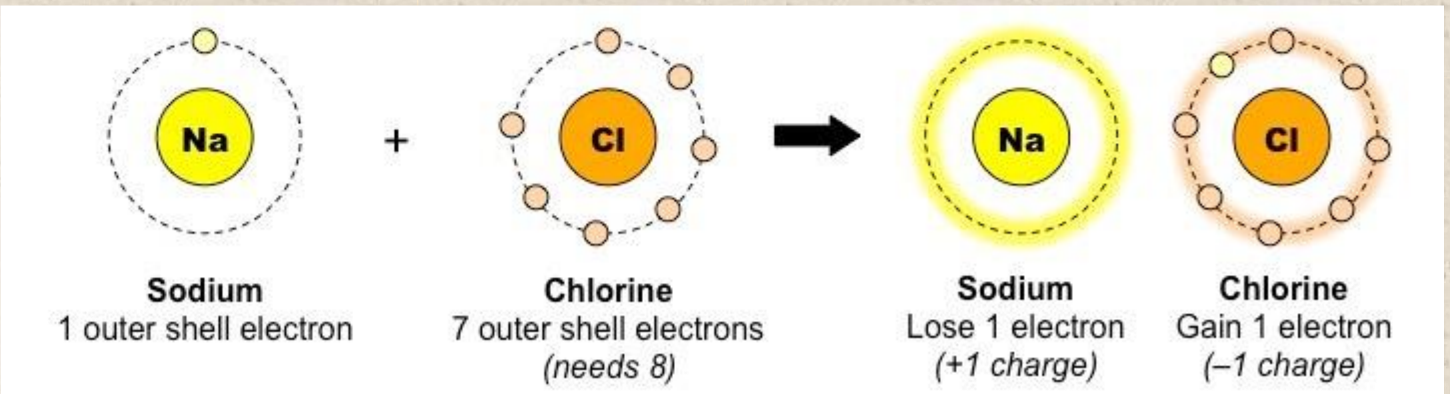
Chemical Bonding

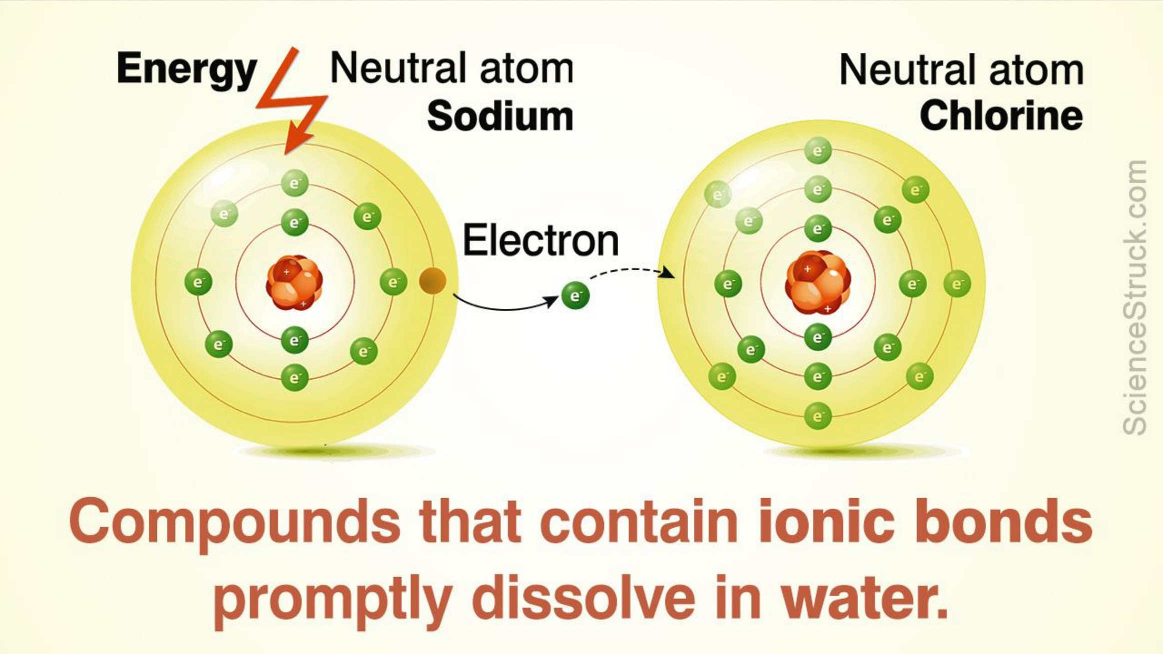
Two or more atoms may combine to form a compound.
The compound is held together by chemical bonds.

There are four basic types of chemical bonding:

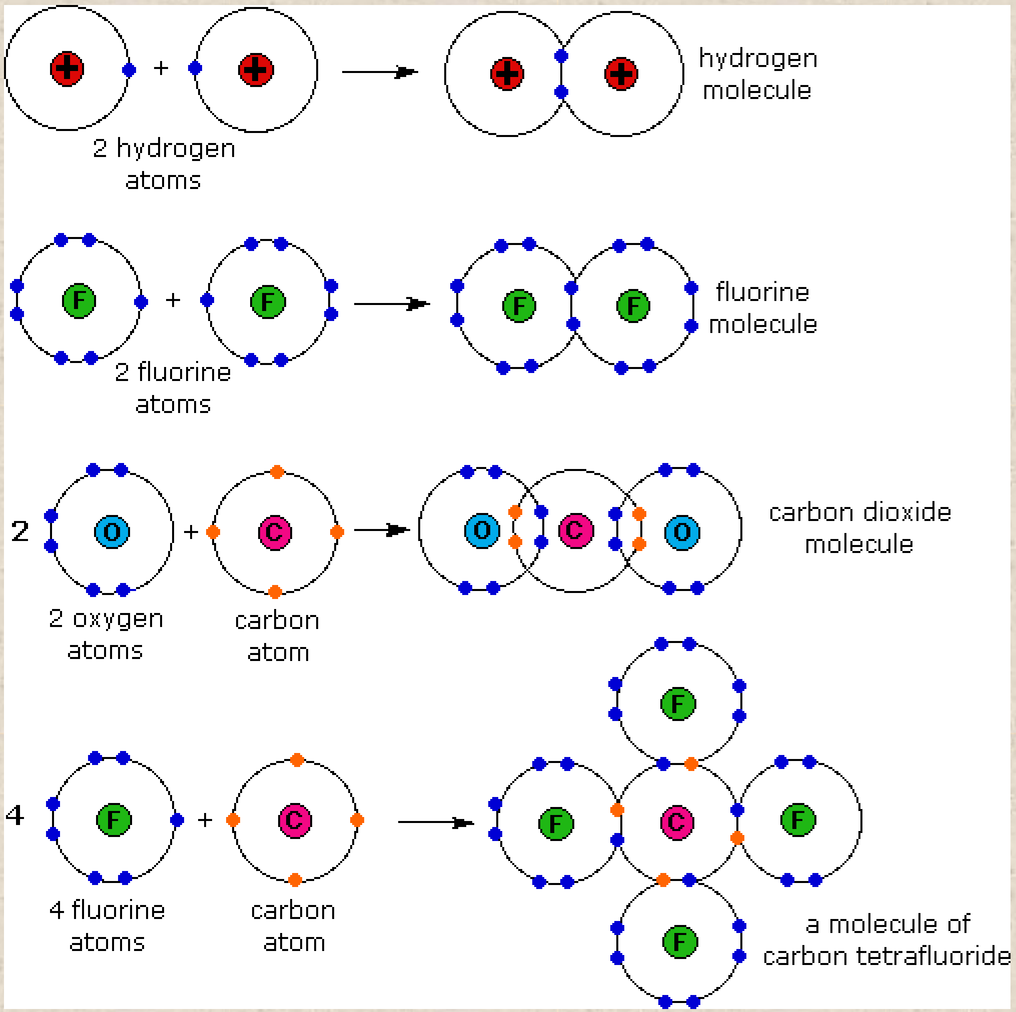
- Ionic Bonding,
- Covalent Bonding,
- Metallic Bonding
- Hydrogen Bonding

Ionic Bonding: occurs when cations and anions combine by electrostatic attraction.





Covalent Bonding: occurs when two or more atoms combine by sharing valence electrons.

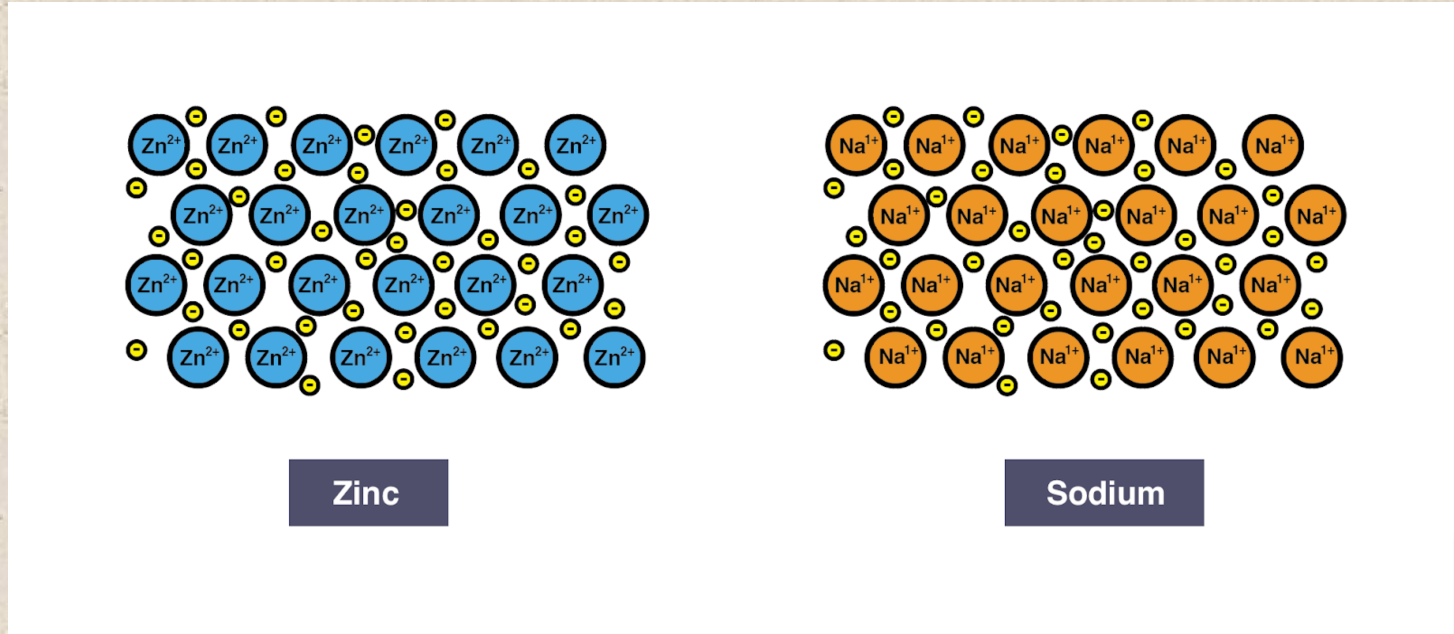


Covalently bonded compounds, with some exceptions, do not readily dissolve in water. This has significant environmental implications. For example, in the case of a petroleum spill the organic liquids persist as a separate phase in groundwater.

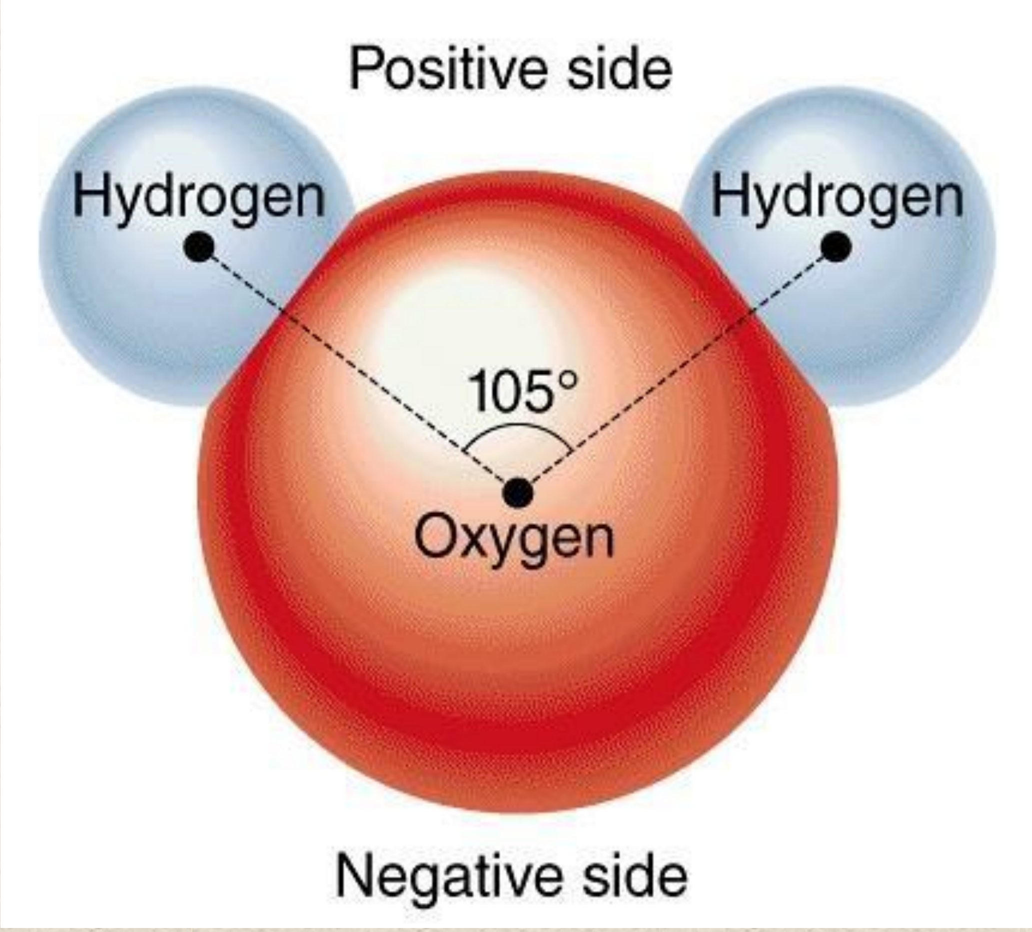
Metallic Bonding: occurs in the case of pure metals in which electrons are freely shared among all of the atoms. These compounds are good conductors of electricity.

Metals generally form cations (ions with a positive charge) and are capable of forming more than one oxidation number.

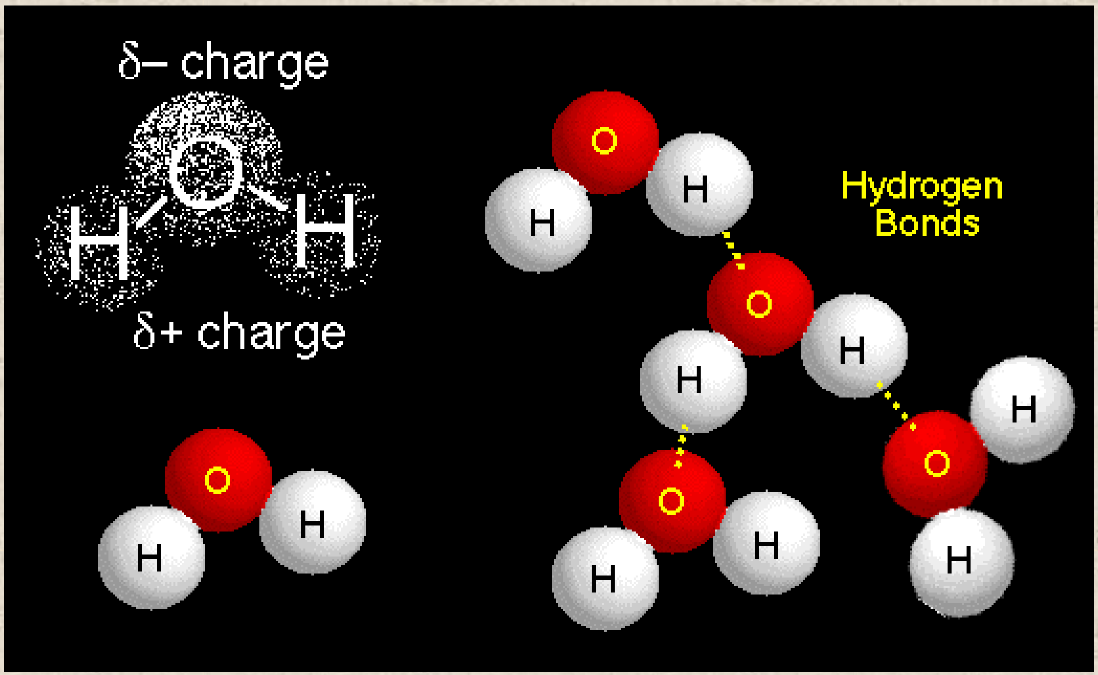
For example: Iron (Fe) may have a 2^+ charge (ferrous) or a 3^+ charge (ferric).

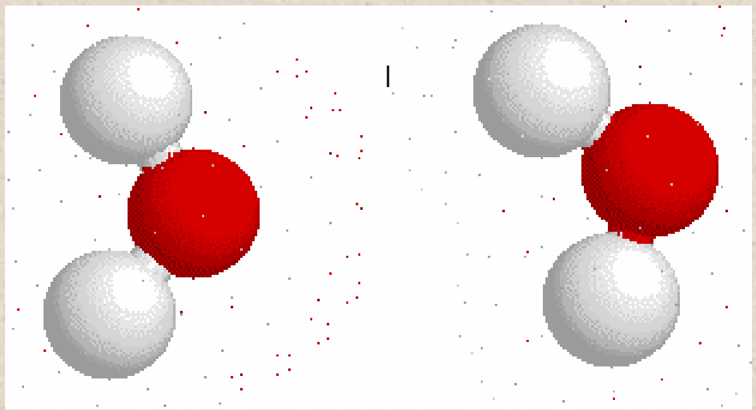


Water is a covalently-bonded molecule. Although the electrons are shared, they are not shared evenly. They tend to spend more time around the oxygen molecule. This results in a polarized molecule that is slightly positive on the H side and slightly negative on the oxygen side.



Hydrogen Bonding: a specific type of intermolecular bonding where at least one of the atoms is H, and the other atom(s) is something other than H. The hydrogen side of the molecule invariably has a slight positive charge bias and the other atom(s) side has a slight negative charge bias.





How does one determine the atomic weight of an element? See the following example.

Carbon as two stable isotopes and may have either 6 or 7 neutrons. To calculate the atomic weight of carbon you need to know the mass and the occurrence of the isotopes.

Element	Isotope	Mass of Isotope	Proportion in element	Mass X Proportion	Sum ^{12}C + ^{13}C
Carbon	^{12}C	12.000amu	0.989	11.868	12.011amu
	^{13}C	13.003amu	0.011	0.143	

Mole: the number of carbon atoms in exactly 12 grams of pure ^{12}C.

Avogadro's number: the number of atoms in a mole (6.022×10^{23}).

Gram-atomic weight: the atomic weight of a mole of an element in grams.

Gram-molecular weight: the weight of a mole of a compound in grams.

Gram-equivalent weight of an ion: the molecular or atomic weight divided by the valence. In the case of an acid or base, it is the number of H^+ or OH^- ions that can be produced when the acid or base is dissolved in water

Measurements of Concentration

Absolute Mass or ***weight per weight*** would be either in SI units or units such as ppt respectively.

Concentrations of Solutions

Solute: the substance that is being dissolved.

Solvent: the material in which the solute is dissolved.

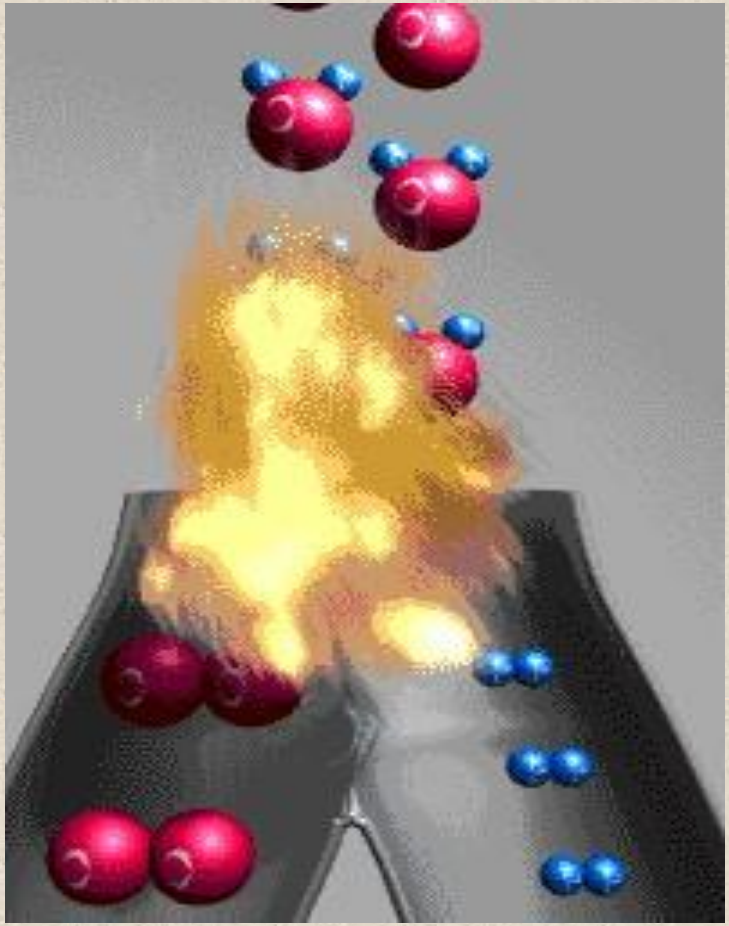
Molarity (M): the number of moles of solute per volume of solution in liters.

Molality (m): the number of moles of solute per kilogram of solvent.

Normality(N): the number of equivalents (often gram-equivalents) per liter of solution.

Mole fraction: the ratio of the number of moles of a given component to the total number of moles of solution.

Chemical Reactions



Species: substances in a chemical reaction that can be either, ions, molecules, solids, liquids, gases, etc.

Reactant: the substances that are the starting materials in a chemical reaction and are found on the left side of the chemical equation.

Product: the substances produced as a result of a chemical reaction and are found on the right side of the chemical equation.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Reactants

Products

There are 3 main types of chemical reactions

- Precipitation
- Acid-Base
- Oxidation-Reduction

Precipitation Reaction: occurs when 2 solutions are mixed and a solid, called a *precipitate*, forms.

$$Ag^{+} + NO_{3_{-}} + Na_{+} + Cl_{-} \rightarrow AgCl_{(s)} + Na_{+} + NO_{3_{-}}$$

The above is a *complete ionic equation*. It includes the spectator ions of NO_3^-, and Na^+. The *net ionic equation* is as follows.

$$Ag^{+} + Cl^{-} \rightarrow AgCl_{(s)}$$

Acid-Base Reactions: involve the transfer of protons.

Acids are proton donors.

Bases are proton acceptors.

An example of a complete ionic equation of an acid-base reaction is as follows.

$$H^+ + Cl^- + K^+ + OH^- \rightarrow H_2O_{(aq)} + K^+ + Cl^-$$

The net ionic equation is written:

$$H^+ + OH^- \rightarrow H_2O_{(aq)}$$

<u>Oxidation-Reduction Reactions</u>: occur when there is a transfer of electrons.

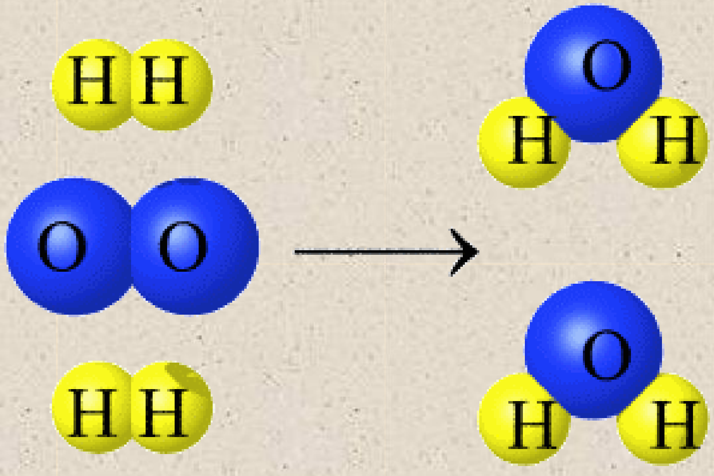
For example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

In this example, the oxidation state of the carbon changes from –4 to +4; 8 electrons are transferred. The oxygen reactant was neutral, but the oxygen in the products carries a –2 charge. There are 4 oxygen molecules. ***(4 X –2 = –8).*** The electrons from the carbon atom were transferred to the four oxygen atoms.

(Note: the oxidation state of the H atoms remain unchanged.)

Balancing a Chemical Equation



$$2H_2 + O_2 \rightarrow 2H_2O$$

When given a chemical equation, you must be certain that the number of atoms of each element on the product side of the equation is equal to that of the reactant side of the equation.

$$2\ Al + 3/2\ O_2 \rightarrow A_2O_3$$

Multiply both sides by 2

$$4\ Al + 3O_2 \rightarrow 2A_2O_3$$

Balancing equations - a summary

1. You may only put numbers in front of molecules, never altering the formula itself. (i.e.H_2O is not the same asH_2O_2)
2. Don't worry if the numbers turn out to be fractions - you can always double or triple all the numbers at a later stage.
3. Balance complicated molecules with lots of different atoms first. Putting numbers in front of these may mess up other molecules, so use the simpler molecules to adjust these major changes.
4. If you recognize the atoms making up a standard group such as sulphate, nitrate, phosphate, ammonium etc. that survive unscathed throughout the chemical reaction, treat them as an indivisible item to be balanced as a whole. This makes life easier and helps understanding of the chemistry.
5. Leave molecules representing elements until last. This means that any numbers you put in front of those molecules won't unbalance any other molecule.

Gases

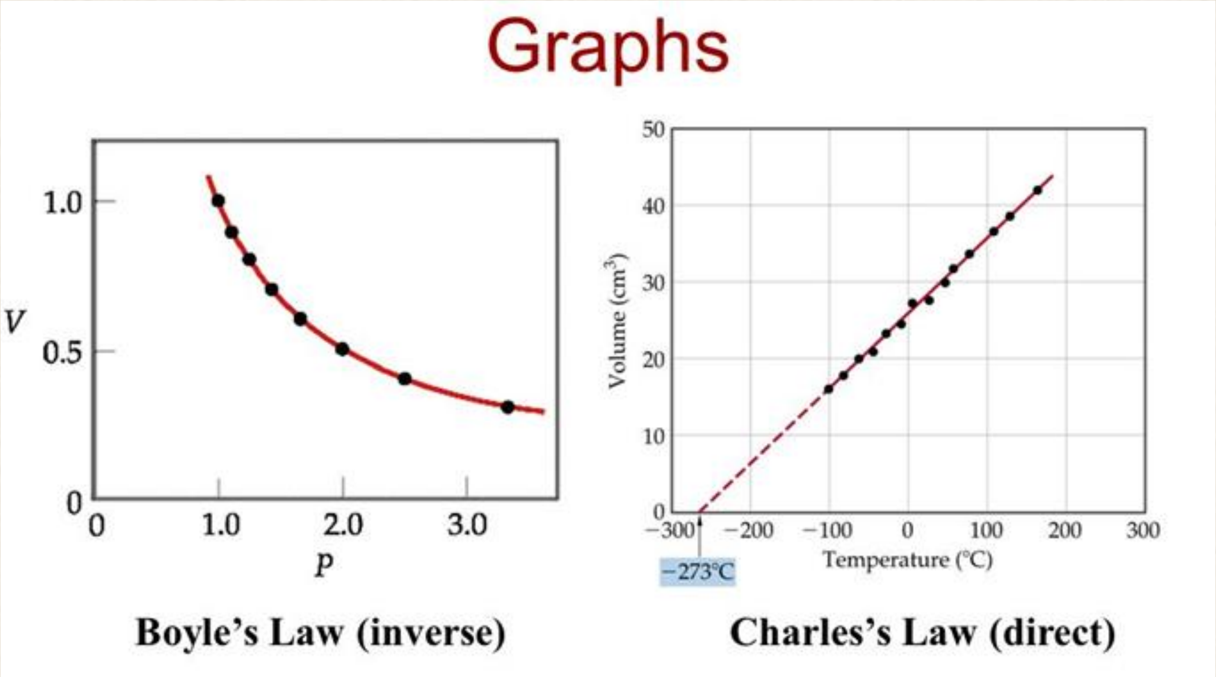
Ideal Gases consist of molecules that move completely independently of one another and occupy a volume much greater than the volume of the molecule.

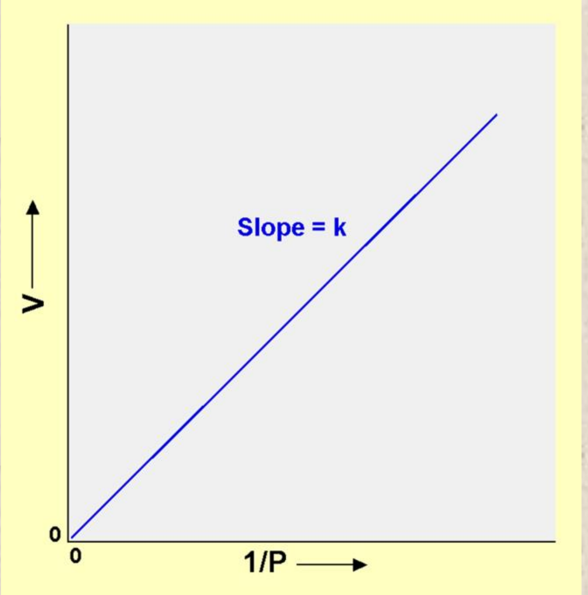
The Ideal Gas Law combines Boyle's ($P_1V_1 = P_2V_2$), Charles's ($V = nT$), and Avogadro's ($V = an$) laws.

$$PV = nRT$$

Where P = pressure, V = volume, n = number of moles, R = universal (or ideal) gas constant, and T = temperature (K).

R combines the standard temperature (273 K), pressure (1 atm) and the fact that 1 mol of gas occupies a volume of 22.4 liters at STP.





An interesting result of the Charles's experiment is that the volume of an ideal gas will become zero at -273^{o}C. The origin of the concept of *absolute zero*.

Ideal gas laws are handy and seem to reflect common sense, however, most gases (especially at high pressure and/or low temperature) deviate from ideal behavior.

This occurs for 2 related reasons.

1. Gas molecules do have a finite volume. When P is increased, the number of molecules/volume of gas will increase. Therefore, gas molecules comprise a significant portion of the volume.

2. Gas molecules do interact with each other, and as the number of molecules/V_{Gas} increases, the number of interactions increases.

Johannes van der Waals introduced two numbers to correct for *non-ideal* gases.

$$V-nb$$

Where n is the number of moles of gas and b is an empirical constant that depends on the gas. V, of course, is the volume of gas. This number corrects for the volume of the gas molecules.

$$a(n/V)^2$$

Where a is an empirical constant, n is the number of moles and V is the volume of gas. This number corrects for the interactions between the gas molecules.

The ideal gas equation with the corrected numbers :

$$P_{obs} = \frac{nRT}{V - nb} - a(n/V)^2$$

Table 1-6 lists van der Waals constants for some common gases.

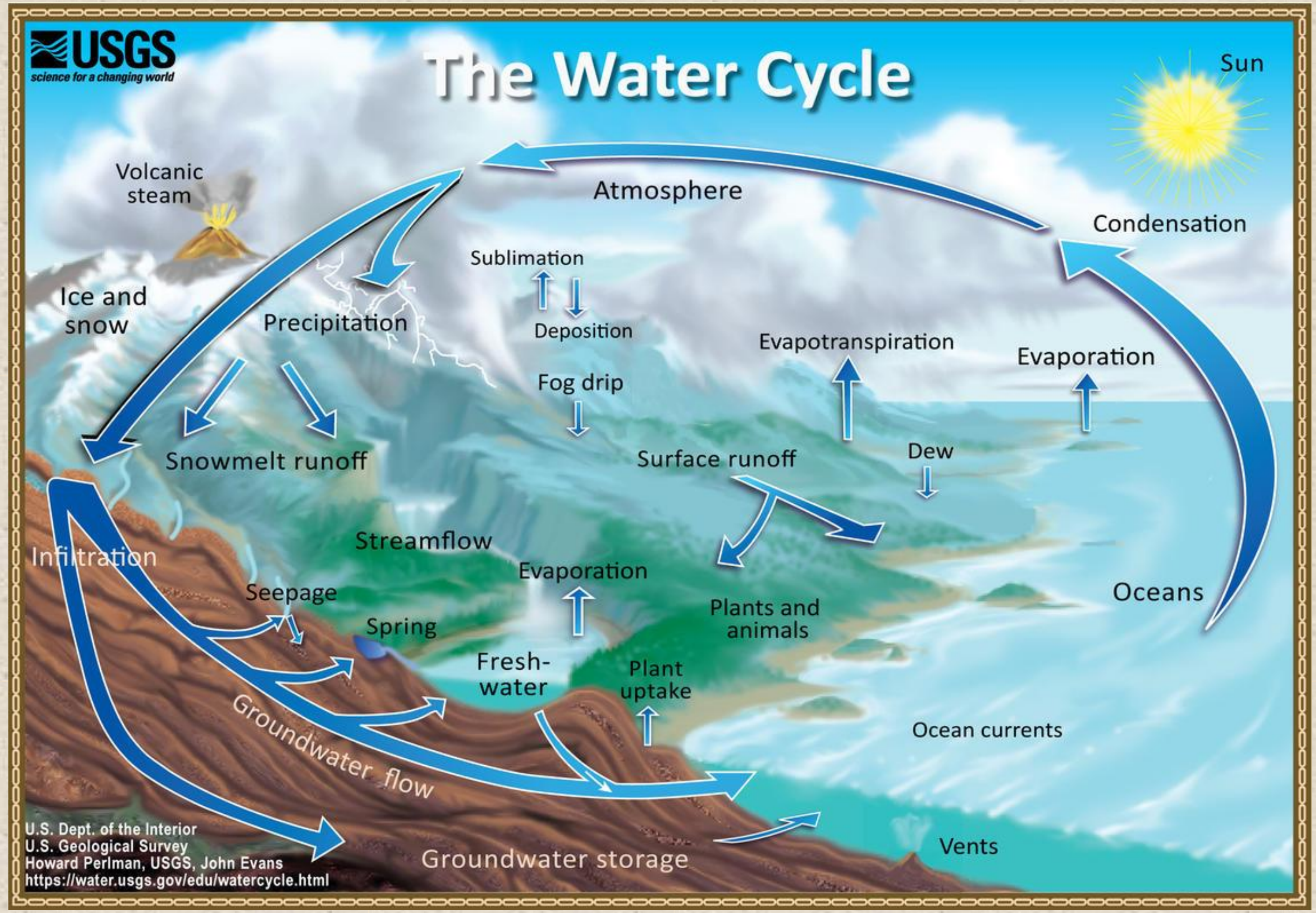
Example 1-11

A cylinder of compressed nitrogen has a volume of 100L and contains 500 mol of N_2. At a temperature of 25°C, calculate the pressure exerted by the gas on the cylinder.

$$P_{obs} = \frac{(500\text{mol})(0.08206\text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298.15\text{K})}{(100\text{L}) - (500\text{mol})(0.0387\text{L}\cdot\text{mol}^{-1})} - (1.37\text{atm}\cdot\text{L}^2\cdot\text{mol}^{-2})(500\text{mol}/100\text{L})^2 = 117.4\text{atm} = 1725\text{psi}$$

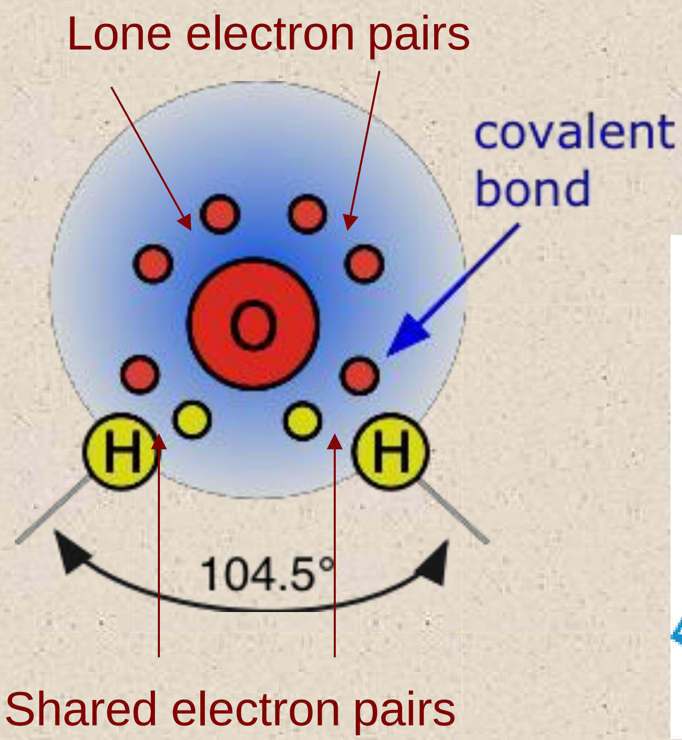
Water

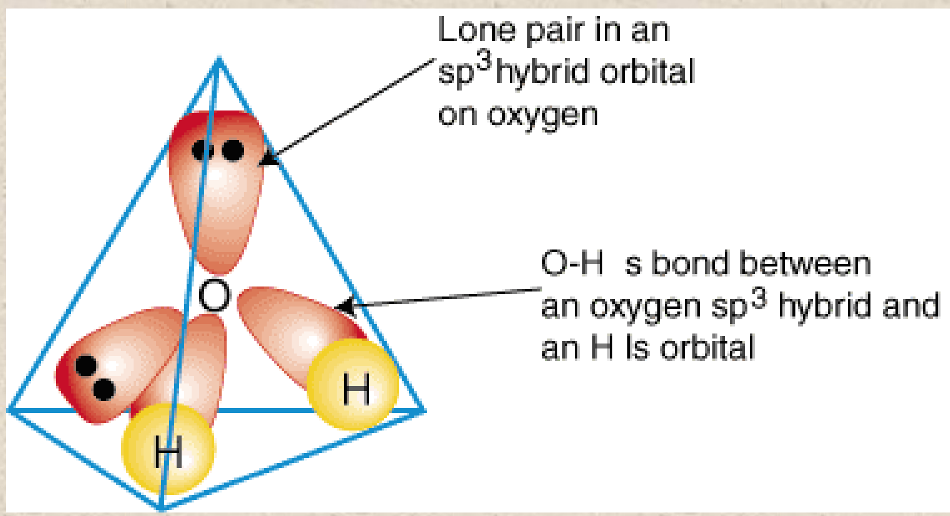
Water is arguably the most important substance on Earth. Without water, life, as we know it, would not exist.



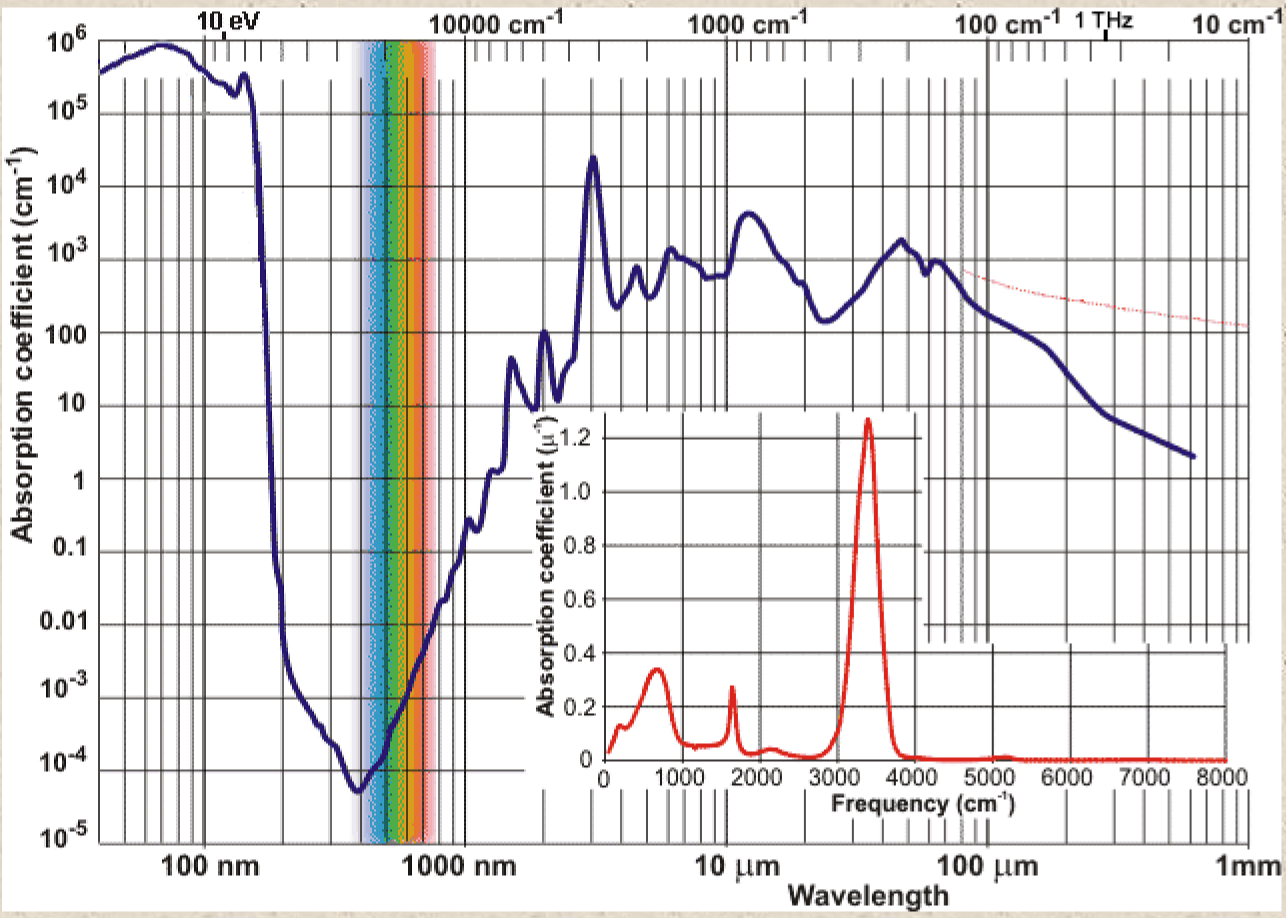
Water is the only substance that occurs in all three states (solid, liquid and gas) at the Earth's surface.

The shape of the water molecule by VSEPR theory (Valence shell electron pair repulsion theory). Oxygen contains 8 electrons ($1s^2$, $2s^2$, $2p^4$). Hydrogen contains 1 electron ($1s^1$).

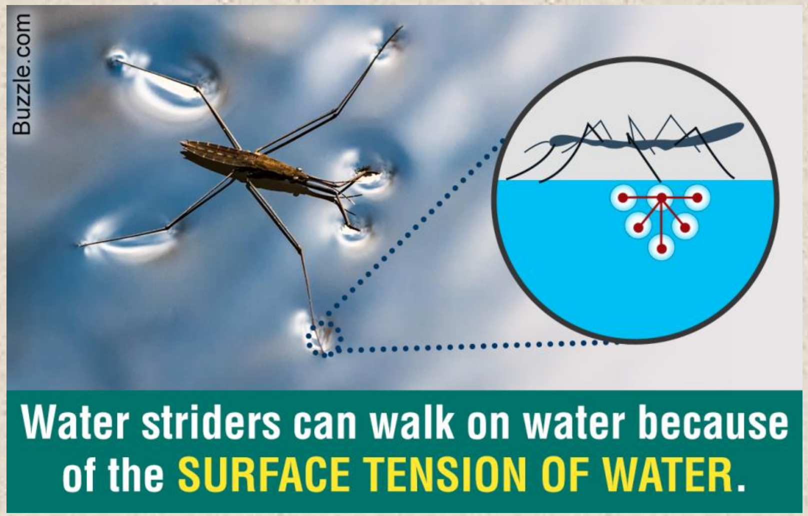




Water has relatively high transparency for visible light. EM radiation of shorter and longer wavelength (higher and lower frequency) are more strongly absorbed.



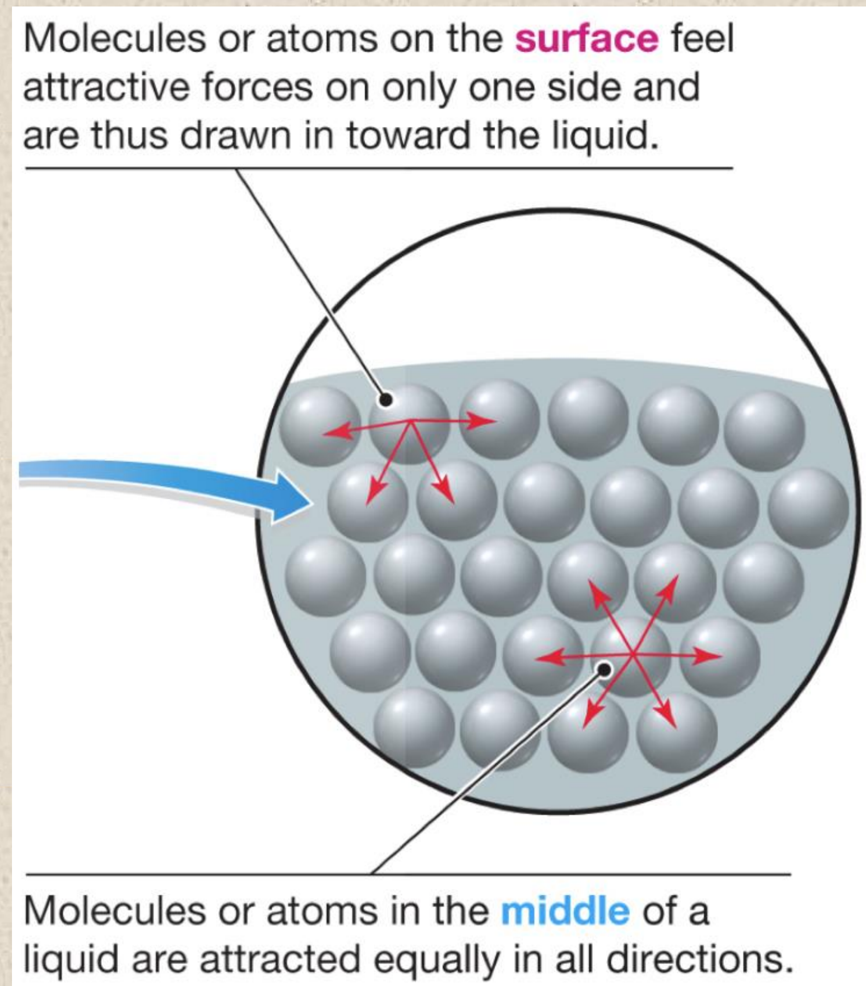
Water has the highest surface tension of all common liquids



Molecular Weight, Density, Surface Tension, and Viscosity for Selected Liquids

Name	Molecular Formula	Mol. Wt.	Specific Density	Surface Tension	Viscosity cP	Viscosity cs
Acetic acid (ethanoic acid)	C2H4O2	60.05	1.043	27	1.06	1.02
Acetone (propanone)	C3H6O	58.08	0.786	23	0.31	0.39
Benzene	C6H6	78.11	0.873	28.2	0.6	0.69
Cyclohexane	C6H12	84.16	0.773	24.7	0.89	1.15
Dichloromethane (methylene chloride, DCM)	CH2Cl2	84.93	1.318	27.8	0.41	0.31
Ethanol (ethyl alcohol)	C2H6O	46.07	0.787	22	1.07	1.36
Ethylene glycol	C2H6O2	62.07	1.111	48.4	16.1	14.5
Formamide (methanomide)	CH3NO	45.04	1.129	57	3.34	2.96
Glycerol	C3H8O3	92.09	1.257	76.2	934	743
Hydrogen peroxide	H2O2	34.02	1.449	74	1.25	0.86
Mercury	Hg	200.59	13.63	474.4	1.53	0.11
Methanol (methyl alcohol)	CH4O	32.04	0.787	22.1	0.54	0.69
Nitromethane	CH3NO2	61.04	1.129	36.3	0.63	0.56
Toluene	C7H8	92.14	0.865	27.9	0.56	0.65
1,1,1-Trichloroethane (methyl chloroform)	C2H3Cl3	133.4	1.33	25	0.79	0.59
Trichloroethylene (TCE, trichloroethene)	C2HCl3	131.39	1.458	28.7	0.55	0.38
Trichloromethane (chloroform)	CHCl3	119.38	1.48	26.7	0.54	0.36
Water	H2O	18.02	0.999	72.7	0.89	0.89

Diversified Enterprises

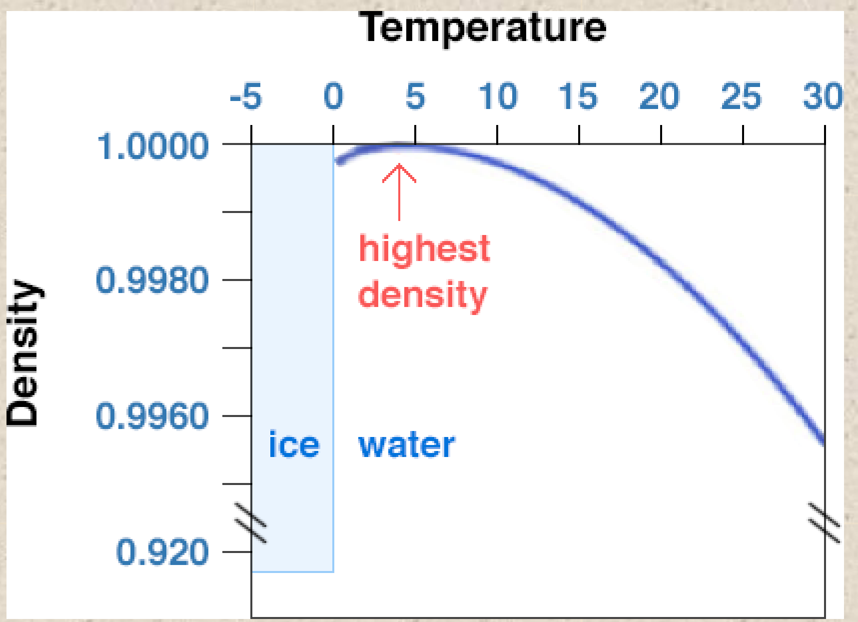


Heat Capacity (specific heat): the amount of energy required to raise the temperature of 1 g of a substance by 1°C. For water, the heat capacity is 1 $cal \cdot g^{-1} \cdot °C^{-1}$.

Latent heat of fusion: The heat absorbed as a substance changes phase from solid to liquid. For water, the latent heat of fusion is 80$cal \cdot g^{-1}$.

Latent heat of vaporization: The heat absorbed when a substance changes phase from liquid to gas. For water, the latent heat of vaporization is 540$cal \cdot g^{-1}$.

Why does ice float? Shouldn't a solid sink?



The highest density for water is at 4°C. Ice (a solid) is significantly less dense than liquid water.