

GENERAL AND INORGANIC CHEMISTRY

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CHEMISTRY

It studies the structure of *matter*, and its *transformations*

matter = all that has mass and volume (living or nonliving)

transformations = passage of the matter through different states (gas, solid, liquid)

➤ **Modern science:**

Newton : newtonian mechanics, universal gravitation, calculus, newton's law of motion;

Copernico : heliocentrism;

Galileo : scientific method;

➤ **Modern chemistry:**

Avogadro: $N_a = 6,02 \times 10^{23}$ particles = 1 mole

Gases with equal V, P, T have the same number of particles

MATTER AND ITS PROPERTIES

matter can be divided in:

- **Pure substances:** constant composition, distinct properties

- Elements: cannot be decomposed into more simple substances
Those are listed in the periodic table:

group

↓

period →

H	
Li	Be

Most of them are unstable, seeable just in labs for a few seconds (ex. Tc)

- Compounds: 2 or more different elements kept together through chemical bonds (obtained through chemical transformations), in a constant simple ratio.

Similar to the molecules but in a molecule the atoms can be of the same element

Elements ⇔ compounds ex: electrolysis of water

- **Mixture of substances** : 2 or more pure substances that maintain their different chemical identities, in a variable ratio

- Heterogenous : macroscopic properties are different throughout the sample
 - Homogeneous (solutions) : macroscopic properties are the same in every part of the sample.

metal alloys are solid homogeneous solutions

Pure substances in a mixture can be separated using physical methods ex: distillation or magnetism

Properties:

- **Physical** : can be studied without altering the identity of the substance

In a physical transformation the chemical identity of the substance is maintained

- **Chemical** : behaviour of a substance in a transformation to yield other different substances.

In a chemical transformation a substance is transformed into another one, with a different identity.

Dalton's atomic theory 1806

- Every element is made of atoms (correct)
- For each element, atoms are identical (not really, isotopes are atoms of the same elements that have a different number of neutrons, they are equal on a chemical level but different on a physical one)
- Atoms of different elements are different (correct)
- Atoms are not changed during chemical transformation (correct)
- Compounds are formed when two or more elements are combined in a chemical reaction, forming chemical bonds (correct)
- Atoms are tiny spheres (no, bohr's atomic model)

Subatomic particles

- Crookes discovered the presence of charged particles composing atoms using cathodic tubes (- =electron, + =proton)
- Thomson determined the m/c ratio of the electron
- Millikan determined the charge of the electron ($e=1.6022 \times 10^{-19} C$)
- Rutherford proved that the largest part of the atomic mass is condoned in a small space, the nucleus (nucleus = 10^{-15} ; atom = 10^{-10})

3 subatomic particles were discovered:

	Charge	mass
Proton:	e	1
Electron:	-e	10^{-4}
neutron:	0	1

Useful numbers of the atoms:

- **Atomic number (Z):** number of protons, equal for the atoms of the same element, in neutral atoms it corresponds to the number of electrons.
If the atom is not neutral it is an *ion* (also valid for molecules):
 - Anion - : $p < e$, negatively charged
 - Cation + : $p > e$, positively charged
- **Mass number (A):** sum of protons and neutrons
Isotopes of the same elements have the same atomic number but different mass number

Identification of an atom: ${}^A_Z \text{Atomic Symbol}$, ex: (1,1) H 1 p, 0 n; (2,1) H (deuterium) 1 p 1 n

Bohr atomic theory

- **Hydrogen atom**

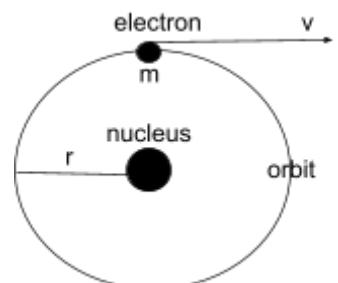
- Energy:

$$\blacksquare E_{tot} = E_k + E_p$$

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}m_e v^2$$

$$E_p = \frac{1}{4\pi\epsilon_0} * \frac{q_1 q_2}{r} = - \frac{1}{4\pi\epsilon_0} * \frac{Ze^2}{r}$$

(only useful if we have 1 electron and 1 or more proton)



$$(\text{hydrogenoids: } q_e * n_p q_p = n_p (q_e q_p)^2 = Ze^2)$$

There are 2 undefined data: v and r .

- Experimental evidences tell us that electrons can have only certain defined energies from which derive the stationary states (in a stationary state the energy is constant)
- Energy is emitted or absorbed when electrons pass from a state to another

- Orbitas:

- Electrons go around the nucleus on well defined orbits
- The only permitted orbits are those for which the **angular momentum** is an **integer multiple of $\frac{h}{2\pi}$** :

$$m_e v r = n \frac{h}{2\pi} \quad n: \text{principal quantum number (number of the orbit)}$$

This equation permits to find the last 2 undefined data of the energy equation, through this we are able to know the speed, position and energy of any electron:

$$r(n) = n^2 * \text{constant} \quad r(1) = 0.529 A = 5.29 * 10^{-8} m = a_0$$

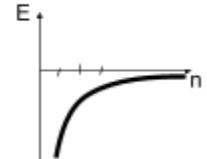
Doubling up n the distance from the nucleus is 4 times longer, a_0 is the closest distance between an electron and the nucleus

$$v(n) = \frac{1}{n} * \text{constant} \quad v(1) = 2.19 * 10^6 m/s$$

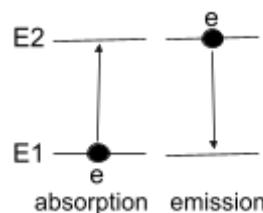
Doubling up n the speed of the electron is halved

$$E(n) = -\frac{1}{n^2} * \text{constant} \quad E(\text{inf}) = 0 \frac{kg m^2}{s^2}$$

$$E(1) = -2.18 * 10^{-18} \frac{kg m^2}{s^2}$$



Doubling up n the energy increases, tending to 0 (to promote an electron are requested precise quantities of energy, maximum from $n1$ to $n2$)



- How do we find the equation that describes the permitted orbits?
 1. The electron is a small particle that behaves also as an electromagnetic radiation, it has a wavelength ($\lambda(m)$) and a frequency ($f(Hz)$)
 2. The energy of an electromagnetic wave is quantized ($E=hv$)
The energy of an electromagnetic wave is linked to the mass of the particle ($E=mc^2$)

The wavelength of an electromagnetic wave depends on the speed of the wave and the speed of the light ($\lambda=c/v$)

So putting all this formulas together:

$$\lambda = \frac{c}{v} = c * \frac{h}{E} = c * \frac{h}{m_e c^2} = \frac{h}{m_e v}$$

3. During his orbit the electron interferes with his own trajectory of the “previous round”, so it must have a path in which, at every round the crests fit with the crests and the valley fit with the valleys (constructive interference) → only certain combinations of orbit circumference and wavelength create constructive interference:

$$2\pi r = n\lambda = n * \frac{h}{m_e v} \rightarrow m_e v r = n \frac{h}{2\pi}$$

- **Polyelectronic atoms:** the bohr model is only valid for hydrogen like atoms (hydrogenoids), having only 1 electron and 1 or more protons, otherwise repulsion forces between the electrons get involved

Heisenberg uncertainty principle

Δx =error on the position

Δv =error on velocity

$\Delta x \Delta v m \geq \frac{h}{2\pi} \rightarrow \Delta x \geq \frac{h}{2\pi \Delta v m}$ this uncertainty is negligible for the macroscopic world

In the case of an atom on the other hand ($m_e = 10^{-30} kg$; $\Delta v = 1 m/s$) Δx results more than $10^{-4} m$ which is nearly 10^6 times the dimension of the atom, it is *impossible to know the trajectory of the electron.*

Schrodinger and orbitals

Chemical properties of the elements depend on the position and energy of the electrons: electronic structure and electron configuration.

Since we cannot have a precise idea of the trajectory and velocity of a general electron Schrodinger found a way to calculate where it is probable (P=probability) to find the electron in a three dimensional region near the nucleus and what energy that electron has.

The equation that Schrodinger found describes an **orbital** and it is a wave function (ψ), it uses quantum numbers to define the geometrical properties of the region in which it is possible to find the electron, Each orbital described by ψ is associated to a given energy

- **Probability density**

The wave function itself doesn't have any physical meaning but it is useful to determine the **probability density** of the electron through the **square of the wave function**.

$$\psi^2 = \text{probability density} = P/dV$$

The probability density (volumic density) of an electron is the probability to find an electron in a given volume, if we take a small volume around the nucleus the probability to find an electron are not so high, on the other hand the probability density is super high (some electrons/tiny volume=great ratio); the probability density is maximum for the volume (depending by r) that has the most “efficient” ratio.

- **Quantum numbers**

For each atom there are several solution to the schrodinger equation, through 4 parameters (quantum numbers) we are able to describe every type of orbital:

- **n** = *principal quantum number*, it is correlated to the **energy** of the orbital.
It is a positive integer number, $n \geq 1$.
- **l** = *secondary quantum number*, it describes the **shape** of the orbital.
It is a positive integer number $0 \leq l \leq n - 1$
- **m** = *magnetic quantum number*, it describes the **orientation** of the orbital.
Integer number, $-l \leq m \leq l$;
- **s** = *spin quantum number*, it is not a property of the orbital but of the electron, it is correlated to the **electron's magnetism**, it describes the direction of the **rotation of the electron**.
It has only 2 values: $+\frac{1}{2}$ clockwise, magnetic field pointing up; $-\frac{1}{2}$ anticlockwise, magnetic field pointing down.

- **Orbitals nomenclature**

$n' l' m'$

- $l = 0$ orbital **s**
 $l = 1$ orbital **p**
 $l = 2$ orbital **d**
 $l = 3$ orbital **f**
- m : combination of **x,y,z**

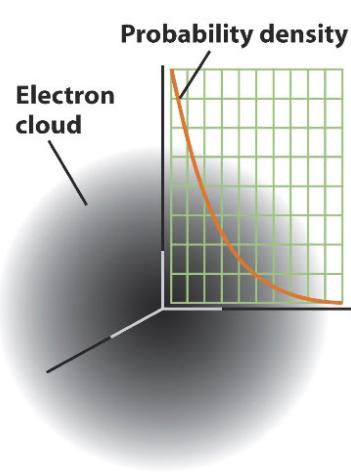
Shell n	Subshell l	Subshell Notation	Orientation m	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1 0 +1	3
3	0	3s	0	1
	1	3p	-1 0 +1	3
	2	3d	-2 -1 0 +1 +2	5
4	0	4s	0	1
	1	4p	-1 0 +1	3
	2	4d	-2 -1 0 +1 +2	5
	3	4f	-3 -2 -1 0 +1 +2 +3	7

- **Graphic interpretation of probability density**

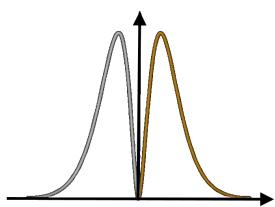
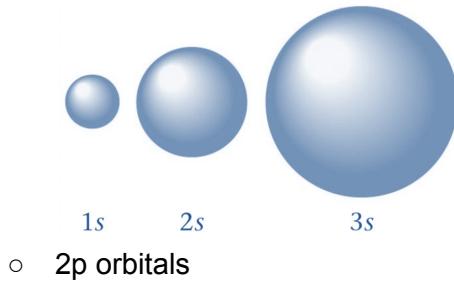
- 1s orbital

By choosing arbitrary spherical volumes around the nucleus the probability density of the electron goes down as the volume increases.

Now we can get rid of the density and pick the set of solutions with the same probability: in a sphere of $r = a_0$ (bohr radius) we have 70% chance to find the electron, while considering a 90% probability the radius is bigger (the probability density in the first one

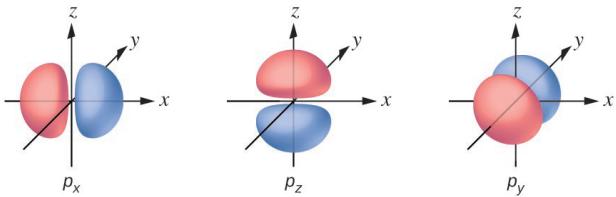


is still bigger than the second one, it has a better probability-volume ratio);
Usually the representations are made considering 90% probability:



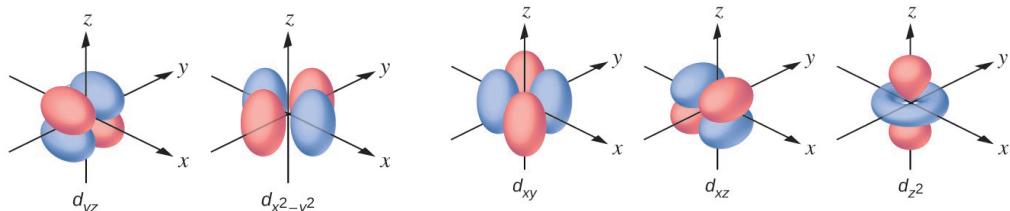
the analysis of the graph of ψ^2 tells us that at the centre of the atom the probability density of the electron is 0, it is impossible to find the electron (nodal plane) and that the electron is distributed in 2 main lobes, symmetrical and with the same density. The orbitals have three possible orientations ($m=-1, 0, +1$) and those are the representations if we pick the

volumes that assure us 90% possibility to find the electron:



○ 3d orbitals

The three dimensional structures of these orbitals, including the electron with a 90% probability, are 5, one for each magnetic quantum number, each of them has 4 lobes.

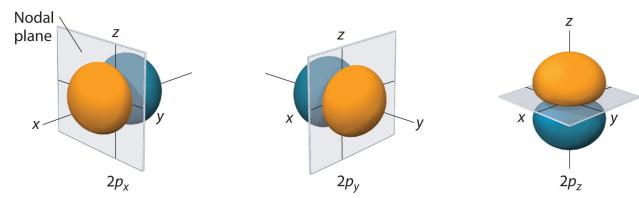


As the n increases every three dimensional region contains a bit of the region with the lower n

● Nodes / nodal regions

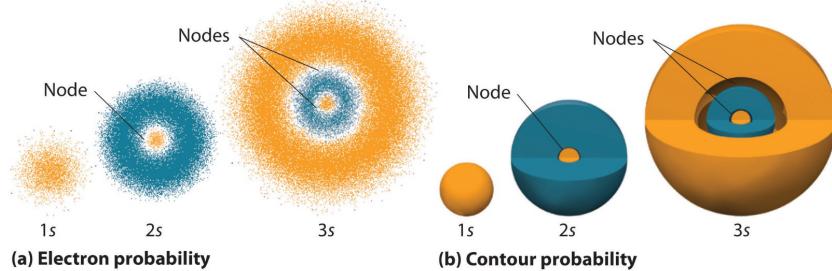
A node is a region of space in which:

- probability density (and the wave function) is equal to 0
- The sign of the wave function changes from a side to the other
- The number of nodes is $n-1$



Nodal region of s orbitals:

In s orbitals the nodes are concentric spheres that surround the region of the smaller sphere



- **Radial distribution**

We can express the wave function through spherical coordinates:

$$\psi(x, y, z, n, l, m) \rightarrow \psi(r, \theta, \phi, n, l, m)$$

In the case of a hydrogen atom we can divide the function into two components:

$$\psi(r, \theta, \phi, n, l, m) = R(r, n, l) * \text{angular wavefunction}$$

↓
Radial wavefunction

This form of the function is useful to get the radial distribution of the electron: the possibility to find the electron in a given empty sphere (surface).

To achieve this we multiply the probability density ψ^2 times the volume of the spherical shell of an infinitely small thickness, $dV(h)$:

$$P = \psi^2 * dV$$

$$V(h) = 4\pi(r^2 h + rh^2 + \frac{1}{3}h^3)$$

$$dV(h) = 4\pi r^2 + 8\pi hr + 4\pi h^2$$

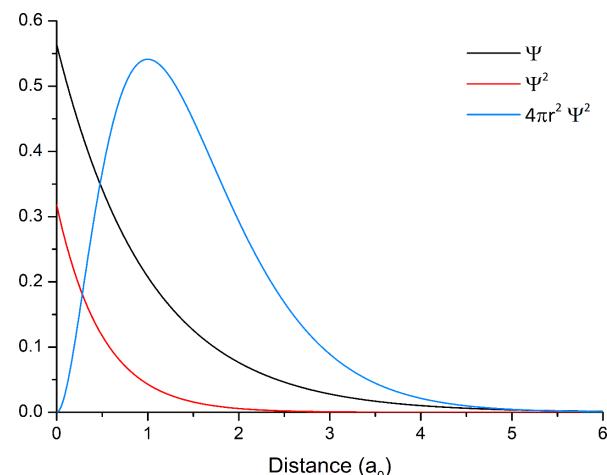
For h infinitely small:

$$dV(h) = 4\pi r^2 \rightarrow P = 4\pi r^2 * \psi^2 \text{ (obtained by } \psi^2 = P/dV)$$

- **Graphic interpretation of radial distribution of this function**

- 1s:

From this graph we can understand that the higher possibility of finding the electron is achieved in the sphere that has the bohr radius, furthermore near the nucleus there is just a little chance to find the electron



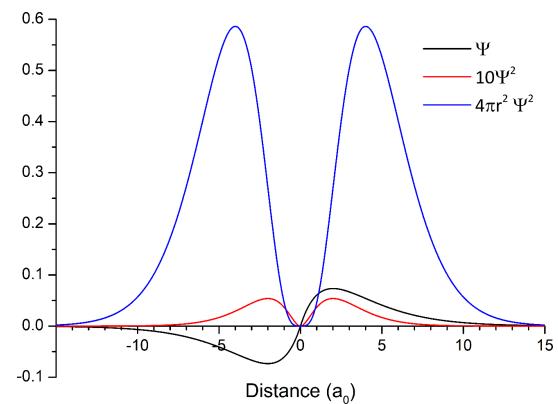
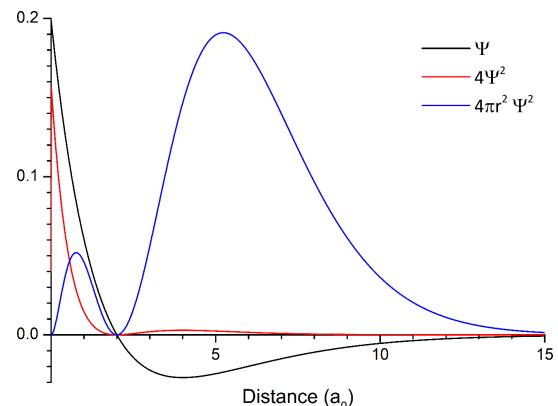
- 2s:

Also in this graph we can see how near the nucleus it's very difficult to find the electron and that the higher possibility of finding it corresponds to the sphere which has $r = 5a_0$

(different from bohr's prediction) a difference from the previous graph is that in this case there is another region in which it is impossible to find the electron, that's the nodal region of the 2s orbital (a concentric sphere with $r = 2a_0$) where it also changes the sign of the wave function

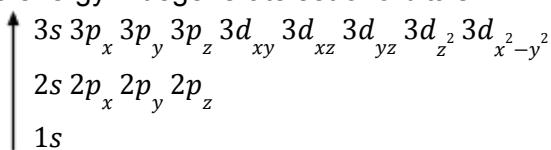
- 2p:

In this graph the nodal plane corresponds to the nucleus, the higher possibility to find the electron is at $r = 5a_0$ and it is equally possible in both the lobes (symmetric behaviour)



- Orbital energy

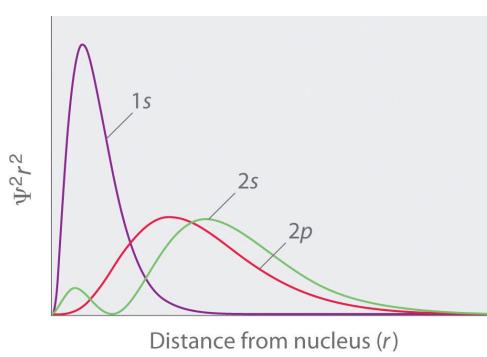
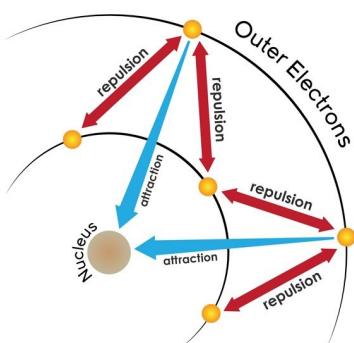
- hydrogenoids: every shell, described by the principal quantum number, has the same energy = degenerate set of orbitals:



$$E_h(n) = -\frac{1}{n^2} Z^2 * \text{constant}$$

- Polyelectronic atoms: there is a non neglectable **repulsion between the electrons**, the value of the equation is difficult to establish, a computer can get closer to it, we will use (to make it simple) a coefficient to decrease the energy because the attraction of the nucleus is lower with multiple electrons (the closer ones cancel some of the positive charge of the nucleus).

Concept of shielding effect:



sometimes an electron of an higher orbital can be closer to the nucleus than the electron of the previous orbital,

so the shielding effect is amplified

To take it into account we use the effective nuclear charge Z_{eff} :

$$Z_{eff} = Z - \sigma \quad \text{where } \sigma \text{ is the shield constant}$$

So the formula of the energy becomes:

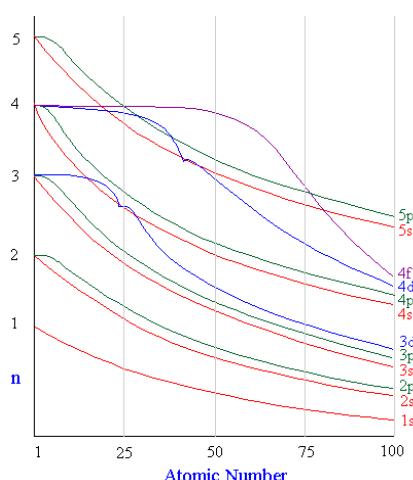
$$E(n) = -\frac{1}{n^2} Z_{eff}^2 * \text{constant}$$

Because of the shield effect, electronic subshells with the same principal quantum number and different secondary quantum number possess different energies: $E(s) < E(p) < E(d) < E(f)$

For polyelectronic atoms the energy depends not only on n but also on l (the value of Z_{eff} changes).

The energy of an orbital with the same n and l depends on the nuclear charge (Z_{eff})

■ Graph of orbital energy:



The relation $E(s) < E(p) < E(d) < E(f)$ is always valid for orbitals with the same principal quantum number.

The energy relation between orbitals with different energies is a bit more complicated, starting by the 4s orbital the energy of the previous orbital (3d) for some values of Z it is more than the next one.

■ Electron configuration

The main consequence of the overlapping of energy in the previous graph is noticeable when we write down the electronic configuration of an atom.

We need to follow three rules:

- Principle of minimum energy: the electrons occupy the orbitals from the one that has the lower energy to the most energetic one
- Pauli exclusion principle: 2 electrons in an atom can't have 4 equal quantum numbers
As a consequence of this principle every orbital can be occupied by up to two electrons
- Hund's rule: when 2 or more electron occupy a degenerate orbital (set of orbital with equal n) they are placed in the maximum possible number of orbitals, with parallel spin

So the energy of a polyelectronic element looks like this:



Each orbital can be:

- Virtual: without any electron
- Semi occupied: with just one electron
- Fully occupied: with 2 electrons

Electron configuration significative examples:

- H: $1s^1$ → Number of electrons in the shell
- He: $1s^2$ it is at the other side of the table because it has the whole outer shell full of electrons, it has a peculiar stability and it is called noble gas (hard to react with other elements)
- Li: $1s^1 2s^2$ = [He] $2s^1$ it can be written also as [the last noble gas element] + configuration of the outer orbital (valent shell)
The valent shell is the shell that it's involved in chemical reaction (same valent shell = same chemical properties)
- C: [He] $2s^2 2p^2$ it has the orbital p partially filled, it is on the right in the periodic table
- Ne: [He] $2s^2 2p^6$ it has all the orbitals of the outer shell fully occupied, it is a noble gas
- Na: [Ne] $3s^1$ his previous noble gas is Neon so it can be written in a very short form, it has just one electron in the outer shell, his chemical properties are similar to the H and Li (periodic behaviour), they all belong to the first group
- Ar: [He] $3s^2 3p^6$ the 3rd shell shouldn't be already completed but Ar is a noble gas because, due to the shielding effect, the next orbital will be 4s, E4s < E3d.

Argon has a super stable electron configuration

Some elements endure weird effects between subatomic particles so their configuration must be determined experimentally.

PERIODIC TABLE

The periodic table is based on the electron configuration of the elements, on the left there are the elements that have an s orbital as valent shell, in the centre there are the d orbitals and on the right there are p orbitals, the first three rows are empty at the centre because 1d and 2d don't exist and 3d has a bigger energy than 4s.

Each orbital corresponds to a group, except for the 3d orbitals, that they all belong to a single group:

- Alkali metals: s^1
- Alkaline earth metals: s^2
- Transition metals: d
- Boron group: p^1
- Carbon group: p^2
- Nitrogen group: p^3
- Oxygen group: p^4
- Halogens: p^5
- Noble gasses: p^6

The first periodic table, created by Mendeleev had already some kind of periodic association between the elements, and basing on these periodic correlations he theorized the existence of still not discovered elements.

- **Periodic properties:**

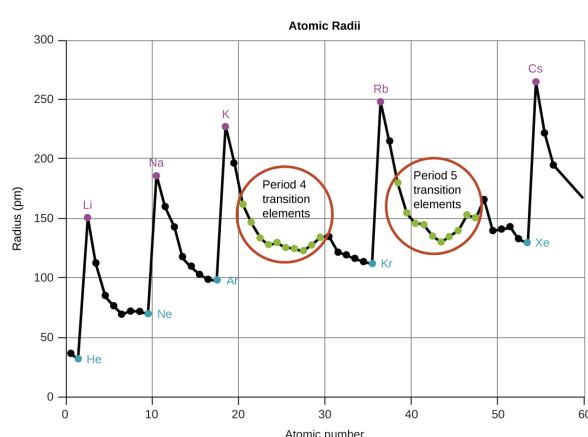
Chemical properties of the elements depend on their electronic structure, which is periodic, so the chemical properties are periodic:

N.b. We will describe 3 behaviours for each graph: the difference between the first and last group (borderline cases), the behaviour along the groups of each period and the behaviour along the periods.

- **Atomic radius:**

To measure the radius we consider a molecule with two atoms of the same element, the radius is half of the distance between the two nuclei.

Arranging the atoms in order of atomic number on the x axis and their atomic radius on y axis allow us to obtain a plot like this:



The length of the radius has a clear periodic trend, the atoms of the first group have a much bigger radius in respect to the successive elements, the noble gasses have the smallest radius of each period.

The chemical explanation of this behaviour is that every time that we go from a noble gas to an alkali a new electron shell

gets filled, and the atomic radius increases drastically;

Then going along the period the nucleus acquires protons while the electrons are always in the same shell, in this case the electrons get attracted a lot more and the radius decreases.

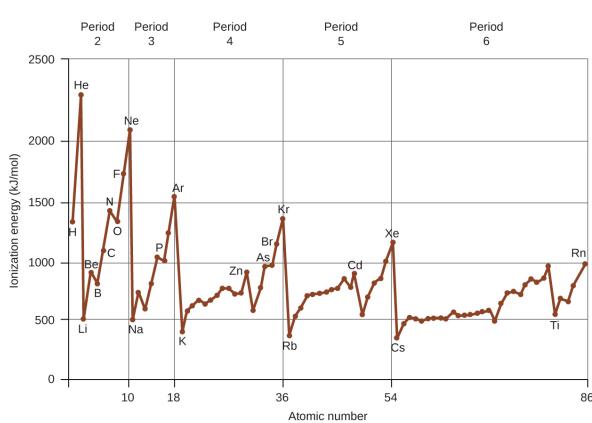
Between the periods the atomic radius increases because the number of electron increases.

When we consider the atomic radius of periods greater than 3 the radius of transition elements has odd behaviours, but we don't care

- **Ionization energy:**

The ionization energy is the amount of energy that is required to remove one electron from the outermost shell of a neutral atom.

Ex: $\text{H(g)} \rightarrow \text{H+(g)} + \text{e}^-$ $I = \text{ionization energy} = 1,321 \text{ kJ/mol}$



Also in this case we can detect a periodicity, the noble gasses have the higher ionization energy, that's because they are very stable elements, they don't want to change their configuration.

According to this, all the other elements tend to reach the configuration of the most near noble gas, so in the case of the ionization energy, it will be very low for the alkali because they

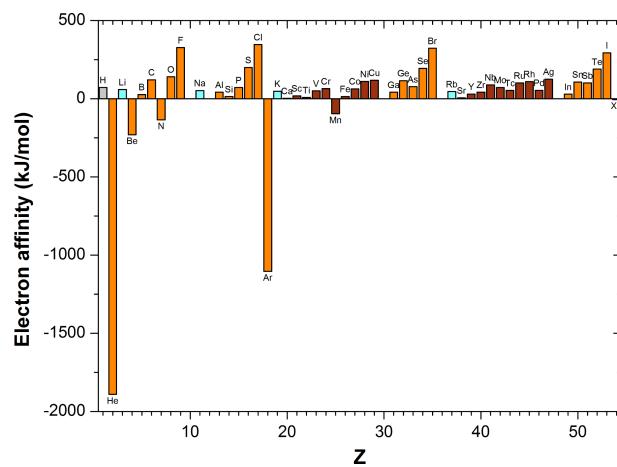
really want to lose 1 electron to reach the configuration of the previous element. Between the groups of each period the energy increases, because at an equal outer shell, the number of protons increases and the electrons are more attracted (the effective nuclear charge, Z_{eff} , is increased).

Finally, the ionization energy goes down along the periods, that's because the electrons are getting farther and farther away from the nucleus so the effect of the nuclear charge is reduced, less Z_{eff} .

- **Electron affinity:**

Energy liberated when an electron is added to a neutral atom

Ex: $\text{A(g)} + \text{e}^- \rightarrow \text{A-(g)}$ $\Delta E = \text{electron affinity}$



If the electron affinity is positive, the process is favoured and energy is transferred from the atom to the environment.

If the electron affinity is negative, the process is disfavored and energy is transferred from the environment to the atom.

The first thing to mention about this graph is that we still don't know the electron affinity of some elements, secondly the bigger most noticeable details are the super low negative energies, associated to the noble gases the behavior is justified by the stability of those elements, they don't want neither to receive an electron (negative electron affinity) neither to give one electron away (high ionization energy).

The higher electron affinity corresponds to the halogens, they miss just one electron to reach the configuration of a noble gas so they are very keen on it.

The electron affinity goes increasing in a single period, until it reaches the noble gas, that's because the effective nuclear charge (Z_{eff}) is higher in the last groups (the nucleus has more attraction power).

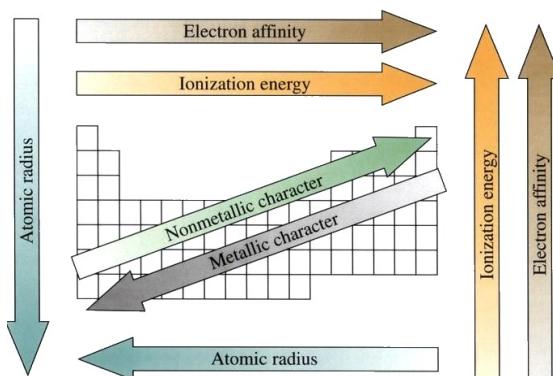
Along the periods the electron affinity tends to increase for the noble gases, less Z_{eff} .

The elements can be categorized on the base of their chemical properties:

Metals are characterized by small ionization energy and small electron affinity

Non-metals are characterized by large ionization energy and large electron affinity.

From the top right to the bottom left of the periodic table goes increasing the metallic character while from the bottom left to the top right goes increasing the non-metallic character.



- **Reactivity:**

- Metal + oxygen → oxide (basic oxide)
- Metal + hydrogen → hydride
- Non-metal + oxygen → oxide (acid oxide or anhydride)
- Non-metal + hydrogen → binary acid
- Basic oxide + water → hydroxide
- Acid oxide + water → oxoacid
- Hydroxide + oxoacid → salt + water
- Hydroxide + binary acid → salt + water

CHEMICAL BONDS

A compound is a substance composed of two or more elements combined in a specific ratio and held together by chemical bond

- Empirical formula: indicates what elements are present in a compound and the whole number ratio between them.
Ex. hydrogen peroxide = HO
- Molecular/chemical formula: indicates the exact number of atoms of each element in a compound.
Ex. H_2O_2
- Structural formula: gives informations about type and position of chemical bonds

2 atoms system

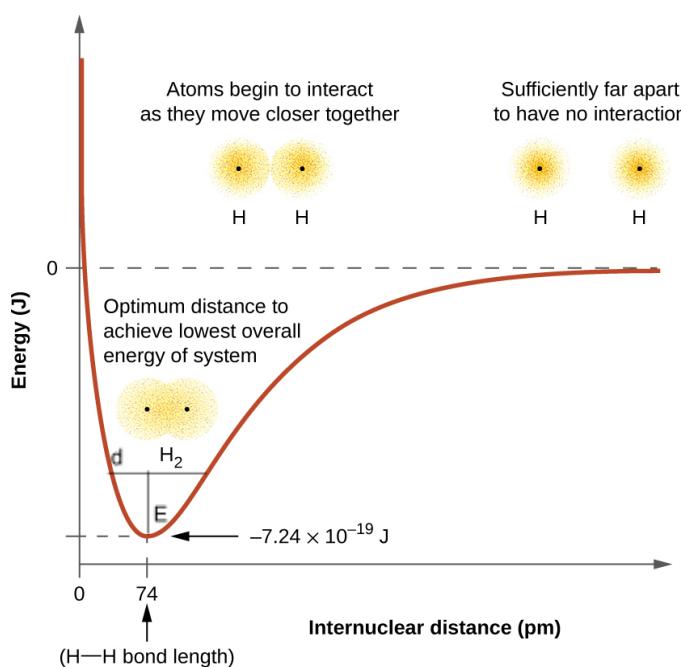
When two atoms are close one to the other several electrostatic forces start acting between the subatomic particles of the different atoms:

- Repulsion between the electrons and repulsion between the protons
- Attraction between protons and electrons

As the atoms get closer the s1 orbitals become more and more deformed, until the orbitals overlap and create a shared orbital; from two elements we achieve a molecule.

This process is spontaneous because the pair of atoms reaches a state of lower energy, releasing energy.

The atoms can't get closer because from the bond distance on the repulsion forces of the nuclei overwhelm the other forces.



A bond that has a greater energy difference between the untied atoms and the bonded atoms is a **strong bond**; when the difference is small the bond is a **weak bond** (in order to break it requires a little amount of energy).

Taking a certain ΔE from the energy of the bonded atoms, a molecule is characterised by a **loose bond** if the distance between the two points of the energy profile that intersect the energy level is large, and **stiff bond** if that distance is small. The atoms in a loose bond can move with a major freedom in respect to the stiff bonded ones,

the movements of the atoms consists in the modification of the bond distance and of the angle between bonds, these movements result in an oscillation of the atoms.

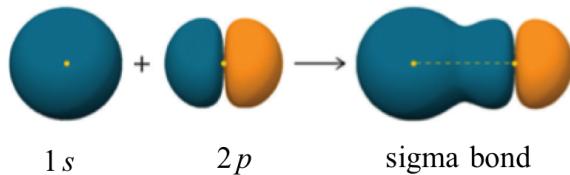
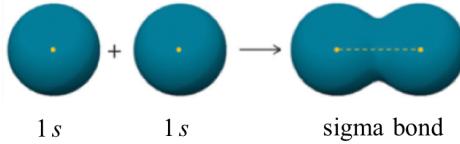
Bonds between classic orbitals

Chemical bond = shared electron pair

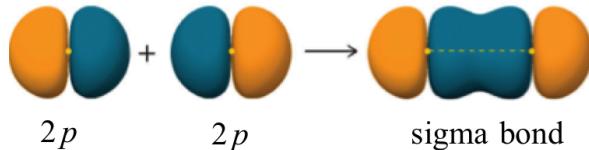
Basing on the position of the electrons in respect to the internuclear axis we can differentiate different bonds:

σ bond: the shared pair stands between the nuclei (high electron density), on the internuclear axis

- 1s+1s: two atoms that have the same spin start getting closer, at some point one of them changes spin and the orbitals overlap
- 1s+2p: same procedure, same electron position

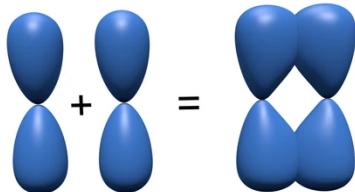


- 2p+2p:

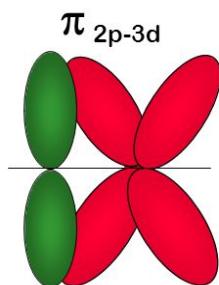


π bond: the shared electron pair is above or below the internuclear axis (π bond is different from a double bond, but if we add a π bond to a σ bond we obtain a double bond)

- 2p+2p: same mechanism of the first bond, it is possible to form it in several directions



- 3d+2p:



Homonuclear molecules

More than two atoms, for example: diamond, graphite

Valence bond theory

Chemical bond = overlap of valence atomic orbitals

Each of the overlapping atomic orbitals must contain a single, unpaired electron.

The chemical bond involves a pair of electrons that become “shared” between the two bonding atoms.

Degree of overlap is proportional to the strength of the bond and inversely proportional to the bond length

The orbital overlap is directional thus the chemical bond is directional.

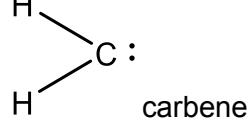
Hybridization of atomic orbitals

C electronic configuration: $1s^2 2s^2 2p^2$

$1\downarrow$	1	1	
$2s$		$2p$	

The outer shell configuration is: $2s^2 2p^2$

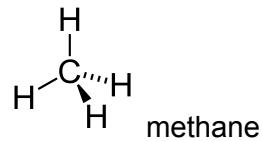
The c atom has only two orbitals with just 1 electron, so a molecule formed by c and h should have the following structure:



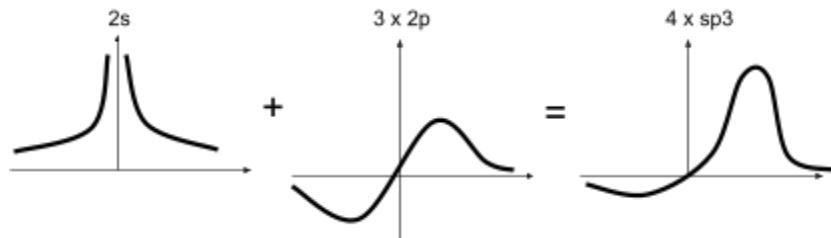
Through the hybridization we can obtain 4 semi occupied orbitals:



Now the carbon can form 4 bonds:

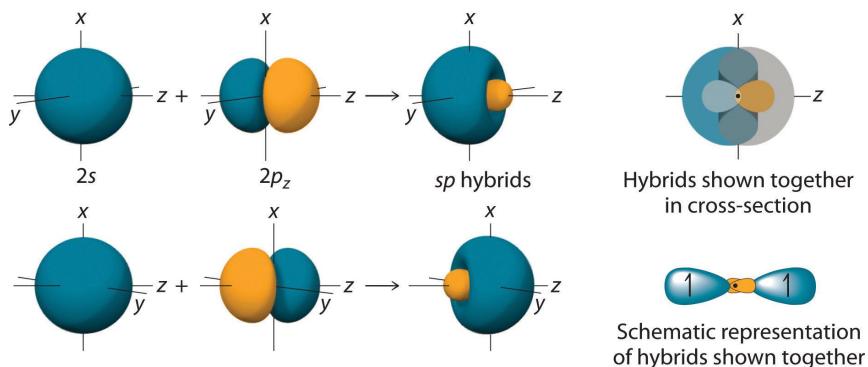


The obtained orbitals are at the same energy level and they are described by a function that is the linear combination of the wave function representing the 2s orbital and the three 2p orbitals, they are called sp^3 orbitals.



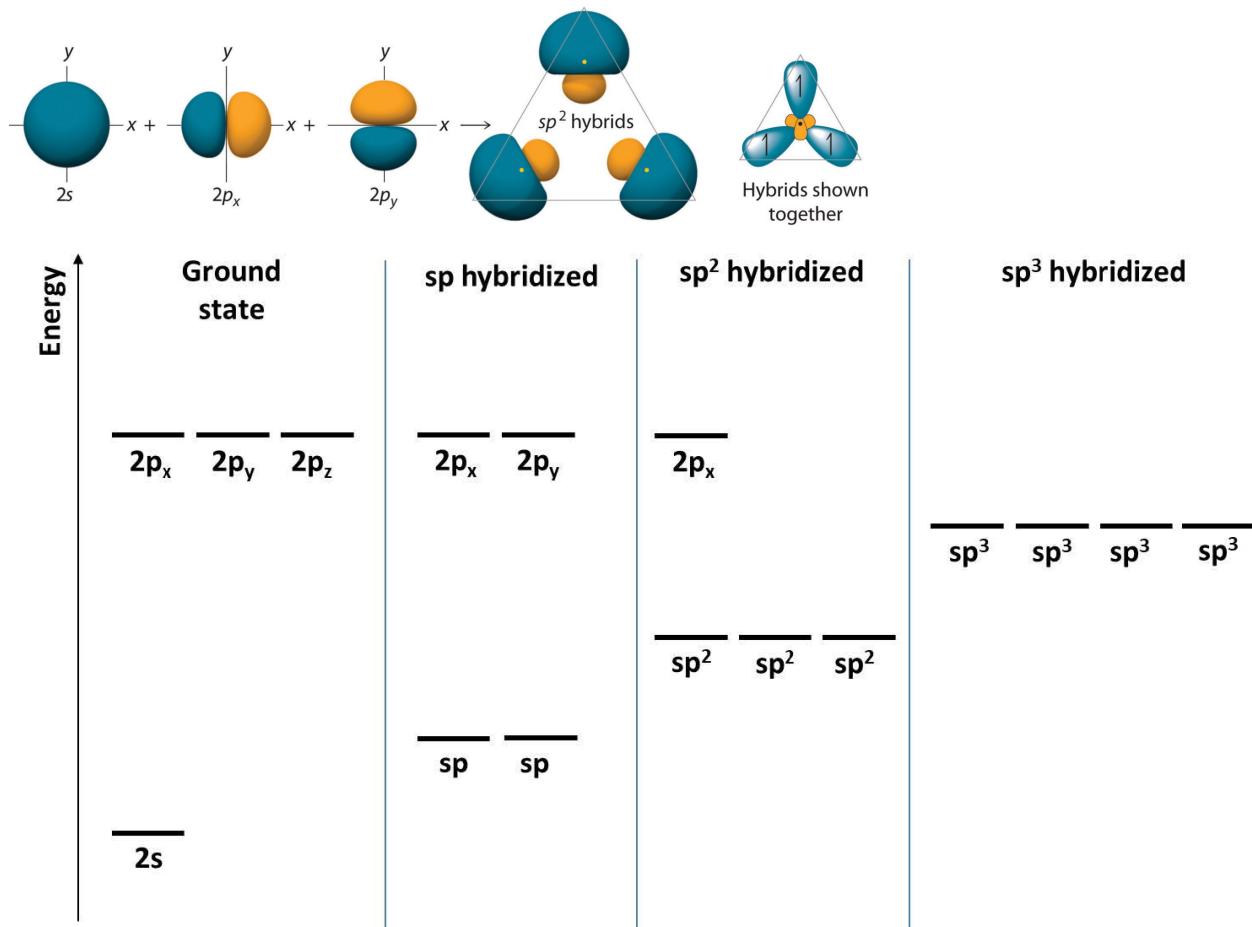
Other hybridizations:

sp : one 2s orbital and one 2p orbital, they form 2 hybrid sp orbitals



The shape of the resulting orbitals always respect some rules: the number of orbital is equal to the initial one, there is always one lobe bigger, one smaller and a nodal region in between and electrons are at the maximum distance.

sp^2 : one 2s orbital and two 2p orbitals, they form 3 hybrid sp^2 orbitals

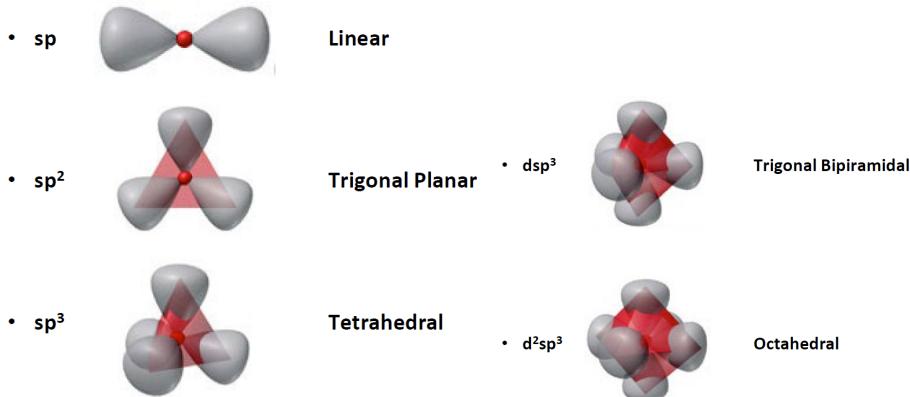


dsp^2 : 5 hybrid orbitals formed by one 3d orbital, 3 2p orbitals and 1 2s orbital

d^2sp^2 : 6 hybrid orbitals formed by two 3d orbitals, 3 2p orbitals and 1 2s orbital

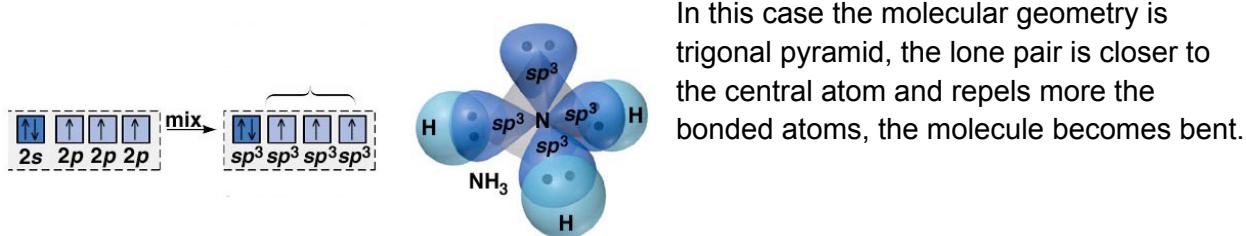
Electron geometry

The hybridization of an atom determines also the tridimensional geometry of his electrons



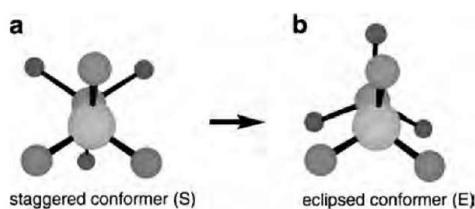
The hybridization is useful even for atoms that have already p orbitals occupied, it sets all the orbitals on the same energy level and permits a symmetrical electron geometry (non-symmetrical molecular geometry).

Ex.



Bond geometry

the σ bond permits the rotation of the 2 atoms that compose it, form the rotation of the atoms derive different molecular conformations:



In a π bond there is no rotation, because the atoms are fixed above and below the internuclear axis.

The π bond is weaker than the σ bond because it has less overlap, but greater is the number of π bonds shorter is the whole bond length: a triple bond has the minimum bond length but it is very easy to break the first π bond.

Electronegativity

Electronegativity is the ability of an atom to draw shared electrons (i.e. in a chemical bond) toward itself.

The electronegativity it's a periodic property and follows the same direction of the metallic character (electron affinity and ionization energy).

It goes from a minimum of 0,6 to a maximum of 4.

Dipole

In a nonpolar covalent bond, the bond pair is shared equally, in a polar covalent bond the more electronegative atom pulls the bond pair towards itself, creating a partial negative charge on it and a partial positive charge on the other atom.

A quantitative measure of the polarity of a bond is the dipole moment, which is calculated as the product of the charge and the distance between the charges: $\bar{\mu} = q \times \bar{d}$; it goes from the least electronegative atom to the most electronegative and has a “module” that can be considered equal to the difference of electronegativity.

Only if the dipole vector has a module >0.4 the bond can be considered polar covalent, otherwise the bond is nonpolar covalent, in the case that the difference is >1.8 the bond is ionic. The molecular dipole is the vector sum of the bond dipoles, usually in symmetric molecules the vectors cancel each other and the molecule results nonpolar.

Lewis structures

The lewis structures are used to predict the structure of the molecules from their molecular formula, to predict the atomic hybridization and to predict the electrostatic properties.

Octet rule = it is a condition of stability to have 8 electrons in the outer shell (reaching the configuration of a noble gas).

In the case of atoms of the third group it is possible to put much more than 8 electrons in the outer shell because it is also available in the 3d orbital.

1. Identify the **central atom** as the **least electronegative** (electronegativity proportional to ionization energy and electron affinity).
2. Make a **sigma bond** between the central atom and each of all other atoms.
3. **Sum all the electrons** in the outermost shell of all atoms in the molecule, adding the molecule negative charges and removing the molecule positive charges.
4. **Place all possible electrons** on the external atoms of the molecule until the octet rule is satisfied.
5. **Place the remaining electrons**, if available, on the central atom as non-bonding electron pairs.
6. Determine the **molecular geometry** using **VSEPR**.

The geometric structure of a molecule depends on the topology of the electron pairs around the atoms (bonding and non bonding electron pairs=n)

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2					
3					
4					
5					
6					

7. **Redistribute the electrons** to have all atoms respect the octet rule and to decrease to a minimum the charge separation.

Charge separation = presence of two atoms with formal charges of opposite sign

Formal charges are determined by comparing the number of electrons associated with an atom in a lewis structure with the number of electrons that would be associated with the isolated atom

Formal charge = valence electrons - (non bonding electrons + bonding electrons / 2)

The Lewis structure with the minimum charge separation is more stable than each structure with a larger charge separation.

To reduce charge separation we move one pair from the one other the terminal atoms to form multiple bonds between the central atom and the terminal atom.

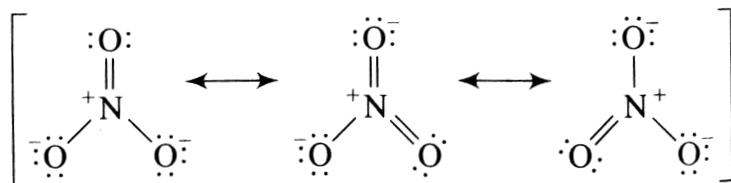
In most cases by reducing the charge separation we are also satisfying the octet rule, when there is no charge separation but the octet rule is not satisfied we have to generate charge separation to fulfil the octet of the central atom (octet rule is more important than charge separation!).

7.5. Represent eventual **resonance structures**: one or two or more equally valid Lewis structures for a single species that cannot be represented accurately by a single Lewis structure.

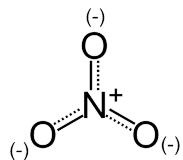
Different resonance structures have the same arrangement of the σ bonds, but differ from the position of the lone pairs and of the π bonds.

Neither resonance structure adequately represents the actual molecule. The actual structure is a mix of all the resonance structures for the same molecule.

Ex. NO_3



The correct and true structure of this molecule is in between these structures, it can be represented as:



8. Determine the presence, direction and verse of the molecular **electric dipole**.

Average charge

In the case of molecules that present resonance structures the charge of each atom must be computed as the mean of the charges of the same atom in the different structures.

First thing first we can determine the bond order of the molecule, it is a measure of stability of the molecule (lower is the bond order more stable is the molecule); it is calculated by dividing the number of bonds of the molecule by the number of resonance structures.

...ex. NO_3

$$\text{Bond order} = (1 + 1 + 2) / 3 = 1,3$$

$$\text{Average charge of oxygen} = (-1 + (-1) + 0) / 3 = -\frac{2}{3}$$

$$\text{Average charge of nitrogen} = (1 + 1 + 1) / 3 = 1$$

Oxidation number

The oxidation number (or oxidation state) is the charge an atom would have if the bonding electrons, of one of the possible molecules, were transferred completely to the most electronegative atom.

Oxidation numbers are determined by comparing the number of electrons associated with an atom in a lewis structure with the number of electrons that would be associated with the isolated atom:

Oxidation number = (valence e-) - (associated electrons, bonding electrons go to the most electronegative atom).

Carbon is in the middle of the period so it can assume a lot of oxidation numbers.

Stoichiometry

Stoichiometry studies the quantitative relationship between the masses of substances taking part in a chemical reaction.

The stoichiometry of reaction indicates in which relationship two or more substances react to each other.

Stoichiometric calculations allow us to calculate the quantities of reagents and products involved in a chemical reaction.

Chemical equations

A chemical process is represented by a chemical equation, each chemical species that appears to the left of the arrow is called reactant

Each chemical species that appears to the right of the arrow is called a product.

The equation must be balanced so that the same number of each kind of atoms appears on both sides of the reaction arrow

Sometimes the physical states of the chemical species of the reaction can be indicated through symbols (s=solid, l=liquid, g=gaseous, aq=aqueous).

The most common types of reaction are:

- Combination reactions
- Decomposition reaction
- Combustion reaction

Quantitative informations

A chemical equation provides quantitative informations on the reaction, we can determine:

- Relative mass of atoms: through the coefficients we know the ratio between the quantities of each species:

Ex.



36 g 4 g 32 g

$$(\text{mass of O}) = 16 \times (\text{mass of H})$$

Originally the masses were defined relatively to the mass of the hydrogen

Relative mass of H = 1 amu

Now atomic masses are defined relative to the mass of ^{12}C :

$$^{12}\text{C} = 12 \text{ amu}$$

$$^1\text{H} = 1.0078 \text{ amu}$$

- Average element mass: the mass on the periodic table is indeed an average mass, it is calculated as the weighted average considering the natural abundance of its isotopes.

Ex. lithium

^6Li : 6.015 amu (abundance: 7.42%)

^7Li : 7.016 amu (92.58%)

$$\begin{aligned} \text{Average mass} &= \\ &= (6.015 \text{ amu} \times 0.0742) + (7.016 \text{ amu} \times 0.9258) = \\ &= 6.941 \text{ amu} \end{aligned}$$

- Percentage composition: we can find the ratio between the species in a compound.

Ex.

Element percentage composition in H_2O :

$$\begin{aligned} 2 \text{H} &= 2 \times 1.0078 \text{ amu} = 2.0156 \text{ amu} \\ 1 \text{O} &= 15.9994 \text{ amu} \end{aligned}$$

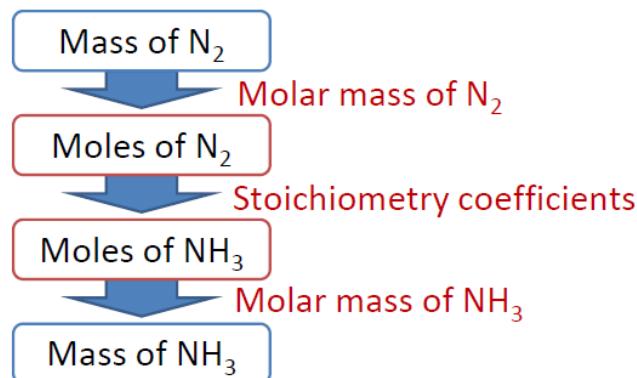
$$1 \text{H}_2\text{O} = 18.0150 \text{ amu}$$

$$\%(\text{H}) = (2.0156 \text{ amu} / 18.0150 \text{ amu}) \times 100 = 11.19\%$$

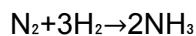
$$\%(\text{O}) = (15.9994 \text{ amu} / 18.0150 \text{ amu}) \times 100 = 88.81\%$$

- Mole: the mole is constituted by 6.02×10^{-23} items
That's defined so that 12 g of ^{12}C correspond to a mole of ^{12}C , an atom of C weights 1.993×10^{-23} g.
 $12 / 1.993 \times 10^{-23} = 6.02 \times 10^{-23}$ items
This number is defined as Avogadro's number (N_A)
- Molar mass: the molar mass of a substance is the mass of 1 mole expressed in grams, it corresponds numerically to the weight expressed in amu.

Stoichiometry calculations



Ex.



Supposing we have 1g of N_2 , using the molar mass we know that it corresponds to: $1\text{g}/(2 * 14.01 \text{ amu}) = 3.57 \text{ E-2 moles of N}_2$.

1 mole of N_2 reacts with 3 moles of H_2 to give 2 moles of NH_3 .

So we obtain double the moles of NH_3 , namely 7.14 E-2 moles ; which correspond to $(7.14 \text{ E-2}) * (3 * 1.008 \text{ amu} + 14.01 \text{ amu}) = 1.216 \text{ g NH}_3$

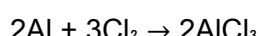
Limiting reactant

Often substances that react with each other are not present in exactly the mass proportion stated by the stoichiometric coefficients of the balanced equation.

The reaction ends when one of the reagents has been completely consumed.

The reactant used up first in a reaction is the limiting reactant, while excess reactants are those present in quantities greater than necessary to react with the quantity of the limiting reactant.

Ex.



Calculate the maximum amount of AlCl_3 that can be prepared starting from

40.0 g of Al

213 g of Cl_2

$$n\text{Al} = 40.0 \text{ g} / 26.98 \text{ g/mol} = 1.48 \text{ mol}$$

$$n\text{Cl}_2 = 213 \text{ g} / (2 * 35.45 \text{ g/mol}) = 3.00 \text{ mol}$$

To compare the quantities we need to determine the equivalents, we have to divide for the stoichiometric coefficient.

$$n\text{eAl} = 1.48 / 2 = 0.74 \quad \text{limiting reactant!}$$

$$n\text{eCl}_2 = 3.00 / 3 = 1.00$$

To form the product chlorine consumes faster than aluminium, more precisely, every two moles of aluminium we consume three moles of chlorine, we have to keep this into account in the determination of the limiting reactant: equivalents are a perfect way to do so.

Reaction yield

The theoretical amount of product formed in a reaction is the theoretical yield of the reaction.

It refers to the end of the reaction, when the limiting reactant is completely consumed.

The theoretical yield is the maximum theoretical amount of product that can be yielded from a reaction.

The actual yield is the amount of product **actually obtained from a reaction**, it is **smaller** than the theoretical one, that is because usually reactions are not completely shifted toward the products or because by mixing several species you could obtain side reactions.

We can define a percent yield for each reaction: $\%yield = \frac{actual\ yield}{theoretical\ yield} * 100$

...ex.

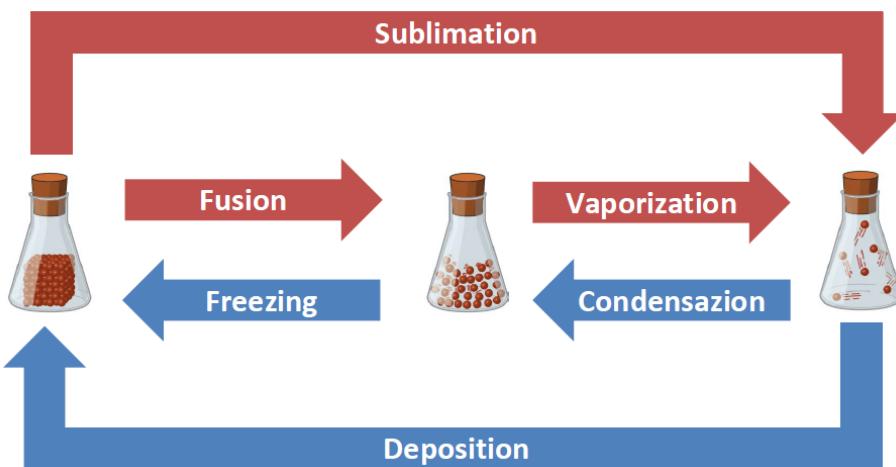
To reach the moles of AlCl₃ we have to multiply the equivalents (moles) of the limiting reactant for the stoichiometric coefficient of AlCl₃.

$$nAlCl_3 = 0.74 * 2 = 1.48 \text{ moles}$$

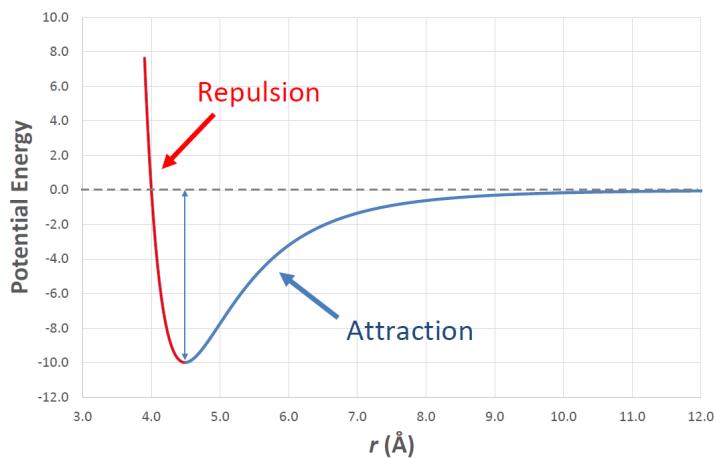
$$mAlCl_3 = n * M_{mol} = 1.48 \text{ mol} * (26.98 + 3 * 35.45) \text{ g/mol} = 167.7 \text{ g} \text{ (theoretical yield)}$$

INTERMOLECULAR BONDS

Every chemical species has all these three physical states:

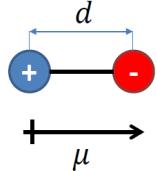


To go from one state to another we need to break or form bonds between the molecules. The intermolecular bonds are equal to interatomic bonds but lower forces are engaged.



Plot of the interaction between two molecules.

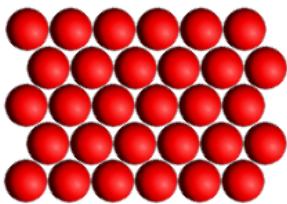
Intermolecular interactions are mainly due to electrostatic interactions between ions and electric dipoles



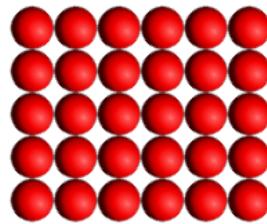
Type of bonds

- **Ion - ion (ionic solids)**

In the ionic bonds the atoms are not at their maximum packing potential:



Maximum packing



Poor packing

The shape of the ionic compounds depends on the ratio between the species.

Ionic radius:

The size of ions is not equal to the size of the uncharged atom of the same element.

- Cations: usually cations come from elements of the first and second group, they lose all the electrons of the outer shell to reach the configuration of the previous noble gas.
That is why cations are smaller than the uncharged atoms, they have completely lost an orbital.
- Anions: usually anions come from elements of the sixth or seventh group, they gain electrons in order to reach the configuration of the nearest noble gas.
Anions have a bigger radius than neutral atoms because the repulsion between the electron increases and the electrons start occupying more space.

Ex. sodium chloride

In sodium chloride the radius of the sodium cation is smaller than the radius of chlorine anion, even though normally sodium is bigger than chlorine.

Properties:

- High melting temperatures
- Hard and brittle, when a line of atoms is shifted, particles with the same sign align, generating repulsive forces all along a plane in the whole lattice
- Soluble in polar solvents
- Low electric conductivity in the solid state
- High electric conductivity in the molten state

- **Ion - dipole**

Interactions occurring in solutions of ionic compounds in polar solvents.

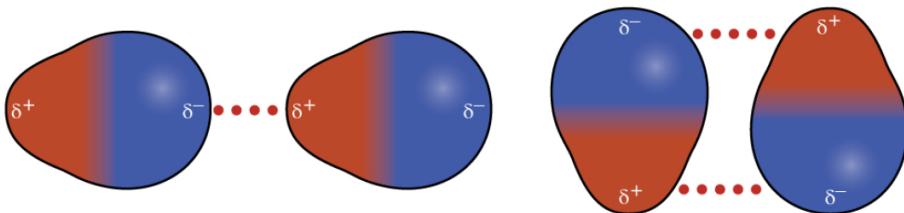
If the ionic compound is negatively charged the polar molecules orient the positive part toward the ion otherwise the positive ion attracts the negative part of the polar molecule.

Ex. salt in water

When we mix salt in water we have a complete dissociation of the ions, the oxygens (with partial negative charge) start to surround the Na^+ cations while the hydrogens (partially positive) get arranged around the Cl^- anions.

- **Dipole - dipole**

Two molecules that present a positive and a negative end can arrange in a way to have an electrostatic interaction. (two possible dispositions in a tridimensional space).



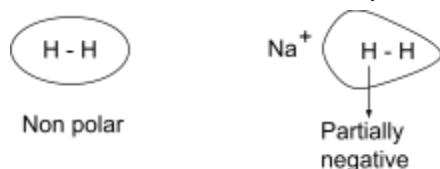
- **Ion - induced dipole**

Interactions between ionic compounds in non-polar solvents.

The force of the interactions depends on the polarisability (α) of the non-polar molecule; a higher polarisability corresponds to a molecule that can become very polar, it increases with the increasing of the number of atoms of the molecules or by increasing the atomic number (large atoms).

Ex.

H-H is neutral, if a positive charge get's near to diatomic hydrogen its orbital gets deformed and the molecule polarises

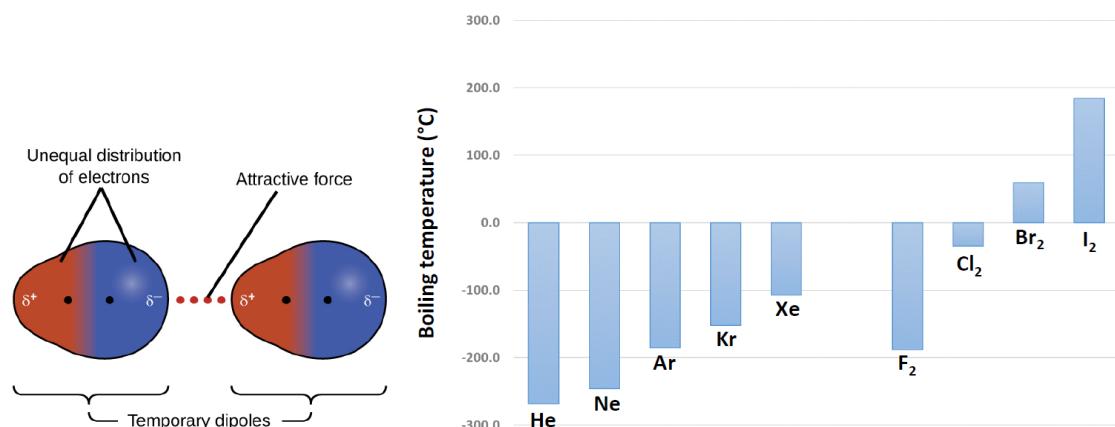


The polarisability is high for the first groups and minimum for the noble gases, it increases as the atom gets bigger (the last periods have higher polarisability)

- **Induced dipole - induced dipole**

The forces engaged in this case are called London forces or dispersion forces.

The interaction verifies between two instantaneous dipoles

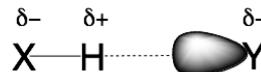


Higher is the polarisability of two atoms, higher is the possibility to form London forces. Larger is the molecule, larger is the polarisability.

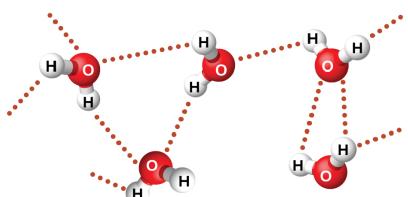
All the forces seen so far can be grouped in the Van der Waals forces.

- **Hydrogen bond**

The hydrogen bond is formed between an atom of a **very electronegative element** (Y) carrying a nonbonding **electron pair**, and an atom of a **very electronegative element** (X) bound to a **hydrogen atom** (H).



The hydrogen bond has both electrostatic (interaction between charges) and covalent (overlap of H orbital and lone pair) character and it is directional (the hydrogen atom is aligned with the two electronegative atoms).



In water there are 4 H bonds for each molecule

In this case oxygen has an sp³ hybridisation, it forms a specific and strict reticoli with big empty space, in liquid water the bonds are formed and destroyed, so the molecules are more free to compact.

For this reason the volume of solid water (ice) is bigger than liquid water.

Hydrogen bonds are the forces that keep together the two strands of the DNA.

Comparison of the Energies Associated with Bonding (Intramolecular) Forces and Intermolecular Forces

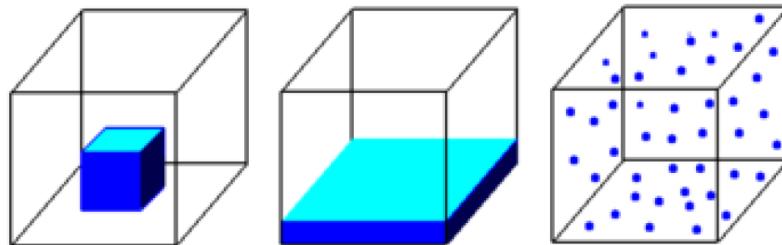
Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Intramolecular				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e ⁻ pair	150–1100	H–H
Metallic		Cations–delocalized electrons	75–1000	Fe
Intermolecular				
Ion-dipole		Ion charge–dipole charge	40–600	$\text{Na}^+ \cdots \text{O}-\text{H}$
H bond		Polar bond to H-dipole charge (high EN of N, O, F)	10–40	$\text{:O}-\text{H} \cdots \text{:O}-\text{H}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \text{I}-\text{Cl}$
Ion-induced dipole		Ion charge–polarizable e ⁻ cloud	3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		Dipole charge–polarizable e ⁻ cloud	2–10	$\text{H}-\text{Cl} \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable e ⁻ clouds	0.05–40	$\text{F}-\text{F} \cdots \text{F}-\text{F}$

States of matter

All substances can exist in either of these three states (solid, liquid, gas) depending on the temperature.

The temperature is a measure of the overall kinetic energy, when the kinetic energy is larger than the interaction energy the molecules are not aggregated anymore, they do not interact and therefore enter the gas phase.

$$\langle E_{kinetic} \rangle = \frac{\frac{1}{2} \sum_{i=1}^N m_i v_i^2}{N} \quad \langle E_{kinetic} \rangle \propto T$$



Solid	Liquid	Gas
Holds shape	Shape of container	Shape of container
Fixed volume	free surface	Volume of container
$\langle E_{kinetic} \rangle \ll E_{intermolecular}$	Fixed volume	$\langle E_{kinetic} \rangle > E_{intermolecular}$
	$\langle E_{kinetic} \rangle < E_{intermolecular}$	

Gases

We consider gases as ideal gases, to give them standard properties.

1. Particles are considered as points with null volume
2. The molecules are in constant chaotic movement
3. The collisions between molecules and between the molecules and the walls are considered elastic, the overall kinetic energy is constant.

From this assumptions we can derive a law to describe a generalised behaviour of gases

We will track four measurable parameters:

- Pressure
- Volume
- Temperature
- Number of atoms/molecules

In order to infer a law we do experiments, it is useful to keep 2 parameters fixed at a time to see the relation between the other two:

- Avogadro's law: T and P constant

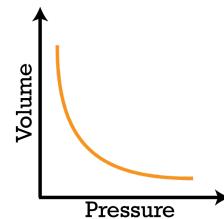
$$V \propto n_{P,T}$$

By increasing the number of molecule on a gas the space that it occupies increases

- Boyle's law: n and T constant

$$V \propto \frac{1}{P_{n,T}}$$

By increasing the pressure of a gas the volume decreases

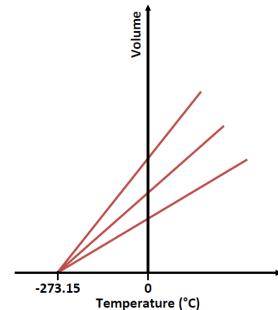


- Charles' law: n and P constant

$$V \propto T_{n,P}$$

By increasing the temperature of a gas the volume increases

By repeating the experiment multiple times we obtain different plots depending on the gas we use; the important result is that all the lines converge to $V=0$, at a temperature of -273°K , defined as absolute zero in the kelvin scale.



General equation of ideal gases

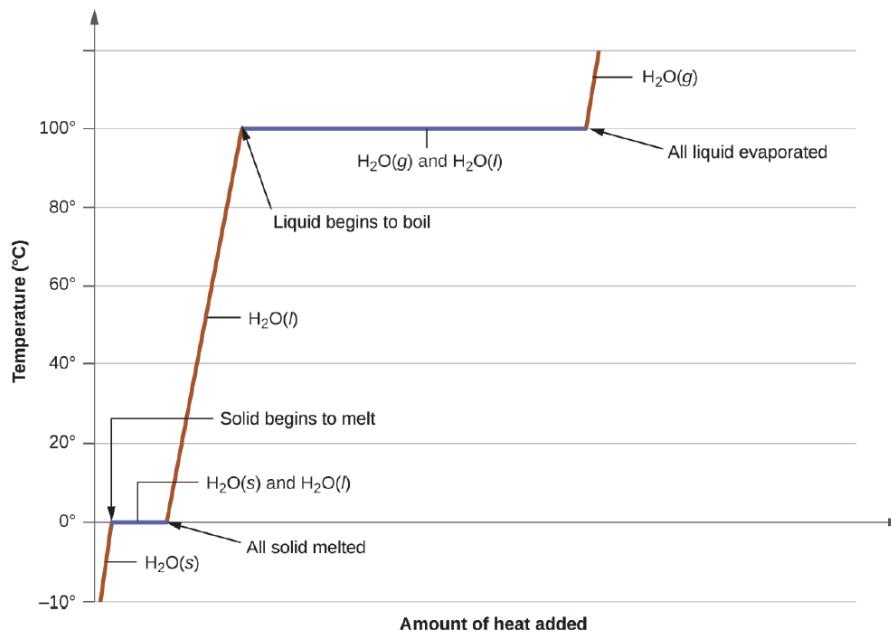
By combining all the results that we have experienced we reach this proportion:

$$V \propto \frac{nT}{P}$$

By adding a constant we can use this formula to obtain precise values for ideal gases:

$$PV = nRT$$

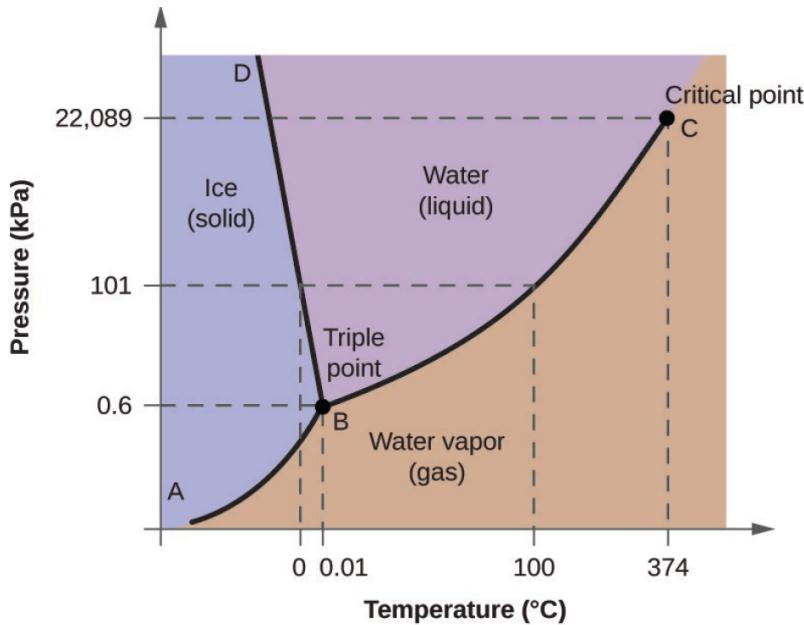
Phase transitions



This is the profile of every chemical compound that gets heated, during the transitions from a physical state to another, even if heat is continuously added, the temperature remains constant. This plot depends on the pressure, if the pressure increases the boiling temperature decreases:

$$P \propto \text{boiling} T$$

We can represent the relationship between the heat and the pressure in a single graph (phase diagram):

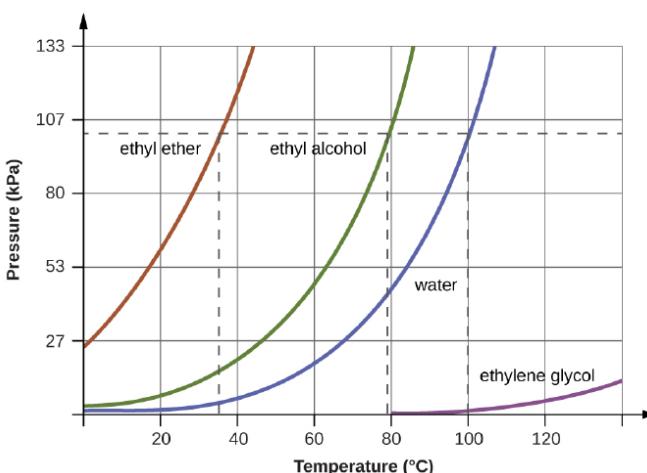


The black lines represent the **phase transitions**, we can see that at normal pressure the first transition for water is at 0°C, the sample will remain at this temperature until it will be all melt, the second phase transition is at 100°C, as far as we are on a line the two phases coexist. If we consider room temperature we can see how, by reducing the pressure, we can go from the liquid state to the gas.

The three lines converge in the **triple point**, it is an equilibrium point that permits the coexistence of the 3 states.

If the pressure is less than the triple point pressure we have only 1 transition phase, from solid to gas (vaporation).

We can also plot the amount of particles in liquid and gaseous state in relation with pressure and temperature:



By doing so we can see the link with the kinetic energy, at room temperature, at sea level, a little amount of particles is in vapour state, by increasing the temperature we can see how the number of gaseous molecules increases (we can measure the number of molecules in gas state by using the equation of noble gases), it is a physical equilibrium. The amount of gaseous particles at room temperature and sea level constitutes the vapour pressure of a liquid.

MIXTURES

Mixtures have variable compositions.

- heterogenous: the macroscopic properties indicate the presence of different substances (different in different parts of the mixture)
- homogenous (solution): if the macroscopic properties are identical in different portions of the mixture (there exist also solid solution)

Solutions

- Solution: homogeneous mixture of a solute in a solvent.
- Solute: substance present in homogeneous mixture in relatively smaller amounts.
If the particles of the solute are small we have an actual solution.
If the particles of the solute are large we have a suspension or a colloid (depending on the nature of the solvent).
- Solvent: substance present in a homogenous mixture in relatively larger amounts.

To describe a solution we need a way to specify the amount of solute and solvent, we can achieve this through the concentration:

The concentration of a solution is the amount of solute dissolved in a given quantity of solvent

- Dilute solution: small amount of solute in solvent
- Concentrated solution: large amount of solute in solvent

Concentration units:

- Percent by mass or percent by weight (wt%):

$$wt\% = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$$

- Percent by volume (vol%):

$$vol\% = \frac{\text{volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$$

- Molarity (M):

$$M = \frac{\text{Moles of solute (mol)}}{\text{Volume of solution (L)}}$$

- Molality (m):

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

- Molar fraction (X):

$$X_A = \frac{n_A}{n_A + n_B + n_C + \dots}$$

Dilution

The dilution is the process of reducing the concentration of a solute in solution, usually simply by mixing with more solvent (it is easy to dilute a solution, it is difficult to concentrate it).

The amount of solute does not change:

Initial concentration $M_1 = n * V_1$

Now we add some solvent: $V_2 = V_1 + \Delta V$

New concentration $M_2 = n * V_2$

The number of moles (n) doesn't change.

We can infer this proportion

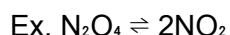
$$M_1 * V_1 = M_2 * V_2$$

CHEMICAL REACTIONS

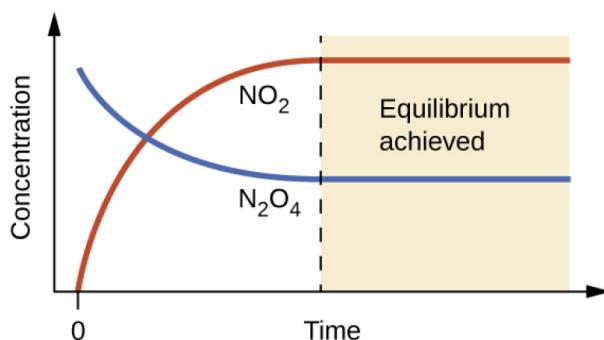
Thermodynamics is the branch of chemistry that studies the initial and final conditions of a chemical transformation process that occurs in a system.

Chemical kinetics on the other hand studies the rate and the mechanism of a chemical reaction.

Every chemical reaction consists in a transformation, the transformation is never complete, at the end of a reaction an equilibrium is reached, we use a double arrow between the reactants and the products to represent that.



After a certain Δt we reach constant concentrations of the reactant and the product.



Apparently the concentration of reagents and products do not change, however, at the microscopic level, both the direct and the inverse reactions are still happening at the same rate. We can demonstrate this through this reaction: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

We have to prepare 2 separate reactions, one of them with normal hydrogen, while the other with deuterium (hydrogen with 2 neutrons).

As long as the reactions remain separated the inverse reaction will form diatomic molecules of hydrogen or deuterium; while when we mix them molecules of hydrogen-deuterium will be formed.

Spontaneity of a reaction

Not all the reactions occur spontaneously, the spontaneity depends on the initial conditions of the reaction, through thermodynamics we can study these conditions:

Types of systems

- Open system: both energy and mass can be exchanged between the system and the environment.
- Closed system: energy, but not mass, can be exchanged between the system and the environment.
- Isolated system: neither energy nor mass can be exchanged between the system and the environment.

The forms of energy that are exchanged between the system and the environment are heat (energy transferred because of a difference in temperature) or work (force x movement).

Exothermic reaction: heat is transferred from the system to the environment

Endothermic reaction: heat is transferred from the environment to the system.

To measure the heat produced by a chemical reaction it can be carried out in a closed system, surrounded by water, and then we can keep track of the temperature of water to see which type of interaction there is between the reaction and the environment.

The ensemble of the closed system and the surrounding environment is a good approximation of an isolated system.

To measure the work carried out by a chemical reaction we can put the reaction into a container, with a piston; by measuring the difference in volume of the container after the reaction (the movement of the piston) we can compute the work.

Internal energy (U)

First principle of thermodynamics:

Every system possesses an internal energy (U), given as the sum of kinetic energy (proportional to T) and the potential energy (function of chemical bonds) of all the components of the system

The internal energy U of an isolated system is constant

The internal energy of a closed system can increase(or decrease) as an effect of a heat transfer from the environment (or form the system) to the system(or to the environment) (increase or decrease of T).

The internal energy of a closed system can increase(or decrease) as an effect of work made on the system(or by the system) by the environment (on the environment).

$\Delta U = q - w$ if $\Delta U = 0$ the system is isolated, we just care about the **variation** in a closed system

The internal energy is a state function: a property that is determined by the state of the system, regardless of how that condition was achieved.

If a transformation occurs at constant volume, the work exchanged between the system and the environment is null, so the variation of the internal energy corresponds to the exchanged heat.

$$\Delta U = q_v$$

Enthalpy (H)

Enthalpy is defined as: $H = U + PV$

(internal energy + pressure of the system * volume of the system)

Enthalpy is a state function.

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

At constant pressure: $\Delta P = 0$, then: $\Delta H = \Delta U + P\Delta V$

$$\Delta U = q - w$$

$$\Delta H = q - w + P\Delta V$$

$w = P\Delta V$ If the work is only expansion/compression

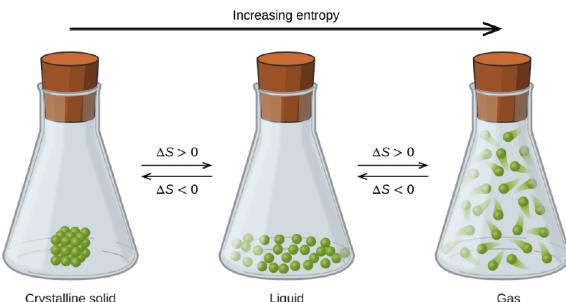
$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q_p$$

In an **exothermic reaction** at constant pressure $\Delta H < 0$
 In an **endothermic reaction** at constant pressure $\Delta H > 0$

Entropy (S)

Entropy is defined as the molecular disorder of a system, it is a state function



The greater the disorder, the greater the entropy

Second principle of thermodynamics:

The entropy of an isolated system increases during a spontaneous reaction

Third principle of thermodynamics:

The entropy of a perfect crystal is zero at T=0K

Gibbs free energy (G)

The gibbs free energy is defined as the amount of heat produced in a chemical reaction that can be transformed in work, it is a state function:

$$\Delta G = \Delta H - T\Delta S$$

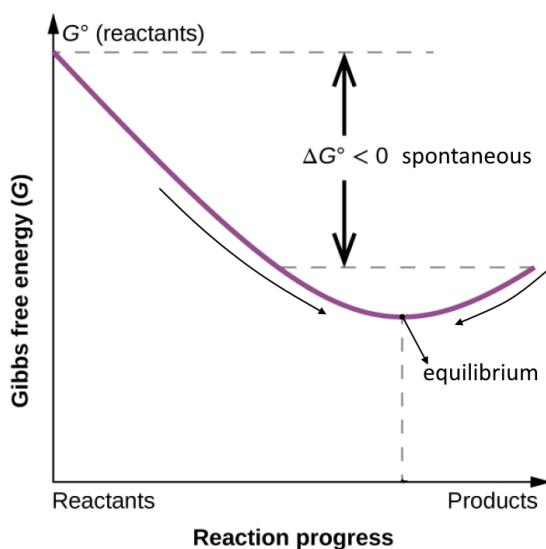
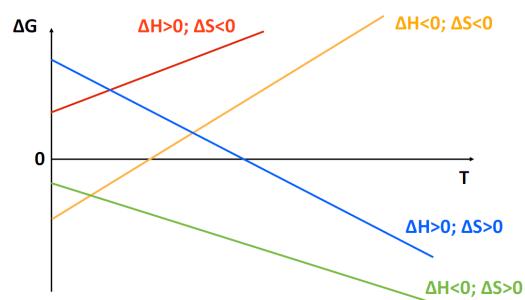
A reaction is spontaneous if $G < 0$

A reaction is not spontaneous if $G > 0$

If $G = 0$ the reaction is at the chemical equilibrium.

spontaneity:

- $\Delta H < 0 ; \Delta S > 0 \Rightarrow \Delta G < 0$ (**spontaneous**)
- $\Delta H > 0 ; \Delta S < 0 \Rightarrow \Delta G > 0$ (**not spontaneous**)
- $\Delta H < 0 ; \Delta S < 0 \Rightarrow$ the spontaneity depends on T
- $\Delta H > 0 ; \Delta S > 0 \Rightarrow$ the spontaneity depends on T

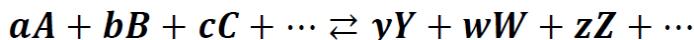


In this example, a certain quantity of products is produced spontaneously, we reach a ratio between reactants and products, this is the equilibrium, from now on the reaction is not spontaneous.

Any movement from the equilibrium is not favoured

Equilibrium constant

For any chemical reaction:



It is possible to show that:

$$Q_c = \frac{[Y]^y[W]^w[Z]^z \dots}{[A]^a[B]^b[C]^c \dots}$$

Where Q_c is the reaction quotient and the concentrations are **not those at the equilibrium**.

We can compute the reaction quotient in any moment of the reaction, when products are not yet formed the reaction quotient is equal to zero.

Moreover is possible to show that:

$$\Delta G = \Delta G^\circ - R T \ln Q_c$$

ΔG° is the variation of gibbs free energy at standard conditions: all species in solution are 1M, $P=1$ atm for gas species, $T=298.15$ K

Through the standard variation we can compare chemical reactions, we can calculate a value of energy by measuring the concentrations.

If we are at the equilibrium, $\Delta G = 0$:

$$0 = \Delta G = \Delta G^\circ + R T \ln Q_c$$

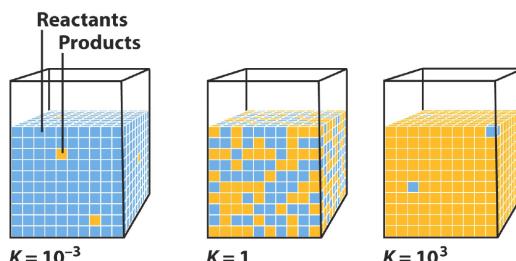
In this case we have to use a particular reaction quotient, the equilibrium quotient or equilibrium constant K_c .

$$\Delta G^\circ = -R T \ln K_c$$

$$K_{eq} = K_c = \frac{[Y]^y[W]^w[Z]^z \dots}{[A]^a[B]^b[C]^c \dots}$$

K_{eq} is a constant, it depends only on temperature.

K_c is a measure of the spontaneity of a reaction to occur, more negative is ΔG° , largest is K_c , the reaction is spontaneous.



The knowledge of K_{eq} allows us to predict if a reaction will evolve towards the products or the reagents: we will only have to compare K_{eq} and Q_c :

- If $Q_c < K_{eq}$, the reaction will form more products.
- If $Q_c > K_{eq}$, the reaction will form more reagents.
- If $Q_c = K_{eq}$, the reaction will be at equilibrium.

Le Chatelier - Brown principle

If we have a reaction at a chemical equilibrium, the parameters that determine it are: T, P, V. When we change one of these the system will go off from the equilibrium, and it will evolve in a direction that will **contrast the changes** imposed from the environment..
Ex. $Q=[P]/[R]$ if [R] increases, Q_c decreases and the reaction will form products, until the equilibrium will be reestablished ($Q_c=K_c$).

Heterogeneous equilibria

The concentration of a pure solid or liquid is independent from the amount of substance and it is, therefore, constant during a reaction.

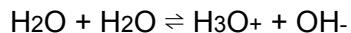
The equilibrium constant for heterogeneous equilibria does not contain the expression for the concentration of pure solids or liquids taking part in the reaction.

Chemical equilibria in aqueous solutions

We consider equilibria in water because water has some useful properties:

- It forms dipole-dipole interaction
- It forms up to 4 hydrogen bonds
- It has high vapour pressure
- It has high surface tension: the terminal molecules of a drop of water are only attracted by the inner ones, this results in a strong film along the surface.
- It is amphiprotic

In pure water or in aqueous solution the following equilibrium always occurs:



Water is amphiprotic, that is a molecule which can act as either a donor or an acceptor of protons (H^+ ions).

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1 * 10^{-14}$$

This means that, In pure water:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 1 * 10^{-7}$$

Operator p

p is a mathematical operator: $p(f) = -\log(f)$:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

ex. pH in pure water is equal to $-\log(10^{-7}) = 7$, it is considered the neutral pH.

$$\text{pOH} = -\log[\text{OH}^-] = 7 \text{ in pure water}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

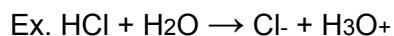
$$\text{pKw} = -\log(K_w) = \text{pH} + \text{pOH} = 14$$

Acids and bases

Arrhenius

By adding a substance in water we can see what effect it produces:

An acid is a substance that, added to water, produces H_3O^+ .



A base is a substance that, added to water, produces OH^- .



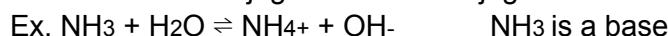
This definition is limited to the reaction of compounds with water.

Bronsted - Lowry

An acid is a substance that transfers a proton (H^+ ion) to another substance behaving like a base, forming its conjugate base.

A base is a substance that accepts a proton from another substance behaving like an acid, forming its conjugate acid.

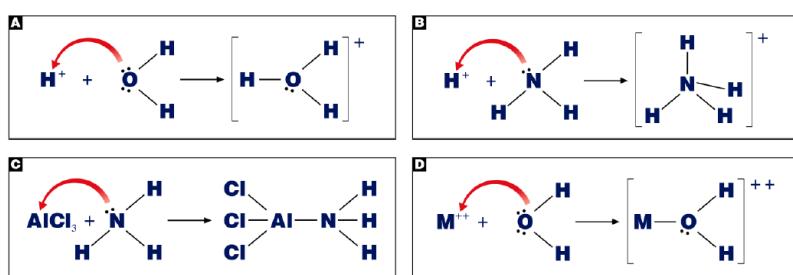
Conjugate acid/base pairs:



This definition is limited to proton transfer.

Lewis

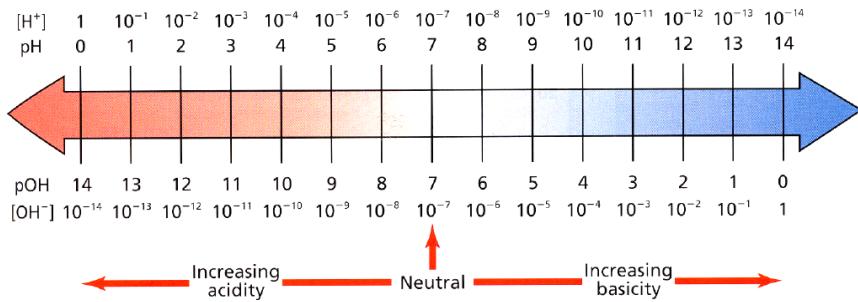
A lewis acid is a substance that accepts a non-bonding electron pair from another substance, which behaves like a lewis base



pH

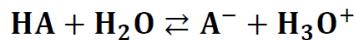
$$pK_w = pH + pOH = 14$$

- In **acidic solution**: $[\text{H}_3\text{O}^+] > 10^{-7} \Rightarrow pH < 7$
- In **acidic solution**: $[\text{OH}^-] < 10^{-7} \Rightarrow pOH > 7$
- In **basic solution**: $[\text{H}_3\text{O}^+] < 10^{-7} \Rightarrow pH > 7$
- In **basic solution**: $[\text{OH}^-] > 10^{-7} \Rightarrow pOH < 7$
- **pH can be > 14 (pOH can be < 0)**
- **pH can be < 0 (pOH can be > 14)**



Solution of an acid or base in water

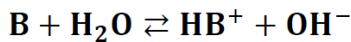
acid:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \text{acid dissociation constant}$$

$$pK_a = -\log(K_a) \quad K_a = 10^{-pK_a}$$

base:



$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} = \text{base hydrolysis constant}$$

$$pK_b = -\log(K_b) \quad K_b = 10^{-pK_b}$$

Acid-base conjugate pair

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ ; \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- ; \quad K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]}$$

$$K_a * K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} * \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

$$pK_a + pK_b = pK_w = 14$$

K_a is inversely proportional to K_b .

A strong acid has $K_a > 1$ ($pK_a < 0$)

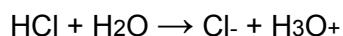
A weak acid has $K_a < 1$ ($pK_a > 0$)

In a conjugate acid-base pair, the strength of the acid is inversely proportional to the strength of the base.

Reactions

Strong acid or base in water

Acid:



$K_a = 10000$, we can assume that the reaction is completely shifted to the products.

	HCl	H_2O	Cl^-	H_3O^+
Initial	C_a	-	0	10^{-7}
Change	$-C_a$	-	$+C_a$	$+C_a$
Equilibrium	0	-	C_a	$C_a + 10^{-7}$

$$K_a = \frac{[\text{Cl}^-][\text{H}_3\text{O}^+]}{[\text{HCl}]}$$

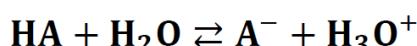
To measure the pH of a reaction we need to measure the concentration of H_3O^+ ions at the equilibrium; we assume that the initial concentration of the acid is far bigger than the quantity of ions produced by the autoprotolysis of water.

Eventually, in the case of a strong acid we have:

$$\text{pH} = -\log(C_a)$$

Weak acid or base in water

Acid:



Concentrations →	HA	H_2O	A^-	H_3O^+
Initial	C_a	-	0	10^{-7}
Change	$-x$	-	$+x$	$+x$
Equilibrium	$C_a - x$	-	x	$10^{-7} + x$

(10^{-7} is the concentration of $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ from water auto-protolysis)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(10^{-7} + x)x}{(C_a - x)}$$

approximations:

$$1) x \gg 10^{-7} \Rightarrow 10^{-7} + x \cong x$$

$$2) C_a \gg x \Rightarrow C_a - x \cong C_a$$

$$[\text{H}_3\text{O}^+] \cong x = \sqrt{K_a C_a}$$

True if:

$$\frac{10^{-7}}{10^{-7} + x} \times 100 < 3\% ; \frac{x}{C_a - x} \times 100 < 3\%$$

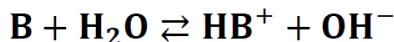
In any case, at the end of the reaction we will have a concentration x of the conjugate base and of H_3O^+ (the two components of the acid).

We can define the percent dissociation (α) as a measure of the quantity of dissociated acid in respect to the initial concentration:

$$\alpha\% = \frac{[\text{H}_3\text{O}^+]}{c_a} * 100 = \frac{x}{c_a} * 100$$

It gives us an idea of how much the equilibrium is shifted to the right.

Base:



Concentrations →	B	H_2O	HB^+	OH^-
Initial	c_b	-	0	10^{-7}
Change	$-x$	-	$+x$	$+x$
Equilibrium	$c_b - x$	-	x	$10^{-7} + x$

(10^{-7} is the concentration of $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ from water auto-protolysis)

$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} = \frac{(10^{-7} + x)x}{(c_b - x)}$$

$$[\text{OH}^-] \cong x = \sqrt{K_b c_b}$$

Percent hydrolysis (or percent protonation):

$$\alpha\% = \frac{[\text{OH}^-]}{c_b} \times 100 \cong \frac{x}{c_b} \times 100$$

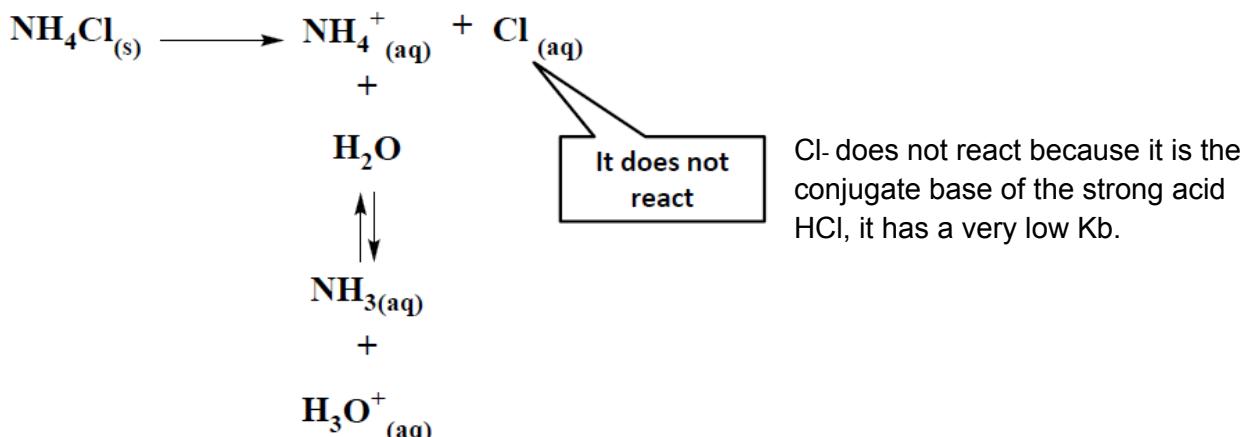
Salt hydrolysis

The ions produced by the dissociation of a salt in solution can react with water to produce either OH^- ions or H_3O^+ ions.

This is called salt hydrolysis

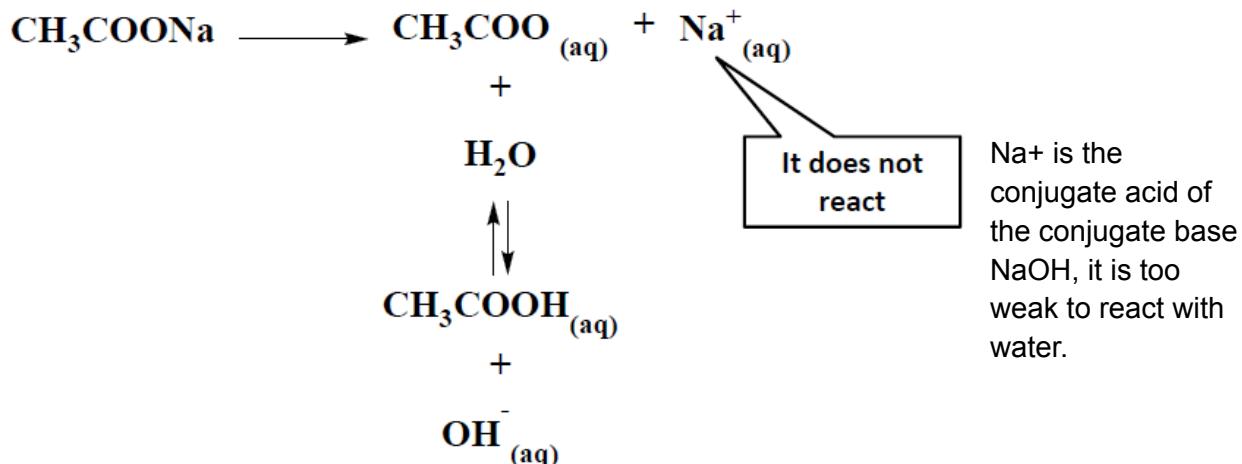
Acid hydrolysis

A cation that is the conjugate acid of a weak base reacts with water to give H_3O^+ ions

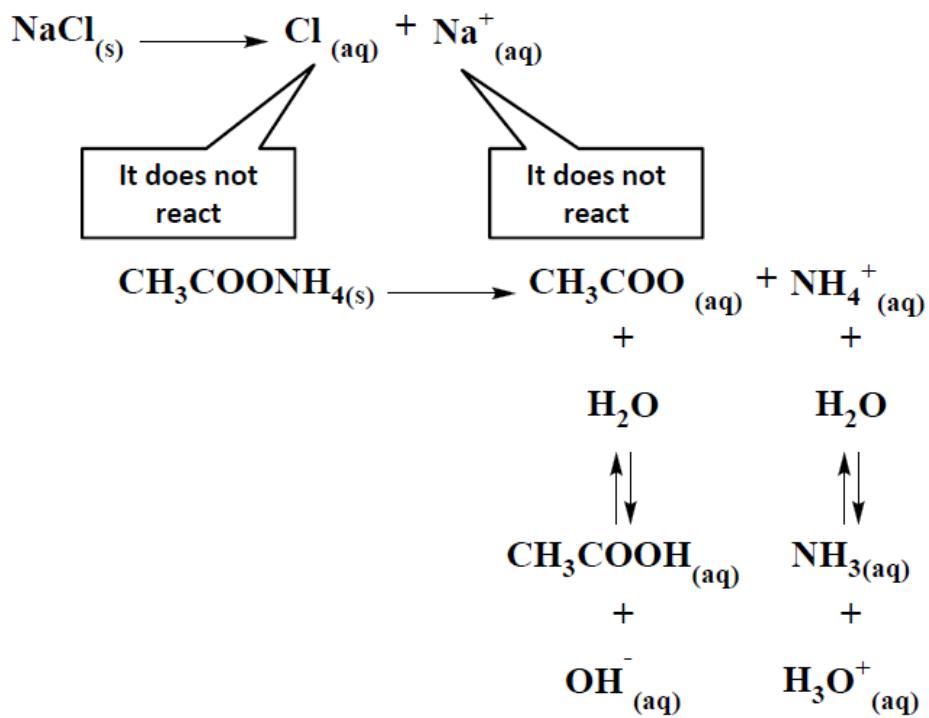


Basic hydrolysis

An anion that is the conjugate base of a weak acid reacts with water to give OH⁻ ions

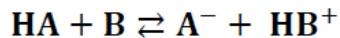


Neutral hydrolysis



- $K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_3) \Rightarrow \text{pH} = 7$

Reactions between an acid and a base



$$K_{eq} = \frac{[\text{A}^-][\text{HB}^+]}{[\text{HA}][\text{B}]}$$

$$K_{eq} \times \frac{K_w}{K_w} = \frac{[\text{A}^-][\text{HB}^+]}{[\text{HA}][\text{B}]} \times \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_3\text{O}^+][\text{OH}^-]}$$

$$K_{eq} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \times \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} \times \frac{1}{[\text{H}_3\text{O}^+][\text{OH}^-]}$$

$$K_{eq} = \frac{K_{a1} \times K_{b2}}{K_w}$$

Depending on the strengths of each reactant we get different cases:

- At least one strong reactant:

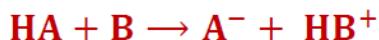
Strong acid with strong base

Strong acid with weak base

Weak acid with strong base

$$K_{eq} = \frac{K_{a1} \times K_{b2}}{K_w} \gg 1$$

The reaction is completely shifted to the right!



- Both weak reactants:

Weak acid with weak base

$$K_{eq} = \frac{K_{a1} \times K_{b2}}{K_w} \gg 1 \quad \text{se} \quad K_{a1} \times K_{b2} \gg K_w$$

The reaction is completely shifted to the right!

$$K_{eq} = \frac{K_{a1} \times K_{b2}}{K_w} \ll 1 \quad \text{se} \quad K_{a1} \times K_{b2} \ll K_w$$

In this case we need to calculate K_{eq} and apply the procedure to calculate the equilibrium concentrations of the reagents and products.

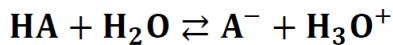
Buffer solutions

A buffer solution is a water solution containing both:

A weak acid and its conjugate base or a weak base and its conjugate acid

Properties:

- pH does not change with dilution
- pH undergoes only small changes upon addition of small amounts of strong acids or bases.



Concentrations →	HA	H_2O	A^-	H_3O^+
Initial	C_a	-	C_b	10^{-7}
Change	$-x$	-	$+x$	$+x$
Equilibrium	$C_a - x$	-	$C_b + x$	$10^{-7} + x$

N.B.: true if $Q_c < K_a$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = (10^{-7} + x) \times \frac{(C_b + x)}{(C_a - x)}$$

Assuming that: $10^{-7} \ll x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = x \times \frac{(C_b + x)}{(C_a - x)}$$

Assuming that: $x \ll C_a, C_b$

$$K_a = [\text{H}_3\text{O}^+] \times \frac{C_b}{C_a}$$

$$[\text{H}_3\text{O}^+] = K_a \times \frac{C_a}{C_b}$$

$$pH = pK_a - \log \left(\frac{C_a}{C_b} \right)$$

$$K_b = [\text{OH}^-] \times \frac{C_a}{C_b}$$

$$[\text{OH}^-] = K_b \times \frac{C_b}{C_a}$$

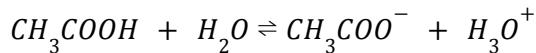
$$pOH = pK_b - \log \left(\frac{C_b}{C_a} \right)$$

Ex.

Calculate the pH of a buffer solution containing 0.321 M acetic acid and 0.281 M sodium acetate.

Buffer solution: $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$

In the solution we have both CH_3COOH and CH_3COO^- , the equilibrium of the dissociation of the acid will be affected:



To state the direction of the reaction we have to compute the reaction quotient:

$Q_c = 0$ because we still don't have any H_3O^+ ion, so $Q_c < K_a$

$$[\text{H}_3\text{O}^+] = k_a * \frac{c_a}{c_b} = 1.8 * 10^{-5} * \frac{0.321}{0.281} = 2.06 * 10^{-5} \text{M}$$

$$\text{pH} = 4.69$$

Adding a strong acid:

If we add $6.25 * 10^{-3}$ M HCl (it is a concentration, we can easily sum and remove it from the others):

$$[\text{H}_3\text{O}^+] = k_a * \frac{c_a + 6.5 * 10^{-3}}{c_b - 6.5 * 10^{-3}} = 1.8 * 10^{-5} * \frac{0.328}{0.275} = 2.15 * 10^{-5} \text{M}$$

$$\text{pH} = 4.67$$

The variation of pH is 0.02, in a non buffered solution it would have been 4.8

Dilution:

In a solution the pH is not affected because:

$$[\text{H}_3\text{O}^+] = K_a * \frac{n_a/V}{n_b/V} = K_a * \frac{n_a}{n_b} \quad \text{the volume simplifies away}$$

Strength:

The strength of the buffer is maximal when $C_a=C_b$, in these conditions $\text{pH}=pK_a$.

To buffer a solution at a given pH, we optimally use an acid/base conjugate pair so that $pK_a=pH$

The buffer best operates when C_a/C_b ratio is:

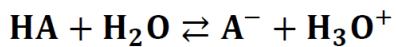
$$0.1 < C_a/C_b < 10$$

$$pK_a - 1 < pH < pK_a + 1$$

Prevalent chemical species at a fixed pH

Now that we are able to fix a solution to a specific pH it could be useful to know what happens to specific compounds at specific pH.

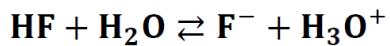
In the case of a buffer solution, by setting an arbitrary pH which quantities of acid and base do we expect to see?



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

What is the most abundant chemical species
at fixed pH?

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{A}^-]}{[\text{HA}]}$$



$$\begin{aligned} pH &= 7.0 \\ K_a &= 6.71 \times 10^{-4} \quad (pK_a = 3.17) \end{aligned}$$

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{6.71 \times 10^{-4}}{10^{-7}} = \frac{[\text{F}^-]}{[\text{HF}]} = 6700$$

For each molecule of HF present in solution
there are 6700 molecules of F⁻

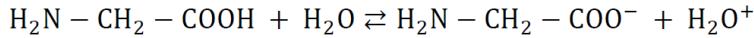
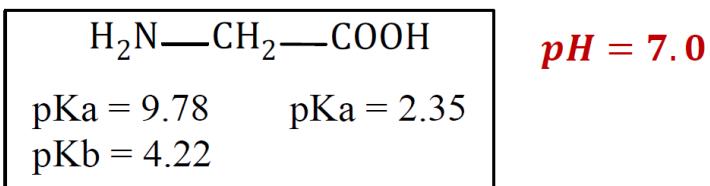
in summary:

$$\text{If: } pH < pK_a \Rightarrow [\text{HA}] > [\text{A}^-]$$

$$pH = pK_a \Rightarrow [\text{HA}] = [\text{A}^-]$$

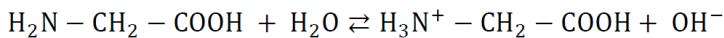
$$pH > pK_a \Rightarrow [\text{HA}] < [\text{A}^-]$$

ex.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-]}{[\text{H}_2\text{N}-\text{CH}_2-\text{COOH}]} = 10^{-pK_a} = 10^{-2.35}$$

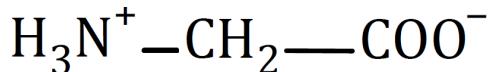
$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-]}{[\text{H}_2\text{N}-\text{CH}_2-\text{COOH}]} = \frac{10^{-2.35}}{1 \times 10^{-7}} \cong 4.5 \times 10^4$$



$$K_b = \frac{[\text{OH}^-][\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}]}{[\text{H}_2\text{N}-\text{CH}_2-\text{COOH}]} = 10^{-(pK_w-pK_a)} = 10^{-4.22}$$

$$\frac{K_b}{[\text{OH}^-]} = \frac{[\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}]}{[\text{H}_2\text{N}-\text{CH}_2-\text{COOH}]} = \frac{10^{-4.22}}{1 \times 10^{-7}} \cong 600$$

Zwitterion



Zwitterion: a molecule with two or more functional groups, of which at least one has a positive and one has a negative electrical charge and the net charge of the entire molecule is zero.
At physiological pH, the amino group of an amino acid is always in the protonated form, while the carboxyl group is always in the deprotonated form.

Titration

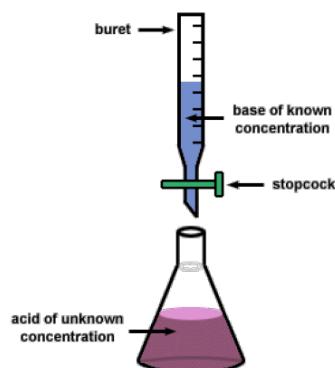
A titration is an analytical technique that has the goal to determine the concentration of a substance in a solution.

During a titration, measured volumes of a solution containing a known concentration of a reagent are added to a solution of another reagent whose concentration is unknown.

The reaction that we have to use must be:

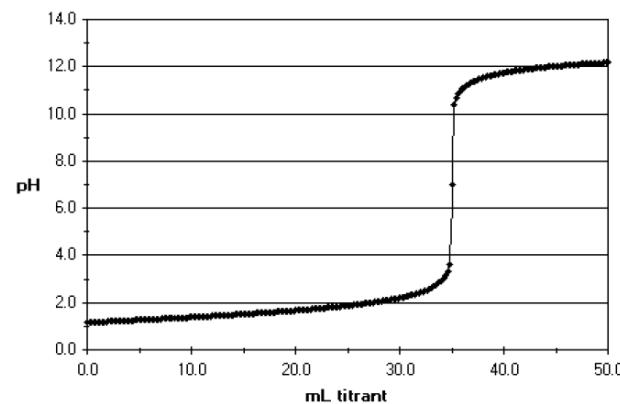
- Quick
- Complete
- With known stoichiometry

To satisfy these requirements the added reagent is usually a strong acid or base.



Strong acid titrated with NaOH:

When the moles of the unknown acid will be equal to the moles of the strong base, in stoichiometric amount, that we are adding, we will reach the equivalence point.



Equivalence point:

Before the equivalence point, the pH is determined by the concentration of unreacted acid (unknown).

The equivalent point occurs at pH=7.0

After the equivalent point the pH is determined by the excess of base.

At the equivalence point the titration is over and we are able to determine the concentration of the acid (or base):

$$[B] = M_B = n_B/V_T \quad (V_T \text{ is the amount of base used during the titration})$$

$$n_B = [B] * V_T$$

$$n_B = n_A \text{ (with respect to the stoichiometric coefficients)}$$

$$[A] = n_A/V_S = \frac{[B]*V_T}{V_S} = M_A \quad (V_S \text{ is the volume of the initial solution})$$

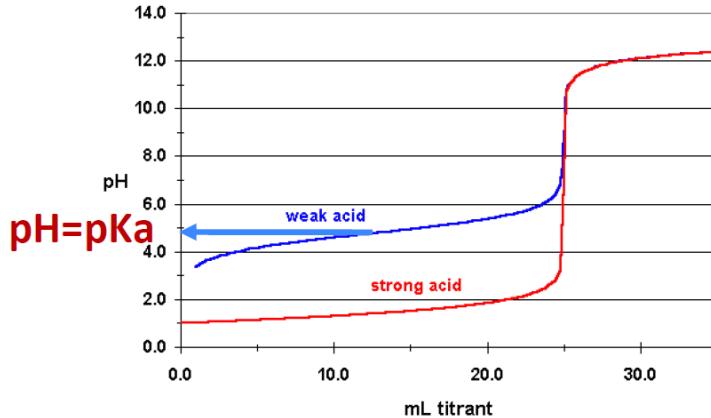
$$(M_A * V_S = M_B * V_T)$$

Weak acid titrated with NaOH:

The initial pH is higher than in the case of a strong acid.

When $0.1 < K_a/C_b < 10$ the solution is buffered and pH does not change much.

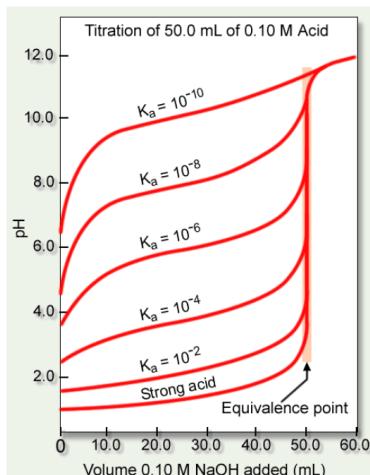
At the equivalence point, all HA has completely reacted with the base, therefore the pH of the equivalence point is determined by the hydrolytic reaction of the conjugate base



For $[HA]=[A^-]$ we have a $pH=pK_a$

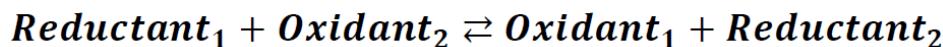
$$[\text{H}_3\text{O}^+] = K_a * C_a/C_b$$

$$K_a = [\text{H}_3\text{O}^+] * C_b/C_a \quad \text{if } C_a = C_b \text{ then } K_a = [\text{H}_3\text{O}^+] \text{ so } pH = pK_a$$



After the equivalent point the situation is always the same, for every acid, and the pH is determined by the excess of strong base

Electron transfer reactions



Reductant is an electron donor.

Oxidant is an electron acceptor.

One or more electrons are transferred from species 1 (reduced) to species 2 (oxidised) to yield the oxidised form of species 1 and the reduced form of species 2.

The reductant is oxidised during the reaction.

The oxidant is reduced during the reaction.

The oxidation number is used to keep count of the electrons transferred from the reductant to the oxidant.

The oxidation number is determined by assigning the electrons shared between two atoms to the more electronegative atom (WRITE THE LEWIS STRUCTURE).

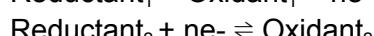
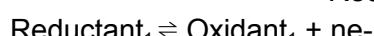
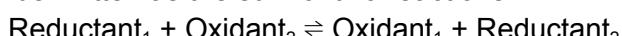
The overall sum of all oxidation numbers in a chemical species must be equal to the total charge of the molecule or ion.

The oxidation produces an increase of the oxidation number.

The reduction produces a decrease of the oxidation number.

Half-reactions

Each redox reaction can be written as the sum of two reactions:



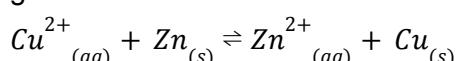
The half-reactions, when balanced, can be used separately to compose several different oxido reduction reactions.

The number of electrons exchanged in both equations is equal, by summing them the electrons simplify and we obtain a total equation.

Battery

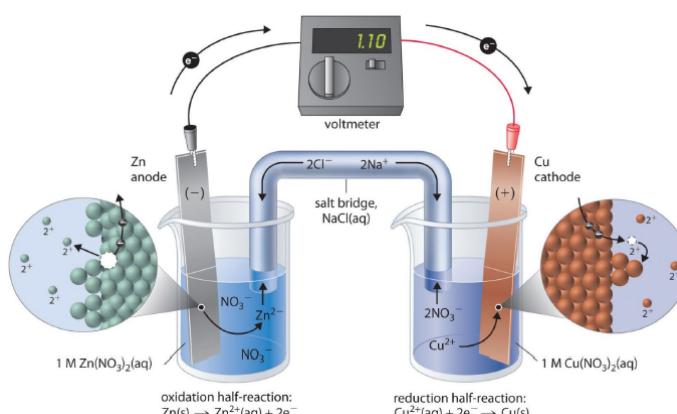
A battery is a source of electric energy that derives from chemical energy.

Most batteries use electron transfer reactions, and produce a movement of electrons that generates a current.

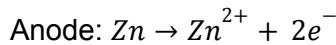
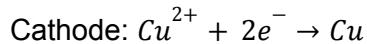


Decrease in oxidation number of Cu (oxidant).

Increase in oxidation number of Zn (reductant).



In the cathode is occurring the reduction while in the anode is occurring the oxidation (RED CAT: reduction cathode).



Physically we have the consumption of the zinc bar and the increasing in volume of the copper bar.

If the two solutions in which the bars are immersed were separated they would accumulate a huge number of charges, so a salt bridge is needed that permits the movement of charged ions to balance the charges; both solutions must have total charge equal to zero.

The electrons are travelling into the wire so we need another charge-travel to balance it.

The flow of electrons in the wire generates a current:

Electromotive force

The electromotive force is the difference between the spontaneity of the two semi reactions, the larger this difference, the larger is the spontaneity of the overall reaction.

$$\begin{aligned} EMF &= \Delta E^\circ = E^\circ_{\text{cat}} - E^\circ_{\text{an}} \\ &= E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \end{aligned}$$

In standard conditions $E = E^\circ$ and for each half reaction we have $E^\circ_{\text{reduction}} = -E^\circ_{\text{oxidation}}$

Nernst' equation

For a generic reaction, in non-standard conditions, we can find the reduction potential with the following formula:

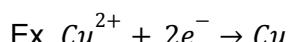
$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} = E^\circ + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

(The reduction potential depends on the concentration of the substances involved)

F = faraday constant; we use to group $\frac{RT}{F} \ln$.

The concentration of a pure solid or liquid in itself is independent of the amount of substance and is therefore constant during a reaction.

The equilibrium constant for heterogeneous equilibria does not contain the expression for the concentration of pure solids or liquids taking part in the reaction.



$$E_{\text{Cu}^{2+}/\text{Cu}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.059}{2} * \log[\text{Cu}^{2+}]$$

We always write $E_{\text{oxidised/reduced}}$; we do not consider the concentration of Cu because it is solid.

We apply this equation to each half reaction, the difference between the two values is the electromotive force:

$$EMF = \Delta E = E_{\text{cat}} - E_{\text{an}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$\Delta E = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2} * \log[Cu^{2+}] - (E^\circ_{Zn^{2+}/Zn} + \frac{0.059}{2} * \log[Zn^{2+}]) = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2} * \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

We can derive a generic case: $\Delta E = \Delta E^\circ - \frac{0.059}{n} \log(K_c)$

After a while the battery is discharged, the system is at the equilibrium: $\Delta E = 0$.

$$0 = \Delta E^\circ - \frac{0.059}{n} \log(K_c)$$

$$\Delta E^\circ = \frac{0.059}{n} \log(K_c)$$

This is the correlation between EMF and the equilibrium constant of the overall oxidoreduction reaction.

$$\Delta E^\circ = \frac{0.059}{n} \log(K_{eq})$$

$$= \frac{RT}{nF} \ln(K_{eq})$$

$$\Delta G^\circ = -RT \ln(K_{eq})$$

$$= -nF\Delta E^\circ$$

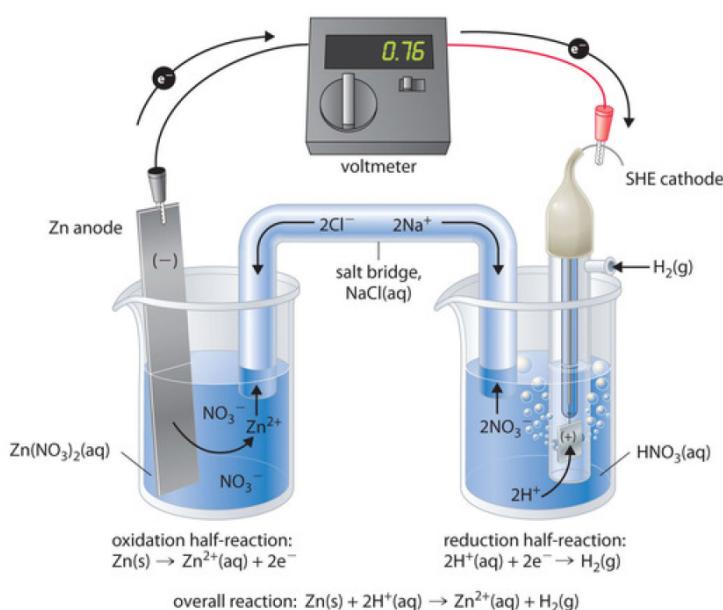
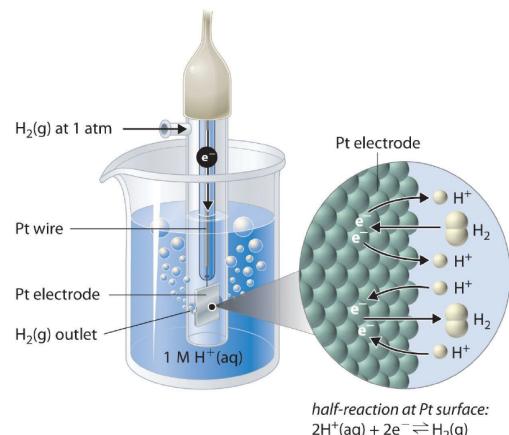
The larger ΔE° , more spontaneous is the reaction, ΔE° is a measurement of the tendency of the overall oxidoreduction reaction to occur.

Standard reduction potentials

ΔE is a difference between two reduction potentials, it is not possible to determine the absolute value.

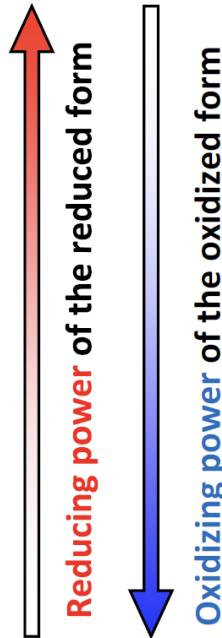
We need to build a scale of electrode reduction potentials relative to the reduction potential of an **electrode taken as reference**.

The reference electrode is the hydrogen electrode (in standard conditions), conventionally taken as $E^\circ = 0$.



Now, by building up a battery with a pole that has the hydrogen electrode, we can full the standard tables:

Reduction semi-reaction	E° (V)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li(s)}$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K(s)}$	-2.93
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na(s)}$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg(s)}$	-2.38
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn(s)}$	-1.19
$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)}$	-0.41
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)}$	+0.80
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$	+1.23
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(l)}$	+1.51
$\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au(s)}$	+1.69
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$	+1.78
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87

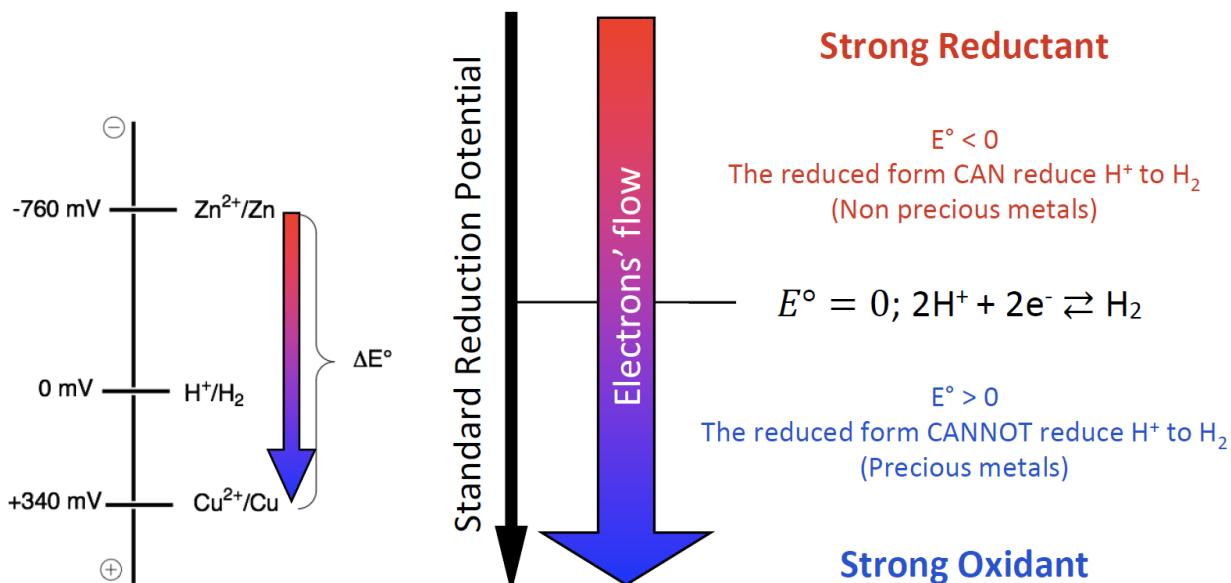


$E^\circ > 0$ for specific elements (silver, gold...).

$E^\circ < 0$ for alkali metals, not precious.

In a spontaneous reaction we go from low potential (anode) to high potential (cathode).

$$\Delta E^\circ = E^\circ(\text{cat}) - E^\circ(\text{an}) \rightarrow \Delta E^\circ > 0 \rightarrow E^\circ(\text{cat}) > E^\circ(\text{an})$$



CHEMICAL KINETICS

In a chemical reaction an equilibrium is always reached, but what about the rate to reach it? Chemical kinetics is the study of the rate and the mechanism of a chemical transformation process that occurs in a system.

Reaction rate

K_{eq} tells us if a reaction occurs spontaneously, to know how long it takes for the reaction to reach equilibrium we have to use a completely different approach.

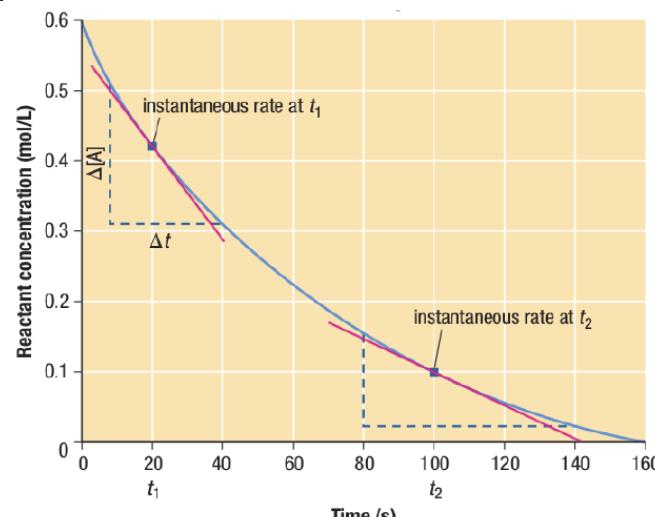
Reaction spontaneity and reaction rate are not correlated.

If we have the reaction $aA + bB \rightarrow cC + eE$

(We want to define the reaction velocity with a positive number)

$$v = -\frac{1}{a} * \frac{d[A]}{dt} = -\frac{1}{b} * \frac{d[B]}{dt} = -\frac{1}{c} * \frac{d[C]}{dt} = -\frac{1}{e} * \frac{d[E]}{dt}$$

The highest is "a" the faster the species is consumed/produced.



Reaction rate law

$$v = k * [A]^n * [B]^m$$

(n, m are not stoichiometric coefficients, they are the order of the reaction with respect of the reactant)

k = kinetic constant

n+m = overall order of the reaction (see the multistep reactions)

We will see how to reach the values of these coefficients in the successive paragraphs.

Reaction mechanism

In general, a reaction occurs through one or more **intermediate steps**, the reaction mechanism describes the detailed sequence of molecular events necessary to yield the products.

We can obtain some information about the reaction mechanism through the reaction order:

Ex.

$$\text{First order reaction: } v = k[A]^1[B]^0 = k[A]$$

the speed of the overall reaction depends only on the concentration of A

$$\text{second order reaction: } v = k[A]^2 \quad v = k[A][B]$$

The mechanism allows the reaction to occur more easily: for example, if we consider the formation of ammonia ($N_2 + H_3 \rightarrow 2NH_3$) we can see how if it would happen all in a single passage the probability to have exactly two atoms of nitrogen and 3 atoms of hydrogen near in the space and with the right energy to combine would be very low.

By some intermediate steps the molecule is built gradually, allowing simpler combinations of atoms.

Collision theory

2 molecules to react need to have a collision, but only effective collisions are cool; we need the right orientation and the right kinetic energy.

Orientation

Ineffective collision:



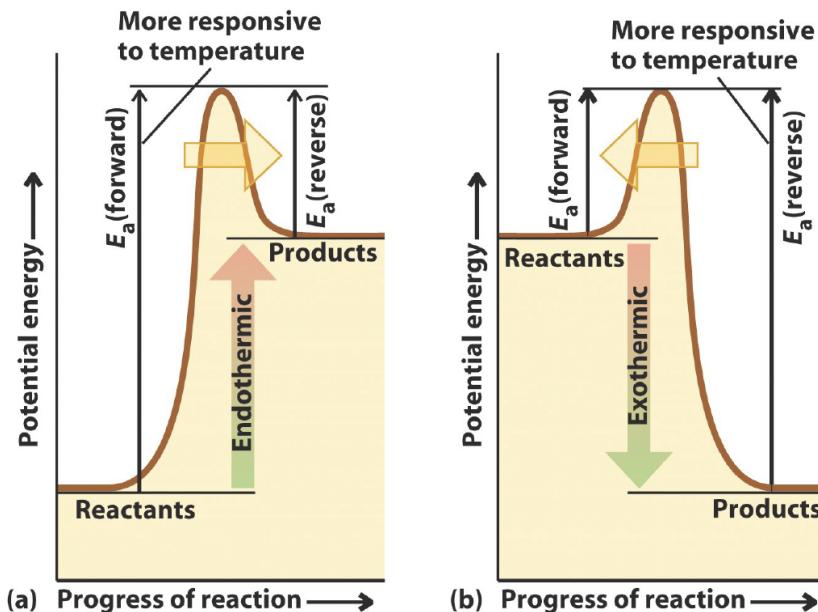
Effective collision:



Activation energy

The activation energy (E_a) is an energy **threshold** for the reaction; it is the energy that the reactants of each step of the reaction have to reach to yield the product.

After that the activation energy has been reached the activated complex is formed and then the products will reach their stability (the energy level of the products can be higher or lower in respect to the reactants, endothermic or exothermic reaction)



Activated complex: geometry of the atom that is intermediate between reactants and products, it is not a stable configuration, it is a transition state and it is not possible to isolate it, we can just isolate the intermediate products between the steps of a reaction

Arrhenius law

We can calculate the K by arrhenius law

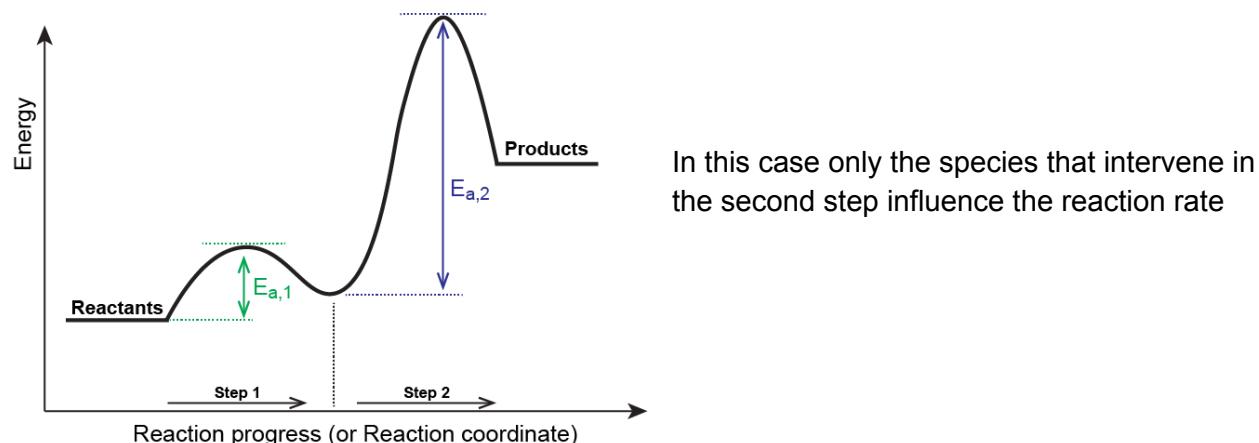
$$k = A * e^{-E_a/RT}$$

Where A is the probability to have an effective collision.

By increasing the temperature the reaction rate increases

Multistep reactions

In a multistep reaction we have several steps, the most important of these steps is the one with the highest activation energy, the slowest, which mainly influences the velocity of the reaction.

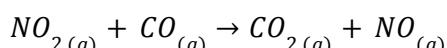


The slowest is the rate-determining step, the slowest is the reaction.

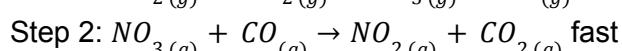
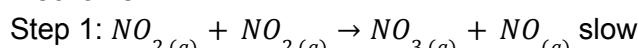
By knowing the coefficients of the main step we can determine which reactants are more important for the reactions.

The coefficients in the reaction rate law (n and m, the order of the reaction) corresponds to the stoichiometric coefficient of each species in the rate-determining step.

Ex.



Mechanism:



The reaction rate law is: $v = k[NO_2]^2$ second order equation, the speed depends only on NO_2

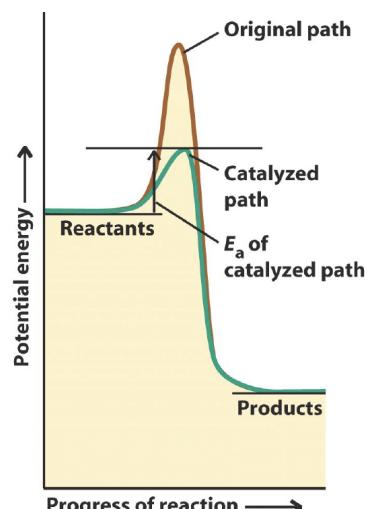
Catalysis

A catalyst is a chemical species able to **increase the reaction rate** providing a different reaction path, having **smaller activation energy**.

A catalyst does not change the position of the final equilibrium, but only decreases the time needed to reach it.

The catalyst is not modified during the reaction

- **Heterogeneous catalysis**: the reactants and the catalyst are in different phases.



- *Homogeneous catalysis*: the reactants and the catalyst are dispersed in the same phase, usually liquid.
- *Enzymatic catalysis*: the catalyst is a protein, it is specific for a chemical reaction. Each enzyme has a peculiar active site where the reactant is oriented in the right position in order to increase the possibility of effective collisions (factor A decreases