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Appunti universitari

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A P P U N T I

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MATERIA: Mathematical Analysis - prof. Saracco

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**ATTENZIONE: QUESTI APPUNTI SONO FATTI DA STUDENTIE NON SONO STATI VISIONATI DAL DOCENTE.
IL NOME DEL PROFESSORE, SERVE SOLO PER IDENTIFICARE IL CORSO.**

SOME FUNDAMENTAL DEFINITIONS

CHEMISTRY: the science that studies matter, its properties, transformations and energy associated

MATTER: everything having a given mass and volume

Energy: the potential of a body/system to perform a work

PHYSICAL PROPERTIES: properties shown by matter by itself, without changing into or interacting with another substance (hardness, density)

CHEMICAL PROPERTIES: shown as a substance changes into or interacts with another substance (flammability, reactivity with acids)

STATES OF MATTER: physical forms.

• A **SOLID** has a fixed shape that does not conform to the container shape

• A **LIQUID** has a varying shape that conforms to the container shape, but only to the extent of the liquid's volume; that is, a liquid has an upper surface.

• A **GAS** has a varying shape, but it conforms to the entire container

same rule:

• if there is a ~~zero~~ decimal point all digits are significant

6500. 4

13.100 5

0.090 3

• if there is no decimal point zeroes are not significant digits

5300 2

• Exponential notation

2.50 $\cdot 10^3$ 3

2.5 $\cdot 10^3$ 2

In calculations if we have too many significant figures we must round off the answers:

• in multiplication and division the answer contains the same number of significant figures as there are in the measurement with the fewest significant figures.

• in addition and subtraction the answer has the same number of decimal places as there are in the measurement with the fewest decimal places.

$$2.2 \times 6.8 \times 0.3744 = 23.4225 \Rightarrow 23$$

$$83.5 + 23.28 = 106.78 \Rightarrow 106.8$$

THE PERIODIC TABLE

There were ~~several~~ ^{noted} several behaviours and properties of elements periodic in the increasing of atomic number. For this reason they were organized in the periodic table.

The atomic number increases from left to right and from ~~top~~ to ~~bottom~~ top to bottom.

The horizontal rows are called periods (from 1 number ~~to~~ from 1 to 7) where properties are changing gradually.

The vertical columns are called groups (1-18) and there are elements with same properties.

COMPOUNDS THAT CONTAINS POLYATOMIC IONS

• POLYATOMIC IONS

- Oxoanions: the ion with most O atoms has the prefix "per-", the atom's root, and the suffix "-ate".

the ion with one fewer O atoms has only the suffix "-ate".

the ion with two fewer O atoms has the suffix "-ite".

the ion with least O atoms has the prefix "hypo-" and the suffix "-ite".

u. of O atoms	↑	per - root - ate
		root - ate
		root - ite
		hypo - root - ite

* memory tid: hypo → less O, like hypothermia → less temperature

• Hydrated Ionic Compounds: compounds having a specific number of water molecules (matched with a greek numerical prefix)

Na_2SO_3	sodium sulfite	sodium (I) sulfite
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	barium hydroxide	octahydrate
$\text{Fe}(\text{ClO}_4)_2$	ferrous perchlorate	iron (II) perchlorate

Oxocids: the name is similar to the oxoanion's name. The suffix changes from "-ate" → "-ite" and "-ite" → "-ous"

* remember the unary id! :)

BINARY COVALENT COMPOUND

Some are so familiar that are used ~~to~~ with their common name (water, ammonia, methane).

Naming them:

- 1) the element with lower group is named first. If the group is the same case first the one with higher period number.
- 2) Greek numerical prefixes are used to indicate the number of atoms of each element. (the first element has a prefix only if more than one atom is present).

CS_2	carbon disulfide
PCl_5	phosphorous pentachloride
N_2O_4	dinitrogen tetroxide

water Cl_2 e
 On ~~the~~ termino
 ca il ~~pre~~ suffisso
 ide cae ~~fosso~~
 dionio e I_2 uo?

CHEMICAL FORMULAS, MOLECULAR STRUCTURE AND ISOMERS.

Do empirical and molecular formulas contain structural information?

- Isomers: different compound with same molecular formula. Their atoms are bonded in different arrangements. Isomers have same molecular formula, and molar mass, but different properties.
- There could exist different compounds with same empirical formula. Such as ethylene (C_2H_4) and propylene (C_3H_6), their empirical formula (C_nH_{2n}) is given by chemical analysis, but their chemical formula needs more research.

How To...

BALANCE CHEMICAL EQUATIONS.

In general balancing is easiest when we - start with the most complex substance, the one with the largest number of different types of atoms.

- End with the least complex

* Remember to specify the state of matter.

* Try to use rational numbers in order to balance.

COVALENT COMPOUNDS IN WATER

Covalent compounds doesn't split in ions, but they can be soluted by water because of the interaction between polar bonds of the covalent compounds and water's ones. This substances doesn't make the water more conductive, and we said nonelectrolytes.

ACID BASE Rx (or SALIFICATION)

- These reactions involve water as reactant or product
- Acid solution arise when certain covalent H-containing compounds dissociates into ions in water.
- We can represent an acid rx with a proton/ H^+ ion or a hydronium ion (H_3O^+)
- * Acids and bases are strong or weak electrolytes.
- The ionic compound produced by acid-base rx is called a SALT.
- Acids and bases are categorized by their strength.

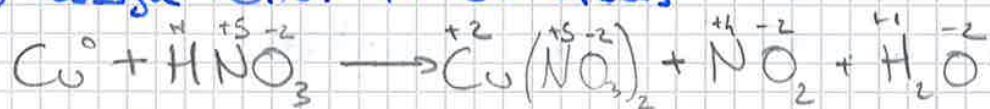
• The Oxidation Number (or oxidation state) is defined as the charge the atom would have if electrons were transferred completely, not shared.

* the O.N. has the sign before the number, whereas ionic charge has the sign after the number.

BALANCING REDOX Rx

• Oxidation Number Method

1) assign O.N. to all atoms

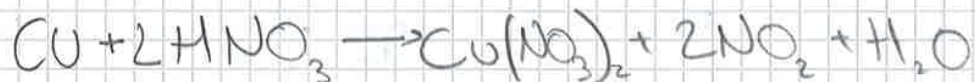


2) identify the oxidized and reduced reactants.

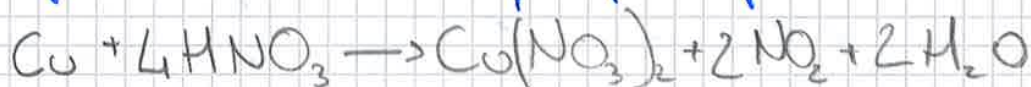


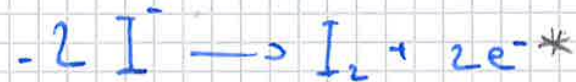
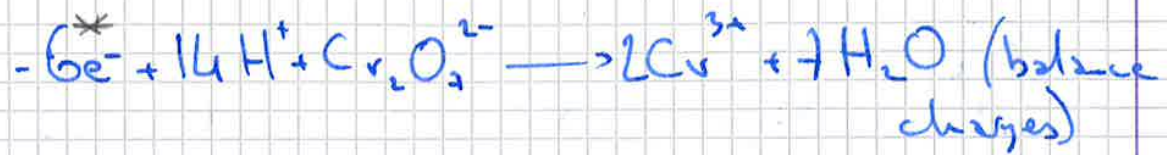
3) Compute the number of e^- lost in the oxidation and gained in the reduction

4) Multiply the numbers of electrons by factors that make the electrons lost equal the electrons gained, and use it as balancing coefficients.



5) Complete the balancing by inspection





4) Check that atoms balance

In case we have a rx in Basic Solution, in order to balance we use OH^- despite H^+ ions. The method is the same but at the end (step 3) we add to the both sides one OH^- per each H^+ in order to combine them in a water molecule in reactants and have OH^- in products.
* H_2O excess are cancelled.

OTHERS REACTIONS

• COMBINATION or SYNTHESIS Rx

Two or more substances react to form one or more products.

Metal + non metal form ionic compound

Non metal + non metal form a covalent compound.

• DECOMPOSITION Rx

One substance breaks down into two or more substances. In these rx the reactants absorb heat (thermal decomposition) or electricity (electrolytic decomposition)

KINETIC MOLECULAR THEORY

- BEHAVIORS THAT DISTINGUISH GASES FROM LIQUIDS AND SOLIDS:

- gas volume changes significantly with pressure
- gas volume changes significantly with temperature
- gases flow much more freely than liquids and solids
- gases have relatively low densities
- gases form a solution in any proportion.

These properties arise because the particles in a gas are much farther apart than those in either a liquid or a solid.

GAS PRESSURE

Gas exerts a pressure on the walls of every container. Pressure is defined as the force exerted per unit of surface area.

To measure the pressure there are several units.

- Pascal (Pa): the SI unit of pressure

$$1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2}$$

- Standard Atmosphere (atm): the average atmospheric pressure measured at sea level and 0 °C

$$1 \text{ atm} = 101,325 \text{ kilopascal (kPa)} = 1,01325 \cdot 10^5 \text{ Pa}$$

• CHARLES' LAW

It describes the relation between volume and temperature

- Volume and temperature are directly proportional
 ↳ At constant P, the volume occupied by a fixed amount of gas is directly proportional to its absolute (K) temperature

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \text{ or } V = \text{constant} \cdot T$$

* Absolute zero (0°K) is the temperature at which an ideal gas would have zero volume.

* The kelvin scale must be used in gas law calculations (for ex: if the temperature changes from 200°K to 400°K the volume doubles, if it changes from 200°C to 400°C the volume increases by 1,4x)

* COMBINED Gas Law

Combination between Boyle's and Charles's laws:

$$P \propto \frac{1}{V} \text{ or } PV = \text{constant} \text{ or } P = \text{constant} \cdot \frac{1}{V}$$

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \text{ or } V = \text{constant} \cdot T$$

$$V \propto \frac{T}{P} \text{ or } V = \text{constant} \cdot \frac{T}{P} \text{ or } \frac{PV}{T} = \text{constant}$$

But R should have different values if different units are used, such as $8.314 \text{ J/mol}\cdot\text{K}$

Given the ideal gas law it's easy to write the three ideal gas laws by fixing 2 parameters:

$$PV = nRT \quad \text{or} \quad V = \frac{nRT}{P}$$

$\xrightarrow[\text{fixed}]{n \text{ and } T}$ $V = \frac{\text{const}}{P}$

$\xrightarrow[\text{fixed}]{n \text{ and } P}$ $V = \text{const} \cdot T$

$\xrightarrow[\text{fixed}]{P \text{ and } T}$ $V = \text{const} \cdot n$

PARTIAL PRESSURE

Ideal gas law holds virtually for any gas at ordinary conditions, whether pure or mixtures, because gases mix homogeneously and any gas solution behaves as if it were the only gas present (assuming no chemical interactions).

DALTON'S LAW OF PARTIAL PRESSURE

He observed that when water vapor is added to dry air the total air pressure increases by the pressure of the water vapor: $P_{\text{w/air}} = P_{\text{dry air}} + P_{\text{vapor}}$
 \Rightarrow each gas in the mixture exerts a partial pressure equal to the pressure it would exert by itself.

STATEMENT: in a mixture of non-reacting gases the total pressure is the sum of the partial pressures of the individual gases.

$$P_{\text{TOT}} = P_1 + P_2 + P_3 + \dots + P_n$$

* Because each gas occupies the same total volume and is at the same temperature the pressure of each gas depends only on its amount n

$$P_{\text{TOT}} = P_{\text{N}_2} + P_{\text{H}_2} = \frac{n_{\text{N}_2} RT}{V} + \frac{n_{\text{H}_2} RT}{V} = \frac{n_{\text{TOT}} RT}{V}$$

$$(n_{\text{TOT}} = n_{\text{N}_2} + n_{\text{H}_2})$$

Now let's state the postulates of the theory:

- 1) Particle volume: A gas consists of a large collection of individual particles with empty space between them. The volume of each particle is assumed to be zero, ~~is~~ when compared to the whole sample \rightarrow each particle is a part of mass.
- 2) Particle motion: the particles are in constant, random, straight-line motion, except when they collide with the container walls or with each other, there are no interacting forces in collisions.
- 3) Particle collisions: the collisions are elastic, which means that the colliding molecules exchange energy but do not lose any energy through friction. \rightarrow Their total kinetic energy is a constant (E_k).

Each particle has a molecule speed (u). In a sample most of particles are moving near the most probable speed, which is related to temperature. In fact most probable speed increases with temperature, because the average kinetic energy of the molecules is proportional to the absolute temperature.

$$\overline{E_k} \propto T \quad \text{or} \quad \overline{E_k} = c \cdot T$$

$\overline{E_k}$ average kinetic energy

c a constant equal for any gas

\Rightarrow At a given temperature all gasses have the same average kinetic energy -

• Avogadro's law: at same starting amount of gas $P_{ext} = P_{gas}$. If n rise the particles hitting the walls rise too. As result P_{gas} increases

Implication of Avogadro's law:

Why don't heavier molecules exert more pressure than lighter ones, at same volume, temperature and volume condition?

As said in the 3rd postulate at given T all gasses have same $\overline{E_k}$.

Mathematically $\overline{E_k} = \frac{1}{2} \cdot \text{mass} \cdot \text{speed}^2$

We know that the lighter the molecule weight, the higher is the molecule speed for this reason $\overline{E_k}$ it's a const.

The meaning of temperature: the temperature "is a consequence" of the average kinetic energy, and it's related with it by the equation:

$$\overline{E_k} = c \cdot T \quad \Rightarrow \quad \overline{E_k} = \frac{3}{2} k \cdot T$$

k is the Boltzmann constant = $1,381 \cdot 10^{-23} \text{ J/K}$
 $= \frac{R}{N_A}$

$$\Rightarrow \overline{E_k} = \frac{3}{2} \frac{R}{N_A} T$$

"Temperature is a measure of the average kinetic energy of the particles"

DEVIATIONS OF REAL GASES FROM IDEAL BEHAVIOUR

Real gases deviate from ideal behavior because two postulates are wrong:

- gas particles are not point
- attractive and repulsive forces do exist among gas particles

These features cause deviations under extreme conditions of low temperature and high pressure

- At moderately high P_{ext} , PV/RT is lower than ideal ones, because the distance between atoms becomes very short, making effective the interparticle attractions. This effect decreases P . Similarly lowering temperature (slowing the atoms particles).
- At very high P_{ext} , PV/RT is greater than ideal values, because at high P_{ext} the particle volume makes the free volume significantly less than V (which refers to the container volume), causing rising of PV/RT .

VAN DER WAALS EQUATION: ADJUSTING THE IDEAL GAS LAW

- Adjust P up
- Adjust V down

$$\left(P + \frac{a^2}{V^2}\right)(V - nb) = nRT$$

* a, b are the Van der Waals constants, experimentally determined for all gases. " a " depends on the number and distribution of electrons, " b " is related to particle volume.

WAVE

Refraction: changing of speed when passing from a medium to another

Dispersion: ~~depends~~ caused by refraction, when a wave passes into a prism it separates.

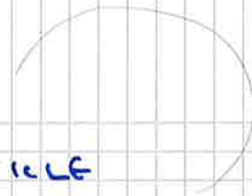
Diffraction: when a wave passes through a hole big as the wavelength, the wave forms semicircles

PARTICLE

It belongs

like

a particle...



PHOTOELECTRIC EFFECT

- **OBSERVATION:** when light shines on metal plate current flows (as light transfers energy that frees electrons). Light must have determined sufficient frequency.
- **EXPLANATION: THE PHOTON TH:** Einstein proposed that light is particulate in photons. Each atom changes its energy when it absorbs or emits one photon

$$E_{\text{photon}} = h\nu$$

ATOMIC SPECTRA

When light from electrically excited gaseous atoms passes through a slit and is refracted it creates a line spectrum, a series of lines at specific frequencies separated by black spaces.

Each spectrum is characteristic of the element producing it.

THE ELECTRON AND ITS PROPERTIES

Nobody knew what electrical current was made of. To study its nature they passed current through a cathodic tube, and observed some rays. Cathode rays consist of negatively charged particles found in all matter, these particles were later called electrons (e^-).

• **THE MASS-CHARGE RATIO:** Thomson measured the ratio of the mass of a cathode ray to its charge. He estimated the weight of the particle was less than $\frac{1}{1000}$ of a hydrogen atom. This implied that atoms contain even smaller particles.

$$\frac{e}{m} = \frac{E}{h\nu}$$

• **CHARGE:** Millikan measured the charge of the electron by observing the movement of oil droplets in a apparatus that carried electrically charged plates and x-ray source. Millikan found the charge $e = -1,602 \cdot 10^{-19} \text{ C}$

↳ early the mass should then be found:

$$9,109 \cdot 10^{-31} \text{ kg} = 9,109 \cdot 10^{-28} \text{ g}$$

⇒ Pudding model by Thomson

ISOTOPES

All elements have same atomic number but not same mass number. Isotopes of an element are atoms with same Z but different A .
Isotopes have nearly identical chemical behaviour.

ATOMIC MASSES OF THE ELEMENTS.

To measure the mass of atoms we use the Dalton (Da) (ex amu) (atomic mass unit), which weights $\frac{1}{12}$ of a $^{12}_6\text{C}$ atom
 $= 1,661 \cdot 10^{-24} \text{ g}$

The atomic mass of an element is the average of the masses of its naturally occurring isotopes weighted according ~~to~~ to their abundance.

3) The atom changes to another stationary state only by absorbing or emitting a photon

FEATURES OF THE MODEL

• Quantum number and electron orbit: the quantum number n is associated to the stationary state where the e^- lays. The lower the n value, the smaller the radius of the orbit, and the lower the energy level

• Ground state and excited states: is called "ground state" the first orbit. If the e^- is in any other orbit the atom is in a excited state ($n=2 \Rightarrow$ first excited state, $n=3 \Rightarrow$ second excited state, ecc...)

• Absorption: if the atom absorbs a photon whose energy equals the difference between lower and higher energy levels the e^- moves to the outer orbit.

• Emission: while an atom is descending to its stationary state the atom emits a photon whose energy equals the difference between the two levels.

↳ A spectral line results because a photon of specific energy (and thus frequency) is emitted. An atomic spectrum then is not continuous because the atom's energy is not continuous.

HEISENBERG'S UNCERTAINTY PRINCIPLE

Heisenberg stated that it is impossible to know simultaneously the position and the momentum of a particle. The more accurately we know the position of the particle (Δx) the less accurately we know the speed (Δv), and vice versa.

$$\Delta x \cdot \underbrace{m \Delta v}_{\substack{\downarrow \\ \text{momentum: mass} \cdot \text{speed}}} \geq \frac{h}{4\pi} \rightarrow \text{Planck constant}$$

* The dual nature of matter and energy and the uncertainty principle culminated in the field of quantum mechanics

QUANTUM NUMBER OF AN ATOMIC ORBITAL

An atomic orbital is specified by three quantum numbers, indicating the size, shape and orientation in space.

- Principal quantum number (n): is a positive integer ($n \geq 1$) and it specifies the energy levels (or shells). The lower n , the greater the probability that e^- is closer to the nucleus.
- Angular momentum quantum number (l): is an integer from 0 to $n-1$, is related to the shape of the orbital. Every level is divided in sublevels (or subshells), given by the l value. l is associated with a letter (the letter derives from ~~the~~ names of spectroscopic lines: sharp, principal, diffuse and fundamental)
 - $l=0 \Rightarrow s$ sublevel
 - $l=1 \Rightarrow p$ sublevel
 - $l=2 \Rightarrow d$ sublevel
 - $l=3 \Rightarrow f$ sublevel
 - $l=4 \Rightarrow g, l=5 \Rightarrow h, l=6 \Rightarrow i, \text{ ecc.}$
- Magnetic quantum number (m_l): an integer from $-l$ to l . It prescribes the three directional orientation of the orbital in the space around the nucleus.

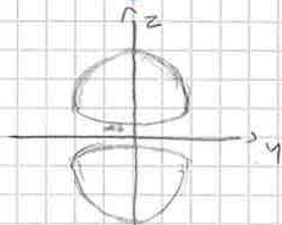
Orbital: each combination of n, l and m_l specifies the size (energy), shape and spatial orientation of one of the atom's orbitals.

• THE P ORBITAL

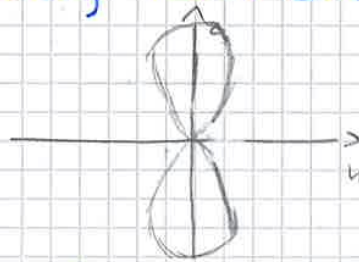
An orbital with $l=1$ has two regions (lobes) of high probability. The nucleus lies at the nodal plane of this dumbbell-shaped orbital. Similar to the pattern for s orbitals, a 3p orbital is larger than a 2p, a 4p larger than a 3p, and so forth.

P orbitals have different spatial orientations (given by m_l).

We associate p orbitals with the x, y and z axes: the p_x lies along the x axis, p_y ...



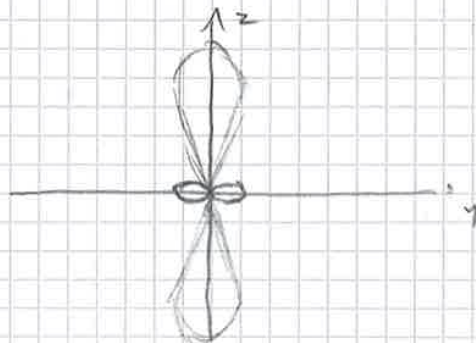
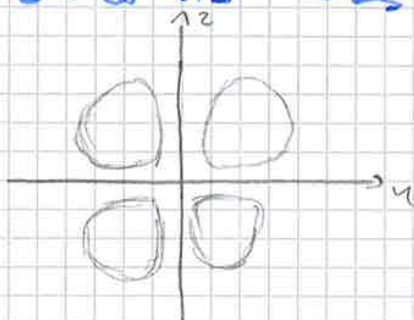
cross section of accurate probability contour



stylized probability contour

• THE D ORBITAL

For $l=2$ there are 5 possible m_l . Four of them have four lobes. The fifth d orbital has two major lobes along the z axis, and a donut-shaped region girdles the center. A electron in a d orbital spends equal time in all of its lobes.

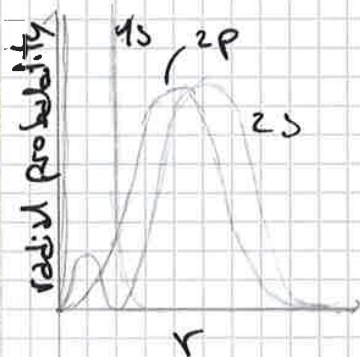


ELECTROSTATIC EFFECTS

This effects play a major role in determining the energy states of many-electron atoms.

- **NUCLEAR CHARGE (Z)**: a higher nuclear charge increases nucleus-electron attractions and, thus lowers sublevel energy.
- **SHIELDING** (electron repulsions on sublevel energy): electrons feels the attraction to the nucleus and the repulsion with other e⁻. We speak of each electron shielding others. Shielding reduces the full nuclear charge to an effective nuclear charge (Z_{eff}): the nuclear charge an electron actually experiences.
- **PENETRATION** (effect of orbital shape on sublevel energy): To see why an electron occupies the 2s sublevel rather than the 2p, we have to consider orbital shapes, that is, radial probability distribution.

Energy ↓
 1s
 2s
 2p
 3s
 3p
 4s
 4p
 5s
 5p
 6s
 4f



A 2p orbital is closer to the nucleus than the major portion of the 2s orbital. But a small portion of 2s orbital distribution peaks within the 1s region, thus an electron in the 2s orbital spends part of its time penetrating very close to the nucleus.

THE QUANTUM-MECHANICAL MODEL

To "build" an atom's configuration we use the Aufbau principle. We start at the beginning of the periodic table, and we add one electron to the lowest energy sublevel available, and so on.

To indicate the electron configuration we have two common ways:

- the electron configuration:



- The orbital diagram



* HUND'S RULE: when orbitals of equal energy are available the electron configuration of lowest energy has the maximum number of unpaired electrons with parallel spins.

* The major connection between quantum mechanics and chemical periodicity is the recurring periodicity of outer electron configurations, which lead to periodical chemical properties.

* For Cr and Cu there is an exception: the Hund rule is violated ^{in 4s orb.} in favor of filling the 3d and 4p orbitals, because it's a more stable configuration.

Within a period it diminishes because the atomic nucleus charge increases (Z_{eff}) thus electrons tend to be attracted more and more.

Within a group it increases because as far as the period number grows more and more shells are occupied.

* Analogously there's a variation :- the ionic radius when an element is reduced or oxidized.

• IONIZATION ENERGY

The ionization energy (IE) is the energy required for the complete removal of 1 mol of e^- from 1 mol of gaseous atoms or ions.

The first ionization energy (IE_1) removes an outermost electron, the second (IE_2) removes a second e^- .

$$IE_2 > IE_1$$

The ionization energy is the inverse of variation in atomic size, because in larger atoms the attraction nucleus- e^- is less.

* the IE increase enormously after valence electrons.

The metallic behavior decrease across periods, and increase down a group (because of the size and IE).

In some groups we find non metals, so at the top there is no metallic behavior at all (same for periods).

PROPERTIES OF MONOATOMIC IONS.

Ions with noble gas configuration have their highest energy level filled, and are called isoelectronic (iso = same) with the nearest noble gas.

Removing or adding more electrons than the isoelectronic configuration would mean the use of too much energy, for this reason we don't have NaCl_2 or Mg_3O_2 .

ELECTRONEGATIVITY (EN)

Is the relative ability of bonded atom to attract shared electrons (it refers to bonded atom attraction, despite EA which refers to atoms formation).

We might expect the H-F bond energy to be the average of H_2 and F_2 bonds, but actually HF is stronger, because F attracts the shared e^- pair strongly. Thus there's a polarization of the atoms, which increase the energy required to break the bond.

THERMODYNAMICS

Is the study of energy and its transformations.

THERMOCHEMISTRY is the branch that deals with the heat in chemical and physical changes

ENERGY TRANSFER

Each particle in a system has **potential and kinetic energy**, the sum is the **INTERNAL ENERGY (E)**. ΔE is the difference between the internal energy after the change and before the change.

A system can change its E by two ways:

- releasing some energy $\Rightarrow \Delta E < 0$
- absorbing some energy $\Rightarrow \Delta E > 0$

HEAT AND WORK

Energy transferred appears in two forms:

- **HEAT**, or **thermal energy (q)**: the energy transferred as result of a difference in temperature between the system and the surroundings.
- **WORK (w)**: all other forms of energy transfer involve some type of work

The total change in a system's E is the sum of energy transfer as heat and work

$$\Delta E = q + w$$

We define the sign from system perspective:

$\Delta E > 0 \Rightarrow$ energy into the system $\Delta E < 0 \Rightarrow$ energy out from the system.

UNITS OF ENERGY

The SI unit is the joule (J) = $\text{kg} \cdot \text{m}^2 / \text{s}^2$

Both heat and work are expressed in joules.

↳ The force (F) times the distance that the mass moves: $w = F \times d$

A force changes the velocity of a mass over time: a force accelerates a mass. Velocity is m/s , then acceleration is m/s^2 .

$$\Rightarrow F = m \times a$$

$$w = F \times d = \text{kg} \cdot \text{m/s}^2 \cdot \text{m} = \text{J}$$

The calorie (cal) is an older unit defined as the quantity of energy needed to raise the T of 1g of water by 1°C from 14.5 to 15.5. Now is defined in terms of joules:

$$1 \text{ cal} = 4,184 \text{ J}$$

$$1 \text{ J} = 0,2390 \text{ cal}$$

ENTHALPY AND INTERNAL ENERGY IN:

- Rxn that do not involve gases: liquids and solids undergo very small volume changes
 $\Delta V \approx 0 \Rightarrow P\Delta V \approx 0, \Delta H \approx \Delta E$
- Rxn in which the amount (mol) of gas does not change: the gases volume is equal in reactants and products
 $\Delta V = 0 \Rightarrow P\Delta V = 0, \Delta H = \Delta E$
- Rxn in which the amount of gas does change:
 $P\Delta V \neq 0$, however q_p is usually much larger than $P\Delta V$, so ΔH is still very close to ΔE

The sign of ΔH indicates whether heat is absorbed or released during the reaction.

$-\Delta H < 0 \Rightarrow H_{\text{products}} < H_{\text{reactants}} \Rightarrow$ exothermic process

$-\Delta H > 0 \Rightarrow H_{\text{products}} > H_{\text{reactants}} \Rightarrow$ endothermic process

HESS'S LAW

Finding ΔH of any rxn

"The enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps."

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \dots + \Delta H_n$$

CALCULATING AN UNKNOWN ΔH

- 1) Identify the target equation, the step whose ΔH is unknown, and note the amount of each reactant and product.
- 2) Manipulate each equation with known ΔH values so that the target amount of each substance is on the correct side of the equation. Remember to:
 - Change the sign of ΔH when you reverse an equation
 - Multiply amount and ΔH by the same factor.
- 3) Add the manipulated equations and their resulting ΔH values to get the target equation and its ΔH .

CHEMICAL BONDS

Why do atoms bond?

• METAL WITH NON-METAL: IONIC BONDING.

Ionic bonding happens between atoms with large differences in their tendency to lose or gain electrons.

A metal atom (low IE) loses its valence electron(s), and a non metal atom (highly negative EA) gains the electron(s).

Electron(s) TRANSFER(s) and each atom forms an ion. The electrostatic attractions draw them into a three-dimensional array to form an ionic solid.

• NON-METAL WITH NONMETAL: COVALENT BONDING

When two atoms differ a little (or not at all) in their tendency to lose or gain electrons we observe electron SHARING and covalent bonding, most commonly between nonmetal atoms.

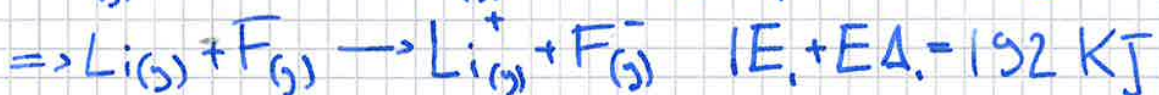
The nucleus of each atom attracts the valence electrons of the other, which draws the atoms together.

IONIC BONDING MODEL

↳ The transfer of electrons from metal atoms to nonmetal atoms to form ions that attract each other by electrostatic forces into a solid compound.

If energy is absorbed during electron transfer, why does ionic bonds occur?

1) the electron transfer process (lithium fluoride)



if > 0 means endoenergetic

2) metallic lithium must be made into gaseous atoms (161 KJ/mol), and fluorine molecules must be broken into separate atoms (79.5 KJ/mol)

3) Steps that RELEASE ENERGY: despite these endothermic steps the standard enthalpy of formation ΔH_f° of solid LiF is -617 KJ/mol!

Because when one mol of LiF is formed $\Delta H^\circ = -1050 \text{ KJ}$ (should be -755 if gaseous, but under standard condition LiF is solid)

$$\Rightarrow (-1050) - (192) - (161 + 79.5) = -617$$

We know that $\text{Li(s)} + \frac{1}{2}\text{F}_2(\text{s}) \rightarrow \text{LiF(s)}$
 $\Delta H_{\text{overall}}^\circ = -617 \text{ kJ}$

applying Hess's law

$$\Delta H_{\text{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

$$\Rightarrow \Delta H_{\text{lattice}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ - \Delta H_{\text{overall}}^\circ$$

$$= 1050 \text{ kJ}$$

* the energy required to form ions is supplied by the attraction among the ions in the solid.

PROPERTIES OF IONIC COMPOUNDS

- PHYSICAL BEHAVIOR: a piece of rock salt is hard, rigid and brittle. These properties arise from the strong attractive forces that hold the ions in specific positions. If ions of like charge are brought next to each other the repulsion between them weak the sample.
- ELECTRICAL CONDUCTIVITY: typically they don't conduct electricity in solid states, but they do when melted or dissolved.

Each atom in covalent bond counts the shared electrons as belonging entirely to itself (shared/bonding pair(s)).

PROPERTIES OF COVALENT BOND

- **BOND ORDER**: the number of e^- pairs being shared by a given pair of atoms:
 - "Single bond", bond order of 1
 - "double bond", two atoms sharing $4e^-$, the bond order is 2

- "Triple bond"...

- **BOND ENERGY (BE)**: is the strength of the bond, the energy needed to overcome the attraction between nuclei. Is defined as ΔH_{BE}° for 1 mol of gaseous molecules; it's always positive (endothermic). When bonds form a sum ΔH° is released (exothermic)

Stronger bonds are lower in potential energy.

The ΔH_{BE} can vary a little between molecules so we use a averaged value.

- **BOND LENGTH**: is the distance between the nuclei, it is as well a averaged value.

* For a given pair of atoms, a higher bond order results in a shorter bond length and higher bond energy. A shorter bond is a stronger bond.

METALLIC BOND

THE ELECTRON-SEA MODEL

This model proposes that all metal atoms contribute their valence e^- to form a delocalized electron "sea" throughout the sample.

Metallic bond differs from others because:

- the metal ions are not held in place as rigidly (ionic bond)
- no particular pair of metal atoms is bonded through a localized electron pair. (covalent bond)
- Instead of forming compounds, metals form ALLOYS, solid mixtures of variable composition.

PROPERTIES OF METALS

- MELTING AND BOILING POINT: moderate to high boiling melting point and much higher boiling point (generally). Melting are relatively lower because cations can move without breaking attraction with electrons, same reason for the high melting point. Larger metal ions have weaker attraction to the electron sea, so the melting point decrease.
- METALS are ductile and malleable.

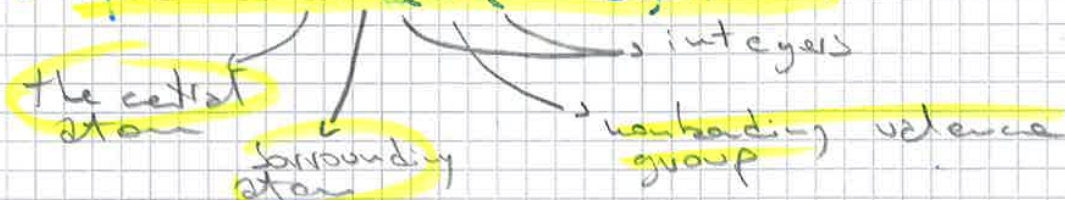
VALENCE-SHELL ELECTRON-PAIR REPLICATION THEORY (VSEPR)

This theory is used to obtain the molecular shape.

Its basic principle is that: to minimize repulsion, each group of valence electrons around a central atom is located as far as possible from the others.

The electron group arrangement is defined by the bonding and non-bonding electron groups, but the molecular shape is defined by the relative position of the nuclei, which are connected by the bonding groups.

To classify molecular shapes we assign each a specific AX_nE_m designation.



Def: The Bond Angle :- the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom as vertex

- with all bonding groups (AX_4): it's a tetrahedral shape ($109,5^\circ$)

- with one lone pair (AX_3E): it's a trigonal pyramidal shape ($107,3^\circ$)

- with two lone pairs (AX_2E_2): it's a bent or V shape ($104,5^\circ$) (H_2O)

* When a double bond occurs the other bonded electron groups are repelled because of the greater electron density of the double bonds. e^- in single bonds more than the single bonds repel each other.

• With FIVE e^- GROUPS: the ideal arrangement is a trigonal bipyramidal arrangement where two pyramids share a common base.

There there are 2 ideal axes: of 120° within ~~the~~ 3 equatorial groups and of 90° between the equatorial plane and the 2 axial groups.

- with all bonding groups (AX_5): trigonal bipyramidal shape (ideal one)

- with one lone pair (AX_4E): seesaw shape. Lone pair first occupies equatorial position. $120^\circ \rightarrow 101,5^\circ$
 $90^\circ \rightarrow 86,8^\circ$

- with two lone pairs (AX_3E_2): T shape. $90^\circ \rightarrow 86,2^\circ$

MOLECULAR POLARITY

Both molecular shape and bond polarity determine molecular polarity.

The dipole moment (μ) is a measure of molecular polarity, given in debye (D).

$$1D = 3,34 \cdot 10^{-30} \text{ C}\cdot\text{m}$$

Carbons \downarrow \uparrow hetero

The presence of polar bonds doesn't result always in ~~the~~ polar molecules.

Ex) CO_2 : $\Delta EN = 1 \Rightarrow$ polar bonds

The linear shape of the molecule counterbalances the two dipole moments (two bonds $\text{C}=\text{O}$)

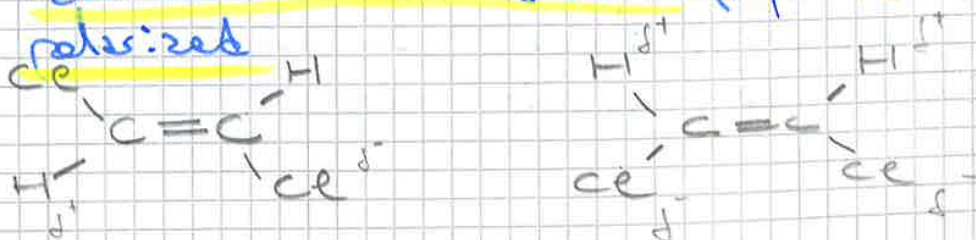
Ex) H_2O : $\Delta EN = 1,4 \Rightarrow$ polar bonds

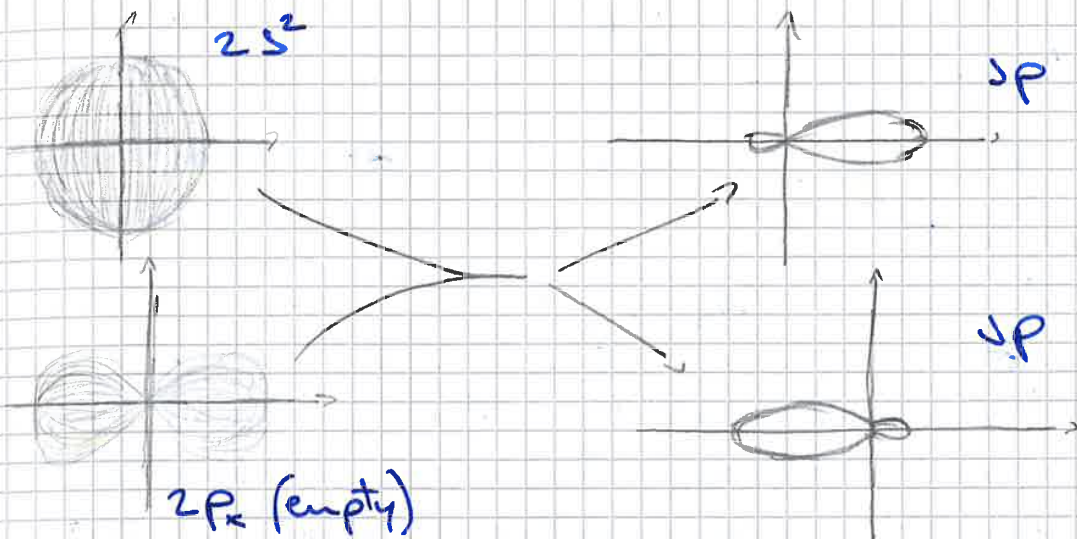
The bond polarities are not counterbalanced because of the \vee shape

Ex) $\text{C}_2\text{H}_2\text{Cl}_2$: this molecule admits isomers.

The trans isomer is not polar, because all the bonds are counterbalanced by their opposite.

But the cis isomer ($\mu = 1,50D$) is polarized





• sp^2 HYBRIDIZATION: one s and two p orbitals are mixed to give 3 sp^2 orbitals at corners of a triangle.

* superscripts in hybridized orbitals correspond to the orbitals involved in the hybridization not to the e^- per orbital.

• sp^3 HYBRIDIZATION: it belongs to any species with a tetrahedral arrangement.

• sp^3d HYBRIDIZATION AND sp^3d^2

linear, T-shaped, trigonal bipyramidal shapes

$3s^0 + 3p^0 + 3d^0$ (empty) forms	$3s^2 + 3p^4 + 3d^0 + 3d^2$ forms
5 sp^3d orbitals	6 sp^3d^2 orbitals

MOLECULAR ORBITAL THEORY (MO)

The VSEPR and valence bond theories are sufficient to explain the geometry of molecules. However in order to explain their magnetic, spectroscopic and catalytic behavior a new theory is needed.

According to this the new orbitals are formed belonging to the entire molecule: molecular orbitals (MOs) of given energies and shapes that are occupied by molecule's e^- .

LCAO (linear combination of atomic orbitals)

A way to obtain MOs is the LCAO method,

Linear: add or subtract atomic wave functions

bonding MO

lower in energy, more stable

HOMO:

highest occupied molecular orbital

are both σ and π bonds because they are cylindrically symmetrical

anti-bonding MO

higher in energy and less stable, the e^- are spending their time outside the intermolecular region

LUMO: lowest occupied molecular orbital

To combine atomic orbitals must be similar (s with s or p_x , not p_y or p_z ; p_x with p_x or p_z but not p_y)

INTERMOLECULAR FORCES

PHASE'S PROPERTIES

Each physical state is called phase: a physically distinct, homogeneous part of a system.

- The potential energy in the form of intermolecular forces tends to draw them together. It depends on the charges and distances.
- The kinetic energy associated with the random motion of the molecules tends to disperse them.

PHASE CHANGES

- As T increases the average kinetic energy goes up, so the faster moving particles overcome attractions more easily
 \Rightarrow phase changes are accompanied by enthalpy changes
- Gas to liquid (condensation), liquid to solid (freezing) and Gas to solid (sublimation) happens because the system particles loses energy (exothermic)
- vice versa (melting or fusion, vaporization, deposition) are endothermic changes

Macroscopically the equilibrium situation seems static, but at molecular level the system has reached a dynamic equilibrium.

Disturbing a system at equilibrium: by changing pressure phase-change rates change. Vaporization increase while decreasing pressure, Condensation while rising it. If a system is disturbed it counteracts the disturbance until it re-establishes equilibrium.

As we saw in kinetic theory, rising temperature cause an higher vapor pressure.

THE CLAUZIUS-CLAPEYRON EQUATION

These relation converts into a linear relation P and T

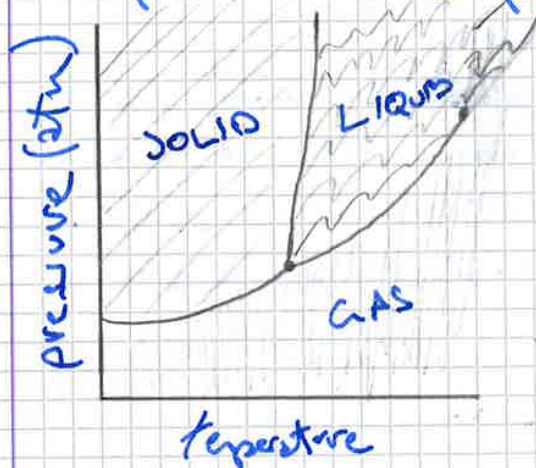
$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Universal gas
constant ($8,314 \frac{J}{mol \cdot K}$)

absolute
Temperature

THE PHASE DIAGRAM

this diagram combines the phase change curves at given condition of temperature and pressure.



- REGIONS: each region presents conditions for which the phase is stable

- LINES: the lines are phase-transition curves, where two phases are in equilibrium.

- TRIPLE POINT: is the point at which all three phases are in equilibrium, few substances can have more than one triple point

- CRITICAL POINT: at the critical point the liquid and gaseous phase become equal in density. The average F_k is so high that the vapor cannot be condensed at any pressure. Pressure and temperature becomes "critical" (T_c, P_c)

• ION-DIPOLE FORCES

When an ion and a nearby polar molecule interact. The most important result is when an ionic compound dissolves in water. The ions separate because the attraction ion-water is stronger than the ion-ion one.

• DIPOLE-DIPOLE FORCES

When poles of molecules interact. Their attraction order the disposition of molecules (obviously not as in a solid). The more strong these forces are, the more energy is needed to separate molecules, thus, the higher is the boiling point.

• THE HYDROGEN BOND

A special type of dipole-dipole force arises between molecules that have an H atom bonded to N, O or F (a small, highly EN, with lone e pairs).

• INDUCED DIPOLE FORCES

Among atoms an electric field can induce a distortion in the e cloud, of a non-polarized atom, pulling the e density and inducing a temporary dipole moment. Smaller atoms are less polarizable (astiers, end-period elements, ...)

LIQUID STATE

SURFACE TENSION

Surface tension is the force needed to increase the surface area.

Surface particles experience a net attraction by intermolecular forces downwards. It's measured in J/m^2 .

CAPILLARITY

The capillary attraction or capillarity results from a competition between the intermolecular forces within the liquid (cohesive forces) and those between the liquid and the tube walls (adhesive forces).

EX1. Water in glass: adhesive forces arise from the bonding forces with the \ominus atoms of the glass.

The liquid rises until the gravity pulling down is balanced by adhesive forces pulling up.

In this case a concave meniscus is formed.

EX2. Mercury in glass: here the cohesive forces are given by metallic bonds, so they're much more stronger. As a result a concave meniscus is formed, by cohesive forces and high surface tension.



SOLID STATE

- Amorphous solids: poorly defined shapes
- Crystalline solids: well defined shapes because their particles occur in an orderly arrangement.

Def: crystal lattice: all points with identical surroundings

Def: unit cell: the smallest portion that gives the crystal if it is repeated in all directions.

Def: coordination number: the number of nearest neighbors of a particle

CUBIC UNIT CELL

- simple cubic unit cell: eight identical particles define the corners of a cube, the coordination number is 6
- body centered cubic unit cell: eight at the corners and one at the center of the cube. Those at the corners don't touch each other. The coordination number is 8
- Face-centered cubic unit cell: particles lie at each corner and at the center of each face of the cube (not at the center itself). Particles at the corners touch those in the faces but not each other. The coordination number is 12.