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TOPIC 0:
Preliminary Concepts

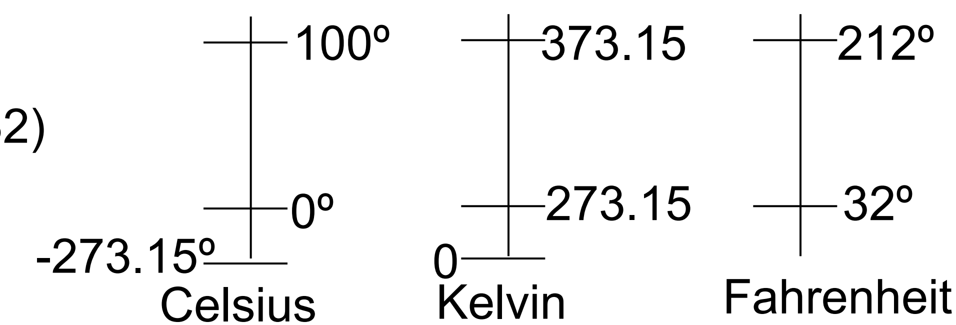
Matter, substance, energy
Atoms and particles
Molecules and mole
Molecular mass
Molecular formula
Chemical equations
Reactions in aqueous media
Acids and Bases
Redox reactions

Matter, substance, energy…

- What is:
  - Matter?
  - Substance?
  - Mixture?
  - Physical property?
  - Chemical property?
  - Element?
  - Compound?

- IS units: m, kg, s, A, K, mol, cd
- Derived units:
  - Volume m^3
  - Velocity $m \cdot s^{-1}$
  - Acceleration $m \cdot s^{-2}$
  - Force $N \equiv m \cdot kg \cdot s^{-2}$
  - Pressure $Pa \equiv N \cdot m^{-2}$ (1 atm = 101,325 Pa)
  - Energy $J \equiv m^2 \cdot kg \cdot s^{-2}$ (1 cal = 4.184 J)
  - Density $kg \cdot m^3$
  - Temperature K

$$°C = (5/9)(°F - 32)$$

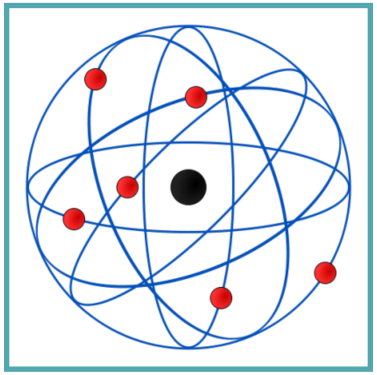


- **Standard Conditions for Temperature and Pressure (STP):** a set of pressure and temperature values for experimental measurements to allow comparison between different sets of data.
  - IUPAC (International Union of Pure and Applied Chemistry) defines:
    - Standard Temperature: 0ºC (273.15K, 32 ºF)
    - Standard Pressure: 100 kPa (14.504 psi, 0.986 atm)
  - NIST (National Institute of Standards and Technology):
    - Standard Temperature: 20ºC (293.15K, 68 ºF)
    - Standard Pressure: 101.325 kPa (14.969 psi, 1 atm)
- **Standard State** of a material is the reference state for the material's thermodynamic properties (H, S, G)
  - Standard Pressure: p^o = 1 bar (100 kPa)
  - Standard Temperature: not defined. Typically 298.15 K.

Atoms and particles

- Atoms:
  - Proton, p: (+), m = $1.672 \cdot 10^{-24}$ g; q = $+1.602 \cdot 10^{-19}$ C
  - Neutron, n: (0), m = $1.675 \cdot 10^{-24}$ g
  - Electron, e^- : (-) m = $9.109 \cdot 10^{-28}$ g; q = $-1.602 \cdot 10^{-19}$ C
  - Atomic number, Z = nº p
  - Mass number, A = nº p + nº n
  - Atoms with ≠ Z → ≠ element
  - Atoms with = Z but ≠ A → isotopes

  $\}\ {}^{A}_{Z}X$

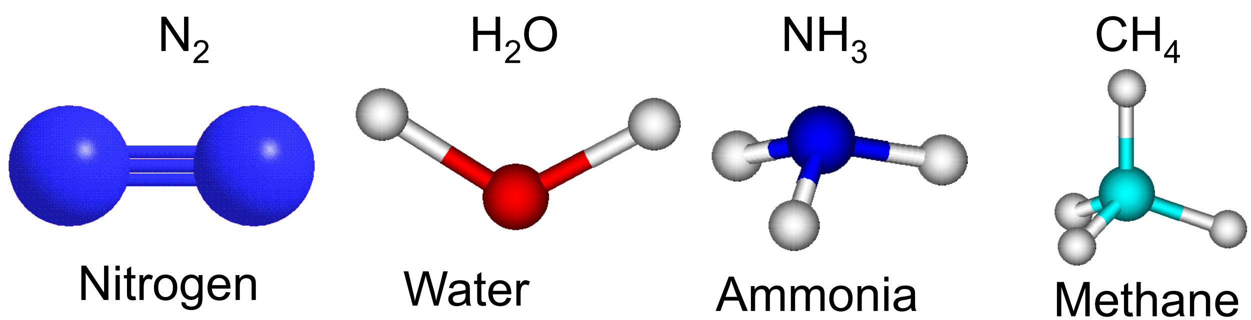


Source: http://es.wikipedia.org/wiki/Átomo

- Atomic mass unit (*u* or *Da*-Dalton)): 1/12 of the mass of a ^{12}C atom
  - Proton: m = 1.00728 u
  - Neutron: m = 1.00867 u
  - Electron: m = $5.489 \cdot 10^{-4}$ u
  - Atomic mass of ^{12}C = 12 u

Molecules and mole

- Neutral atoms: when nº p = nº e
- Atomic Ions: when nº p ≠ nº e (cations or anions)
- Molecules: a collection of atoms linked by covalent bonds (neutral or ion)



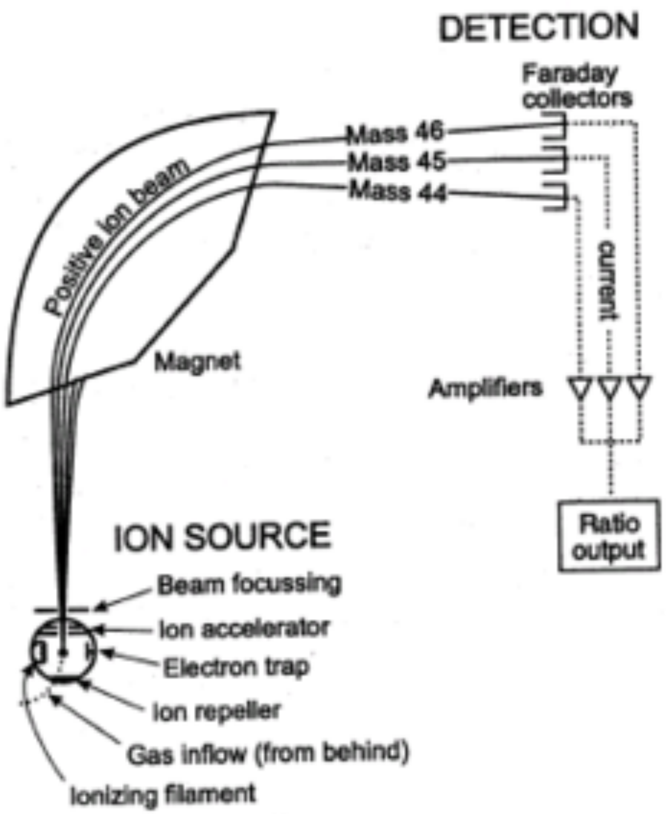
- Avogadro's Number: number of carbon atoms contained in 12 grams of ^{12}C. $N_A = 6.022 \cdot 10^{23}$ [atoms]/mol or mol^{-1}
  - *Deduce that 1 Da = $1.6605 \cdot 10^{-24}$ g*
- Mole (symbol mol): mass of substance that contains as many atoms as in 12 grams of ^{12}C.
- Mole: (generalization) mass of substance that contains N_A particles (ions, atoms, electrons, molecules, etc.). [objects]/mol

Molecular mass

- How molecular masses can be determined (early times)
  - Using the Dulong and Petit law (1819): *the product of the specific heat (cal/ºC·g) times the atomic mass (g/mol) is a constant (6 cal/ºC·mol). Only useful for metals.*
  - Avogadro's Principle (1811): *a mol of any gas occupies the same volume under STP. Not true because of non-ideality of gases. But it can be used:* $M(g/mol) = d_{corr}(g/L) \times 22.414\ (L/mol)$ *if* d_{corr}*, the density of the gas, is extrapolated to pressure = 0.*
  - Combination weights (For interested students, See Mahan).
  - Mass spectrometry (nowadays)

Molecular mass

- Mass spectrometry: separates ions by its q/m ratio.



Source: http://en.wikipedia.org/wiki/Atom

  - Molecules or atoms enter the ionizing camera in gas form.
  - A high energy ray of electrons is produced by a high voltage filament. Electrons collide with molecules, pulling out electrons and/or fragmenting molecules.
  - Positive ions, accelerated by an electric field, enter in a magnet with magnetic field B and describe circular trajectories of radius given by

$$\frac{1}{r^2} = \frac{B^2}{2V}\frac{q}{m}$$

  - Ions collide the detector at a distance given by their q/m ratio. Since probability of having two charges is extremely low, ions separate according to their mass
  - MS can separate isotopes.

Exercise 1.1

In the following Table you may find the abundances of chlorine isotopes as well as their atomic masses. Calculate the average atomic mass of chlorine in Da and g/mol.

	^{35}Cl	^{37}Cl
Abundance (%)	75.77	24.23
Atomic mass (u)	34.96885	36.9659

The average atomic mass is given by
$M = \Sigma A(\%) \cdot M(u) = 0.7577 \times 34.96885 + 0.2423 \times 36.9659 = 35.453\ u = 35.453\ g/mol$

The mass unity u refers to the mass of an atom but it is numerically equivalent to the mass of a mol of atoms, so M = 35.453 g/mol.

Exercise 1.2

Calculate de average distance between two water molecules if the density is 1 $g \cdot cm^{-3}$.

For solving this exercise it is necessary to make some assumptions about what are water molecules.

a) Suppose that water molecules are points in the space. One mole of water <> 18 g <> 18/1 cm^3. Suppose a cube of 18 cm^3 volume. It will contain N_A molecules ($6{,}022 \times 10^{23}$). The edge of the cube has a length given by $18^{1/3}$ = 2,6207 cm. Along this length you may find, in average, $(N_A)^{1/3}$ molecules, i.e. $8{,}445 \times 10^7$ molecules. If the molecules are uniformly distributed, the distance between two water molecules can be calculated as 2,6207 cm/ $8{,}445 \times 10^7$ molecules = $3{,}103 \times 10^{-8}$ cm $\times$ (10^{-2} m/cm) $\times$ (10^9 nm/m) = 0,31 nm = 3,1Å. All these numbers can be grouped in a formula. If M is the molecular mass and d, de density, the distance between two molecules is given by $l = (M/dN_A)^{1/3}$

b) Now let us suppose that water molecules are spheres. If N_A molecules occupy a volume of 18 cm^3, a single molecule will occupy $18/N_A = 2{,}989 \times 10^{-23}$ $cm^3 \times (10^{-2}$ $m/cm)^3 \times (10^9$ $nm/m)^3$ = $2{,}989 \times 10^{-2}$ nm^3. The volume of an sphere is $V=(4/3)\pi r^3$ where r is the radius. The radius of a single molecule is $r=(3V/4\pi)^{1/3}$ = 0,19 nm. If all molecules are in contact, the distance between two molecules will be 2r = 0,38 nm = 3,8 Å

Molecular mass

- Molecular mass (M): is the mass of a single molecule (in *u*) or of a mole of molecules (g/mol). $M = \Sigma M_i$ where M_i is the mass of each atom. *Is this assertion really true?*

Example: molecular mass of phosphoric acid H_3PO_4

- M (H) = 1.008 g/mol
- M (O) = 16.00 g/mol
- M (P) = 30.97 g/mol

$M(H_3PO_4) = 3 \times M(H) + M(P) + 4 \times M(O) =$ 97.99 g/mol

- Percent composition:

In atoms

% P = 1/8 × 100 = 12.5%
% O = 4/8 × 100 = 50.0 %
% H = 3/8 × 100 = 37.5 %

In mass

% P = 30.97/97.99 × 100 = 31.61%
% O = 4×16.00/97.99 × 100 = 65.31 %
% H = 3×1.008/97.99 × 100 = 3.086 %

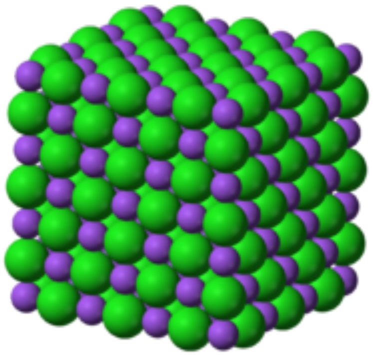
Molecular formula

- Molecular mass also applies to substances that do not form molecules: ionic substances and metals.

Example, sodium chloride NaCl

M (NaCl) = M (Na^+) +M (Cl^-) =

= 22.99 + 35.45 = 58,44 g/mol of ions



Source http://en.wikipedia.org/wiki/Crystalline_lattice

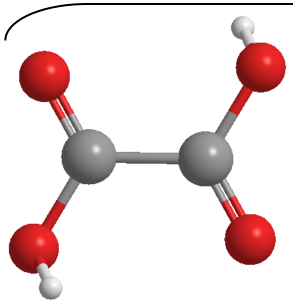
- Molecular formula: Set of element symbols and subscripts (generally integers) describing the number of atoms that form a given substance

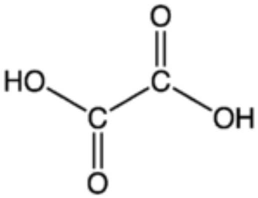
Example: Oxalic acid

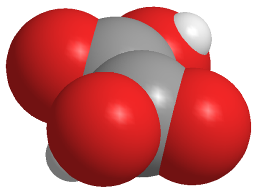
Molecular formula
$C_2O_4H_2$

Empirical formula
CO_2H

Structural formulas







Chemical equations

- **Chemical equations**: *standard way of representing chemical changes*

$$\underline{2}H_2 + (\underline{1})O_2 \rightarrow \underline{2}H_2O$$

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

Left term: reagents
Right term: products
+ means "reacts with".
$\rightarrow$ means "produces"; applies to irreversible reactions.
$\rightleftarrows$ or $\leftrightarrow$: both terms are in equilibrium; applies to reversible reactions.
Numerical coefficients: number of molecules or moles of substance that react or are produced (stoichiometric coefficients).

- **Balanced equations**: number of atoms and charge at each side must be the same

Chemical equations

- Phase transformations

$H_2O_{(l)} \rightarrow H_2O_{(g)}$

$H_2O_{(l)} \rightarrow H_2O_{(s)}$

$H_2O_{(s)} \rightarrow H_2O_{(g)}$

$_{(l), (g), (s)}$ mean liquid, gas or solid, the state in which products and reactants participate in the process

- Precipitation reactions

$BaCl_2 + 2AgNO_3 \rightarrow 2AgCl \downarrow + Ba(NO_3)_2$

↓ means that AgCl precipitates

- Equilibrium reactions in aqueous media

$2H_2O \leftrightarrow H_3O^+_{(ac)} + OH^-_{(ac)}$

$_{(ac)}$ means dissolved in water. Isolated ions do not exist unless shielded (surrounded) by water molecules.

- Decomposition reactions

$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}\uparrow$

Reactions in aqueous media

- Some terms
  - Reactants must be soluble in water (~ 0.1 mol·L^{-1})
  - Solute → Ions: ELECTROLYTES
  - Solute → Molecules: NON-ELECTROLYTES
  - STRONG electrolytes: completely ionized
  - WEAK electrolytes: partially ionized

Soluble compounds	**Insoluble compounds**
Compounds of Group 1	Carbonates, chromates, oxalates, phosphates except Group 1 and NH_4^+
Ammonium compounds (NH_4^+)	Sulfides except Group 1 and NH_4^+
Chlorides, bromides, iodides except Ag^+, Hg_2^{2+}, Pb^{2+}	Hydroxides, oxides except Groups 1 and 2
Nitrates, acetates, chlorates, perchlorates	
Sulfates except Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Hg_2^{2+}, Ag^+	

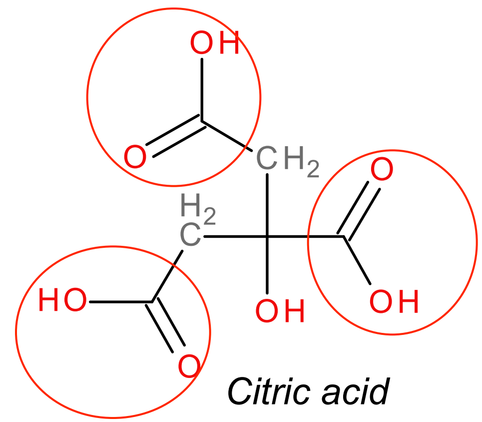
Acids and Bases

- Arrhenius theory:
  - Acid: Compound that contains H and gives H^+ when reacts with water
  - Base: Compound that produces OH^- when reacts with water

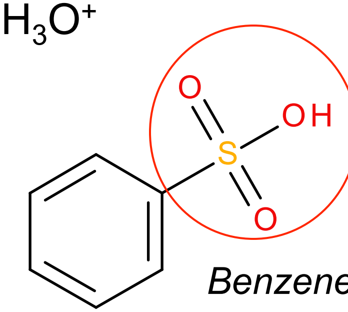
- Brønsted and Lowry: generalization
  - Acid: substance that donates protons
  - Base: substance that accepts protons
    - MONOPROTIC acids: HCl, HNO_3,
    - POLYPROTIC acids: H_3PO_4, H_2SO_4, Citric acid
    - Organic acids: the groups –COOH and $–SO_3H$ (carboxylic and sulfonic)

$$R\text{-}COOH + H_2O \leftrightarrow RCOO^- + H_3O^+$$

    - STRONG and WEAK acids and bases



Citric acid



Benzenesulfonic acid

Acids and Bases

STRONG acids	**WEAK acids**	**STRONG bases**	**WEAK bases**
HCl, HBr, HI	All other inorganic acids	Hydroxides Groups 1 and 2	Ammonia (NH_3)
HNO_3	Organic acids	Oxides Groups 1 and 2	Amines
$HClO_3$, $HClO_4$			
H_2SO_4			

- Neutralization: reaction between an acid and a base

$$2\,HNO_3 + Ba(OH)_2 \rightarrow Ba(NO_3)_2 + 2\,H_2O$$

$$2\,H^+ + 2\,NO_3^- + Ba^{2+} + 2\,OH^- \rightarrow Ba^{2+} + 2\,NO_3^- + 2\,H_2O$$

$$2\,H^+ + 2\,OH^- \rightarrow 2\,H_2O$$

Redox reactions

- Oxidation and reduction

$$2\ Ca_{(s)} + O_{2(g)} \rightarrow 2\ Ca^{2+}_{(s)} + 2\ O^{2-}_{(s)} \quad (CaO)$$

$$Ca_{(s)} + Cl_{2(g)} \rightarrow Ca^{2+}_{(s)} + 2\ Cl^{-}_{(s)} \quad (CaCl_2)$$

  – Oxidation: incorporation of oxygen
  – Generalization: oxidation consists of loosing electrons
  – Generalization: reduction consists of gaining electrons
  – Oxidation plus reduction : REDOX process

  – Oxidizing agent (oxidant): induces oxidation (O_2, Cl_2) and reduces itself
  – Reducing agent (reductant): induces reduction (Ca) and oxidizes itself

  – Redox process: a change in the oxidation state of substances