2_ Basic concepts and quantities in chemistry

Formula weight (molecular mass)

Given a compound its **formula weight (molecular mass, m.m.)** is given by the sum of the atomic masses (a.m., see Periodic Table of the Elements) of the atoms that make it up.

Ex.:

m.m. H_2O = 2x (a.m. H) + a.m. O = 2x1,008 + 16,00 =18,016 amu

m.m. NaCl = a.m. Na + a.m. Cl = 23 + 35,45 = 58,45 amu

m.m. $Mg(OH)_2$= a.m. Mg+2x(a.m. O+ a.m. H)=24,3+2x(16,00+1,008)=58,3 amu

atomic mass unit , *amu* = 1/12 of the massa of the ^{12}C isotope = *1,6605665 x 10^{-24} g*

PERIODIC TABLE OF THE ELEMENTS

Università degli Studi di Bologna

Facoltà di Farmacia
www.farmacia.unibo.it

Il colore di fondo indica le proprietà della specie elementare a 25 °C e 1 bar: bianco = atomica; giallo = metallica solida; rosso = metallica liquida; verde = covalente solida; viola = covalente liquida; turchese = covalente gassosa

Numero atomico → 1 | 1,008 ← Peso atomico (1)
Simbolo (2) → H
idrogeno ← Nome
Configurazione elettronica esterna fondamentale → $1s^1$

(1) Numero di massa dell'isotopo più rappresentativo per gli elementi naturali con solo isotopi a vita breve e per gli elementi artificiali

(2) elementi artificiali: simbolo rosso e fondo grigio

Periodo	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1,008 H idrogeno $1s^1$																	2 4,003 He elio $1s^2$
2	3 6,941 Li litio $2s^1$	4 9,012 Be berillio $2s^2$											5 10,81 B boro $2s^22p^1$	6 12,01 C carbonio $2s^22p^2$	7 14,01 N azoto $2s^22p^3$	8 16,00 O ossigeno $2s^22p^4$	9 19,00 F fluoro $2s^22p^5$	10 20,18 Ne neon $2s^22p^6$
3	11 23,00 Na sodio $3s^1$	12 24,30 Mg magnesio $3s^2$											13 26,98 Al alluminio $3s^23p^1$	14 28,09 Si silicio $3s^23p^2$	15 30,97 P fosforo $3s^23p^3$	16 32,07 S zolfo $3s^23p^4$	17 35,45 Cl cloro $3s^23p^5$	18 39,95 Ar argo $3s^23p^6$
4	19 39,10 K potassio $4s^1$	20 40,08 Ca calcio $4s^2$	21 44,96 Sc scandio $3d^14s^2$	22 47,87 Ti titanio $3d^24s^2$	23 50,94 V vanadio $3d^34s^2$	24 52,00 Cr cromo $3d^54s^1$	25 54,94 Mn manganese $3d^54s^2$	26 55,85 Fe ferro $3d^64s^2$	27 58,93 Co cobalto $3d^74s^2$	28 58,69 Ni nichel $3d^84s^2$	29 63,55 Cu rame $3d^{10}4s^1$	30 65,41 Zn zinco $3d^{10}4s^2$	31 69,72 Ga gallio $3d^{10}4s^24p^1$	32 72,64 Ge germanio $3d^{10}4s^24p^2$	33 74,92 As arsenico $3d^{10}4s^24p^3$	34 78,96 Se selenio $3d^{10}4s^24p^4$	35 79,90 Br bromo $3d^{10}4s^24p^5$	36 83,80 Kr cripto $3d^{10}4s^24p^6$
5	37 85,47 Rb rubidio $5s^1$	38 87,62 Sr stronzio $5s^2$	39 88,91 Y ittrio $4d^15s^2$	40 91,22 Zr zirconio $4d^25s^2$	41 92,91 Nb niobio $4d^45s^1$	42 95,94 Mo molibdeno $4d^55s^1$	43 99 Tc tecnezio $4d^55s^2$	44 101,07 Ru rutenio $4d^75s^1$	45 102,91 Rh rodio $4d^85s^1$	46 106,42 Pd palladio $4d^{10}$	47 107,89 Ag argento $4d^{10}5s^1$	48 112,41 Cd cadmio $4d^{10}5s^2$	49 114,82 In indio $4d^{10}5s^25p^1$	50 118,71 Sn stagno $4d^{10}5s^25p^2$	51 121,76 Sb antimonio $4d^{10}5s^25p^3$	52 127,60 Te tellurio $4d^{10}5s^25p^4$	53 126,90 I iodio $4d^{10}5s^25p^5$	54 131,29 Xe xeno $4d^{10}5s^25p^6$
6	55 132,91 Cs cesio $6s^1$	56 137,33 Ba bario $6s^2$	La - Lu	72 178,49 Hf afnio $4f^{14}5d^26s^2$	73 180,95 Ta tantalio $4f^{14}5d^36s^2$	74 183,84 W wolframio $4f^{14}5d^46s^2$	75 186,21 Re renio $4f^{14}5d^56s^2$	76 190,23 Os osmio $4f^{14}5d^66s^2$	77 192,22 Ir iridio $4f^{14}5d^76s^2$	78 195,08 Pt platino $4f^{14}5d^96s^1$	79 196,97 Au oro $4f^{14}5d^{10}6s^1$	80 200,59 Hg mercurio $4f^{14}5d^{10}6s^2$	81 204,38 Tl tallio $4f^{14}5d^{10}6s^26p^1$	82 207,2 Pb piombo $4f^{14}5d^{10}6s^26p^2$	83 208,98 Bi bismuto $4f^{14}5d^{10}6s^26p^3$	84 209 Po polonio $4f^{14}5d^{10}6s^26p^4$	85 210 At astato $4f^{14}5d^{10}6s^26p^5$	86 222 Rn radon $4f^{14}5d^{10}6s^26p^6$
7	87 223 Fr francio $7s^1$	88 226 Ra radio $7s^2$	Ac - Lr	104 261 Rf rutherfordio $5f^{14}6d^27s^2$	105 262 Db dubnio $5f^{14}6d^37s^2$	106 263 Sg seaborgio $5f^{14}6d^47s^2$	107 262 Bh bohrio $5f^{14}6d^57s^2$	108 255 Hs hassio $5f^{14}6d^67s^2$	109 256 Mt meitnerio $5f^{14}6d^77s^2$									

57 138,91 La lantanio $5d^16s^2$	58 140,12 Ce cerio $4f^26s^2$	59 140,91 Pr praseodimio $4f^36s^2$	60 144,24 Nd neodimio $4f^46s^2$	61 145 Pm promezio $4f^56s^2$	62 150,36 Sm samario $4f^66s^2$	63 151,96 Eu europio $4f^76s^2$	64 157,25 Gd gadolinio $4f^75d^16s^2$	65 158,93 Tb terbio $4f^96s^2$	66 162,50 Dy disprosio $4f^{10}6s^2$	67 164,93 Ho olmio $4f^{11}6s^2$	68 167,26 Er erbio $4f^{12}6s^2$	69 168,93 Tm tulio $4f^{13}6s^2$	70 173,04 Yb itterbio $4f^{14}6s^2$	71 174,97 Lu lutezio $4f^{14}5d^16s^2$
89 227 Ac attinio $6d^17s^2$	90 232,04 Th torio $6d^27s^2$	91 231 Pa protoattinio $5f^26d^17s^2$	92 238,03 U uranio $5f^36d^17s^2$	93 237 Np nettunio $5f^46d^17s^2$	94 244 Pu plutonio $5f^67s^2$	95 243 Am americio $5f^77s^2$	96 247 Cm curio $5f^76d^17s^2$	97 247 Bk berkelio $5f^97s^2$	98 251 Cf californio $5f^{10}7s^2$	99 254 Es einstenio $5f^{11}7s^2$	100 257 Fm fermio $5f^{12}7s^2$	101 258 Md mendelevio $5f^{13}7s^2$	102 259 No nobelio $5f^{14}7s^2$	103 260 Lr lawrenzio $5f^{14}6d^17s^2$

Ordini dei Farmacisti
di Bologna e di Rimini

Università degli Studi di Bologna

PERIODIC TABLE OF THE ELEMENTS

Facoltà di Farmacia
www.farmacia.unibo.it

Elemento: metallo · semimetallo · non-metallo

Simbolo → H; Elettronegatività (Pauling) → 2,2; Gradi di ossidazione (1) → +1 / 0 / −1; Proprietà acido/base (2) → ab; Proprietà redox a pH 0 (3); Proprietà redox a pH 14 (3)

(1) in rosso: g.o. importanti; in verde: g.o. rappresentati prevalentemente da complessi

(2) A = acido forte; a = acido debole; ab = anfotero; b = base debole; B = base forte

(3) O = ossidante forte; o = ossidante medio; r = riducente medio; R = riducente forte

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 2,2 +1 ab - - 0 - - r −1 - R R																	**He** 0 -
2	**Li** 1,0 +1 B - - 0 - R R	**Be** 1,6 +2 ab - - 0 - R R											**B** 2,0 +3 a - - 0 - r R −3	**C** 2,6 +4 a - - +2 - o R 0 - - r −4 - - r	**N** 3,0 +5 A O - +4 - O o +3 a O o +2 - O o +1 - O o 0 - - - −1 b O R −2 b O R −3 b - r	**O** 3,4 0 - O o −1 a O o −2 ab - -	**F** 4,0 0 - O O −1 a - -	**Ne** 0 -
3	**Na** 0,9 +1 B - - 0 - R R	**Mg** 1,3 +2 B - - 0 - R R											**Al** 1,6 +3 ab - - 0 - R R	**Si** 1,9 +4 a - - 0 - r R	**P** 2,2 +5 a - - +3 a r r +1 a r R 0 - r R −3 - - r	**S** 2,6 +6 A O - +4 a o r +2 0 - - r −2 a - r	**Cl** 3,2 +7 A O o +5 A O o +3 a O o +1 a O o 0 - O O −1 A - -	**Ar** 0 -
4	**K** 0,8 +1 B - - 0 - R R	**Ca** 1,0 +2 B - - 0 - R R	**Sc** 1,4 +3 ab - - 0 - R R	**Ti** 1,5 +4 ab - - +3 b - R +2 b r R 0 - R R	**V** 1,6 +5 ab o O +4 ab o o +3 b - - +2 b r r 0 - R r	**Cr** 1,7 +6 a O - +3 ab - - +2 b r R 0 - r R	**Mn** 1,6 +7 A O o +6 a O o +4 - O - +3 b O - +2 b - - 0 - R R	**Fe** 1,8 +6 a O o +3 ab o - +2 ab - r 0 - r r	**Co** 1,9 +3 ?b O - +2 ab - - 0 - - r	**Ni** 1,9 +2 b - - 0 - r r	**Cu** 1,9 +2 ab o - +1 ab o - 0 - - r	**Zn** 1,7 +2 ab - - 0 - r R	**Ga** 1,8 +3 ab - - +1 b r ? 0 - r r	**Ge** 2,0 +4 a - - +2 0 - - r	**As** 2,2 +5 a o - +3 ab - r 0 - - r −3 - r R	**Se** 2,6 +6 A o - +4 a o - 0 - - r −2 a r r	**Br** 3,0 +7 A O o +5 A O o +3 +1 a O o 0 - O O −1 A - -	**Kr** +2 0 -
5	**Rb** 0,8 +1 B - - 0 - R R	**Sr** 1,0 +2 B - - 0 - R R	**Y** 1,2 +3 b - - 0 - R R	**Zr** 1,3 +4 b - - +3 0 - R R	**Nb** 1,6 +5 a - ? +4 0 - r ?	**Mo** 2,2 +6 a o - +5 b o ? +4 b - r +3 b - ? 0 - - R	**Tc** 1,9 +7 A o ? +4 - o ? 0 - - ?	**Ru** 2,2 +8 ? O o +7 a O o +6 a O ? +4 - O - +3 b o - +2 b o ? 0	**Rh** 2,3 +6 a O o +4 - O o +3 b O - +2 b o ? 0 - - -	**Pd** 2,2 +4 - O O +2 b O - 0 - - -	**Ag** 1,9 +3 a O o +1 ab o o 0 - - -	**Cd** 1,7 +2 ab - - 0 - r r	**In** 1,8 +3 b - - +1 b r ? 0 - r r	**Sn** 2,0 +4 ab - - +2 ab - r 0 - - r	**Sb** 2,1 +5 a o - +3 ab - r 0 - - r −3 - r R	**Te** 2,1 +6 a O - +4 ab o - +2 0 - - r −2 a r R	**I** 2,7 +7 a O o +5 a O o +3 +1 a O o 0 - o o −1 A - -	**Xe** 2,6 +8 a O O +6 a O O +4 +2 0 - - -
6	**Cs** 0,8 +1 B - - 0 - R R	**Ba** 0,9 +2 B - - 0 - R R	La - Lu	**Hf** 1,3 +4 b - - 0 - R R	**Ta** 1,5 +5 a - ? 0 - r ?	**W** 2,4 +6 a - - +5 b - ? +4 b - R +3 0 - - R	**Re** 1,9 +7 A o - +6 a o r +4 ? - r +3 ? o R 0 - - r	**Os** 2,2 +8 a O o +6 a o - +4 - o - +2 0	**Ir** 2,2 +6 a O o +4 - o - +3 b O - 0 - - -	**Pt** 2,3 +4 a o - +2 ab o - 0 - - -	**Au** 2,5 +3 a O o +1 b O ? 0 - - -	**Hg** 2,0 +2 b o - +1 b o - 0 - - -	**Tl** ~1,8 +3 b O - +1 B - - 0 - r r	**Pb** 2,3 +4 a? O - +2 ab - - 0 - - r	**Bi** 2,0 +5 a O ? +3 b o - 0 - - r	**Po** 2,0 +4 ab o - +2 b o ? 0 - - r −2 a r R	**At** 2,2 +5 a O o +1 a o - 0 - o - −1 A - -	**Rn** +2 0 - - -
7	**Fr** 0,7 +1 B - - 0 - R R	**Ra** 0,9 +2 B - - 0 - R R	Ac - Lr	**Rf** +4	**Db**	**Sg** +6	**Bh**	**Hs**	**Mt**									

La 1,1 +3 b - - 0 - R R	**Ce** 1,1 +4 b O - +3 b - r 0 - R R	**Pr** 1,1 +4 ? O o +3 b - - 0 - R R	**Nd** 1,1 +3 b - - +2 ? R ? 0 - R R	**Pm** +3 b - - 0 - R R	**Sm** 1,2 +3 b - - +2 b R ? 0 - R R	**Eu** +3 b - - +2 b r ? 0 - R R	**Gd** 1,2 +3 b - - 0 - R R	**Tb** +4 ? O o +3 b - - 0 - R R	**Dy** 1,2 +3 b - - 0 - R R	**Ho** 1,2 +3 b - - 0 - R R	**Er** 1,2 +3 b - - 0 - R R	**Tm** 1,2 +3 b - - 0 - R R	**Yb** +3 ab - - +2 b R ? 0 - R R	**Lu** 1,3 +3 ab - - 0 - R R
Ac 1,1 +3 b - - 0 - R R	**Th** 1,3 +4 b - - 0 - R R	**Pa** 1,5 +5 b - ? +4 b -r ? 0 - R ?	**U** 1,4 +6 ab o - +5 b o ? +4 b - r +3 b r R 0 - R R	**Np** 1,4 +7 ab O o +6 b o o +5 b o o +4 b - - +3 b - R 0 - R R	**Pu** 1,3 +7 a ? o +6 ab o o +5 b o o +4 b o - +3 b - R 0 - R R	**Am** 1,3 +6 b O o +5 b O o +4 b O o +3 b - - +2 b R ? 0 - R R	**Cm** 1,3 +4 b O o +3 b - - 0 - R R	**Bk** 1,3 +4 b O ? +3 b - ? 0 - R ?	**Cf** 1,3 +3 b - ? 0 - R ?	**Es** 1,3 +3 b - ? +2 b R ? 0 - R ?	**Fm** 1,3 +3 b - ? +2 b r ? 0 - R ?	**Md** 1,3 +3 b - ? +2 b - ? 0 - R ?	**No** 1,3 +3 b O ? +2 b - ? 0 - R ?	**Lr** 1,3 +3 b - - 0 - R R

Ordini dei Farmacisti
di Bologna e di Rimini

MOLE (mol)

quantity of an element or a chemical species equal to its atomic or molecular weight expressed in grams.

Ex.: a.m of C = 12,01 amu, 1 mole of C has mass equal to 12,01 g

Ex.: m.m. of H_2O= 18 amu, 1 mole of H_2O has mass equal to 18 g

Hence, a.m. and m.m. can also be expressed in **g/mol**

A mole of any element or chemical compound contains the same number of elements or compounds and this number is the AVOGADRO NUMBER (*N*).

$$N = 6{,}02 \times 10^{23}$$

✓1 mol of C weighs 12.01 g (atomic weight 12.01 uma) and contains 6.02×10^{23} (N) C atoms

✓1 mol of H_2O weighs 18 g (weight formula 18 uma) contains 6.02×10^{23} (N) H_2O molecules

AVOGADRO NUMBER

A mole of any element contains the same number of atoms

Ex:

- ✓ **a.m. of C = 12,01 amu,**
- ✓ **1 mole of C has a mass of 12,01 g**
- ✓ conversion of the a.m. from amu to grams :

1. relation amu/grammi: *1 amu* = *1,6605665 x* 10^{-24} *g*
2. Proportion:

a.m. in grams : m.a. in amu = 1,6605665 x 10^{-24} *grammi : 1 amu*

a.m.* C *in grams= a.m. in amu x 1,6605665 x 10^{-24} *:1 =*

= *(12,01 x 1,6605665 x* 10^{-24}***) g***

- ✓ **Number of atoms in 1 mole of C** =

=total grams /a.m. in grams=

=12,01 g /(12,01 x 1,*6605665 x* 10^{-24} *g*)=

= 1 / 1,*6605665 x* 10^{-24} =

= ***6,02 x*** 10^{23}

AVOGADRO NUMBER

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AVOGADRO NUMBER

A mole of any chemical compund contains the same number of molecule

Ex:

- ✓ **m.m. of H_2O = 18 amu**, or in grams =(18 x 1,*6605665 x 10^{-24}) g*
  (1 amu = 1,6605665 x 10^{-24} g)
- ✓ **1 mole of H_2O has a mass of 18 g**
- ✓ **number of molecules in 1 mole of H_2O**

=total grams / m.m. in grams=

= 18g / (18x 1,*6605665 x 10^{-24} g*)=

= 1 / 1,*6605665 x 10^{-24}* =

= ***6,02 x 10^{23}***

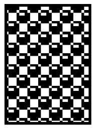
AVOGADRO NUMBER

AVOGADRO NUMBER and MOLE

AVOGADRO NUMBER (*N*) = ***6,02 x 10^{23}*** it is the reciprocal of the value of the a.m.u and corresponds to the number of atoms or molecules contained respectively in a mole

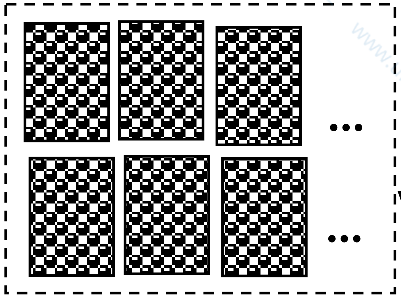
- ✓ 1 mol of Na contains 6,02x10^{23} (*N*) atoms of Na and has a mass of 23 g (a.m. Na = 23 amu)
- ✓ 1 mol of NaCl contains 6,02x10^{23} (*N*) *formula units* of NaCl and has a mass of 58.45 g (formula weight NaCl= 58.45 amu)
- ✓ **1 mol of elecrons contains 6,02x10^{23} (*N*) electrons, corresponds to 1 Faraday and has a total electric charge of -96485 Coulomb**

MASS, MOLE and MOLAR MASS



1 mole has
N molecoles
and mass = m.m.

∘= molecola



"n" moles

Each mole contributes with its mass to the total mass (m_{tot})

The total mass (m_{tot}) of n moles of a chemical compound is
m_{tot} = number of moles x molecular mass

$$\mathbf{m_{tot} = n \times m.m.}$$

Indeed

Total mass of moles : n moles = m.m. : 1 mole
Total mass of n moles = m.m. x n moles / 1 mole

Therfore, if we want to calculate the number of moles of a chemical species contained in a given total mass
number of moles = total mass of n moles / m.m.

$$\mathbf{n = m_{tot} / m.m.}$$

Indeed

n moles : total mass of n moles = 1 mole : m.m.
n moles = 1 mole x total mass of n moles / m.m

Excercises

1) Calculate the molar mass of and the mass of 0.1 moles of

- PbO_2 (lead oxide)
- $LiCoO_2$ (lithium cobaltite, LCO, first Sony Lithium ion batteries)
- Graphite (C_6)
- $LiMnO_2$ (Lithium manganate, LMO, layered oxide)
- $LiMn_2O_4$ ((Lithium manganate, LMO, spinel))
- $Li(Ni_{0.5}Mn_{0.5})O_2$ (Lithium Nickel Mnganese oxide, NMO)
- $LiFePO_4$ (Lithium iron phosphate, LPO, olivine)
- $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC)
- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA, Panasonic cells!)
- $LiPF_6$ (Lithium hexaflourophosphate, salt in LP30 Lithium battery electrolyte)

2) How many moles of lare contained in 1 kg of:

- Li
- Pb
- Si
- O_2
- S
- H_2

3) Calculate the charge of $5{,}0.10^{-2}$ moles of electrons

4) Cobalt is considered a critical element for cost, low abundance and low envirnonmental compatibility. Calculate the mass and weight percentage of Co in 1kg g of a) $LiCoO_2$, b) $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and c) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

Percentage purity and composition

✓percentage by weight = quantity by weight of a component contained in 100 parts of the total mass of the sample

$$\%p/p = \frac{massa_{component} \times 100}{massa_{total}} \quad [dimensionless]$$

The same unit for the component and total mass!
ex: grams of the component in 100 grams total

The solutions

They are physically homogeneous but chemically heterogeneous material systems, made up of different chemical species in variable ratios

They can be:
- gaseous (gas/gas)
- liquid (liquid / liquid, liquid / dissolved gas, dissolved liquid / solid)
- solid (alloys, mixed crystals)

The solutions consist of at least one solvent (the component present in greater quantity) and a solute.

Examples:
Lithium-ion battery catohodes: mixed oxides
Anodes LixSi, LixSn alloys (Si and Sn are the solvents)
LP30 electrolyte solution:
1 M $LiPF_6$ in EC (ethylene carbonate):DMC (dimethyl carbonate) 1:1 (Liquid)

The electrolyte solutions electrochemical cells

The electrolyte solutions are ionic conductors, charge is carried by the movement of ions. To be useful in an electrochemical cell, the solvent/electrolyte system must be of sufficiently low resistance (i.e., sufficiently conductive) and high electrochemical stability for the electrochemical processes that drive the cell response.

- liquid solutions containing ionic species, such as, H^+, Na^+, Cl^-, Li^+ in either water or a nonaqueous solvent.

Examples:
Lead-acid batteries
Aqueous solution: 35% sulphuric acid (H_2SO_4) and 65% water

Lithium-ion batteries (LP30 electrolyte solution)
Organic solution:
1 M $LiPF_6$ in EC (ethylene carbonate):DMC (dimethyl carbonate) 1:1

- fused salts (e.g., molten salt batteries and fuel cells)
- ionically conductive polymers (e.g., Nafion, polyethylene oxide (PEO)-$LiClO_4$).
- solid electrolytes (e.g. ceramics,[glass,lithium sulfide, sodium b-alumina, where charge is carried by mobile sodium ions that move between the aluminum oxide sheets).

Molarity

n= moles, V= volume

✓ **molarity** = number of solute moles in **1 liter of solution**

$$M_{solute} = \frac{n_{solute}}{V_{solution} \text{ in L}} \qquad [\text{mol L}^{-1}]$$

Molality

✓ **molality** = number of solute moles in **1 kg of solvent**

$$m_{solute} = \frac{n_{solute}}{mass_{solvent} \text{ in kg}} \qquad [\text{mol kg}^{-1}]$$

Ex: Calculate the molarity and the molality of a solution obtained by dissolving 1 g of $LiPF_6$ in 500 mL of EC:DMC (density of EC:DMC = 1.28 g/mL at RT)

Molar fraction

n= moles

✓ molar fraction = ratio between the moles of a component and the sum of the moles of all the components of the solution

$$X_{component} = \frac{n_{component}}{n_{total}} \quad \text{[dimensionless]}$$

the sum of the molar fractions of all the components is 1

ex: calculate the molar fractions of each element in the compund $Li(Ni_{0.5}Mn_{0.5})O_2$

CHEMICAL REACTIONS

A chemical reaction leads to individual variation in the composition of the reagents and therefore leads to variation of their chemical properties.

Example: in the reactions between acids and bases there is the neutralization of the reagents

To describe the chemical reactions we use CHEMICAL EQUATIONS, in which the reagents are written on the left and the products on the right; the arrow between reagents and products means "react to give"

Ex.: $2\ H_2 + O_2 \rightarrow 2\ H_2O$ *PEM Fuel Cell reaction*

Symbols (l), (g), (s), (acq) or (aq) placed AFTER each reagent or product indicate the respective states of aggregation liquid, gas, solid or if the substance is dissolved in water.

Es.: $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$

The reactions may involve reagents and products in the same phase (homogeneous reactions) in solution (gaseous, solid or liquid) or having different aggregation states (heterogeneous reactions)

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Stoichiometry of the chemical reactions

The stoichiometry of a chemical reaction is the quantitative description of the relative quantities (in moles) of the substances involved in the reaction.

All reactions must be balanced, ie the same number of atoms of each element must be present on the left and right of the chemical equation (principle of conservation of the mass).

In order to balance a chemical equation, the STECHIOMETRIC COEFFICIENTS are used. They are suitable numbers put BEFORE the reagents and products that indicate the relative quantities of the products both in moles and in molecules.

Es.: $2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(l)$

Also $4\,H_2\,(g) + 2\,O_2\,(g) \rightarrow 4\,H_2O\,(l)$

$2Li + S \rightarrow Li_2S$

Total mass of reagents + products in constant.
In general, the total number of moles is not preserved!

Never change the subscripts to balance a chemical equation, it will change the compound chemistry

LIMITING REAGENT

The limiting reagent is the one present in a lower quantity than the stoichiometric quantity defined by the chemical equation

Given a chemical reaction, if the reagents are not present in stoichiometric ratio, the products will be formed according to their stoichiometric ratio with the limiting reagent

REACTION YIELD

absolute yield: grams or moles of product which has been experimentally obtained from a chemical reaction

theoretical yield: grams or moles of product obtainable according to the reaction stoichiometry and based on the quantity of limiting reagent.

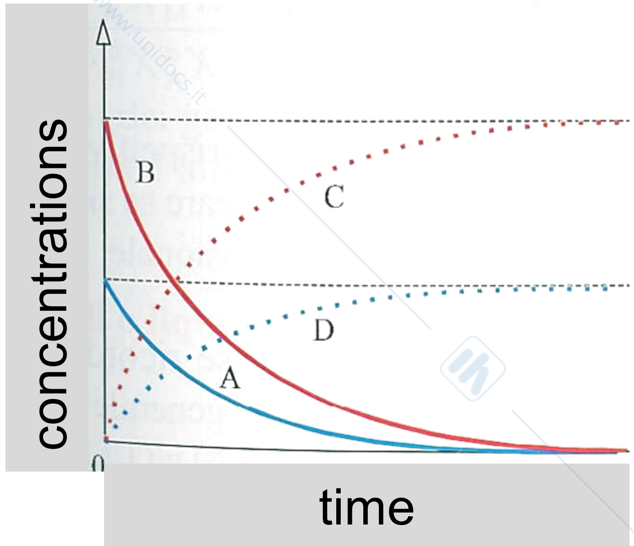
percentage yield: percentage of product obtained with respect to the quantity theoretically obtainable on the basis of the reaction stoichiometry, in the hypothesis that the limiting reagent reacts completely. The latter is calculated as:

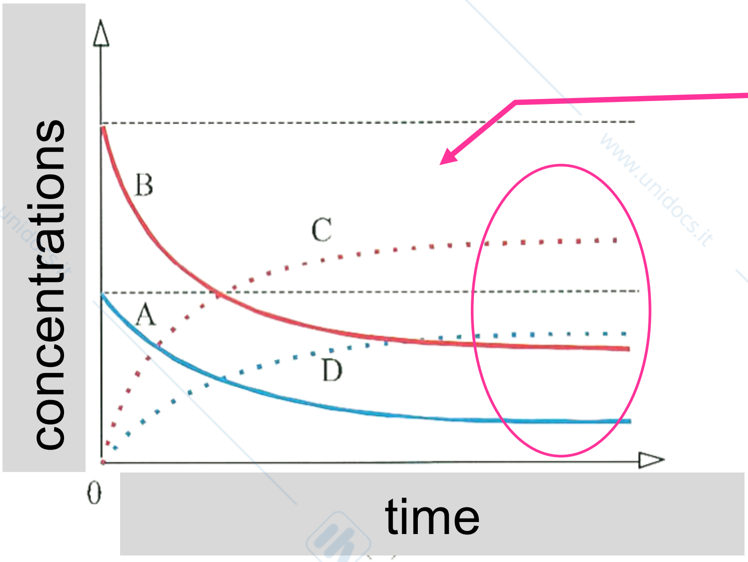
$$\text{percentage yield} = (\text{mol}_{\text{obtained}} / \text{mol}_{\text{theoretical}}) \times 100\ .$$

Chemical Equilibrium

✓ *For complete reactions (single arrow), reagents A and B are consumed over time and products C and D are produced. If A and B are initially present in stoichiometric ratio, only C and D are present at the end of the reaction*

$$aA + b\,B \rightarrow cC + dD$$





✓ *When a chemical equilibrium is established, the direct reaction (from right to left) and inverse (from left to right) occur at the same speed (double arrow). There is a dynamic equilibrium, there are both the C and D products and the reagents and the relative concentrations do not vary over time.*

$$aA + b\,B \rightleftarrows cC + dD$$

Law of the Chemical Equilibrium

At a constant temperature, the ratio of the product of the equilibrium concentrations of the reaction products, elevated to the respective stoichiometric coefficients, and the product of the reactant concentrations, elevated to the respective stoichiometric coefficients, is constant.

$$aA + bB \rightleftarrows cC + dD$$

$$\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K_{eq}$$

[C], [D], [A], [B] molar concentrations

K_{eq} High $\Rightarrow$ $[C]^c\,[D]^d >> [A]^a\,[B]^b$ formation of products is favored

reaction shifted to the right

$$aA + bB \rightleftarrows cC + dD$$

K_{eq} Low $\Rightarrow$ $[C]^c\,[D]^d << [A]^a\,[B]^b$ formation of reactants is favored

reaction shifted to the left

$$aA + bB \rightleftarrows cC + dD$$

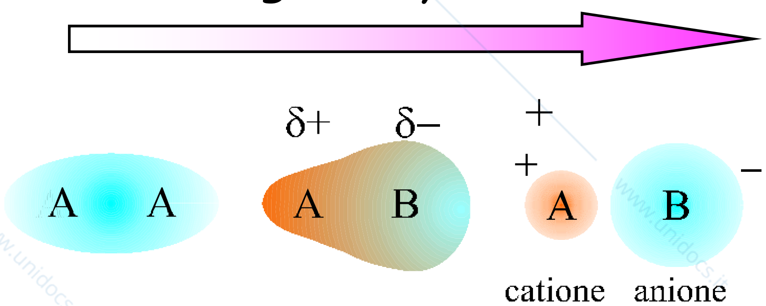
For heterogeneous reactions (products and or reagents in different aggregation states), K is given by placing the concentrations of pure liquid or solid compounds = 1 (their concentrations are constant). Only molar concentrations and the partial pressures appear.

TYPES OF CHEMICAL REACTIONS

- Ionic double exchange reactions
- Acid-base reactions
- **Redox reactions:** reactions with electron transfer between atoms of different molecules, with consequent variation of the oxidation number of the atoms involved.

Oxidation state (oxidation number, valence)

Electronegativity difference



A-A	(δ^+) (δ^-) **A-B**	A^+ B^-
H-H	**H-Cl**	Na^+ Cl^-
unpolarized covalent molecules	**polarized covalent**	**ionic**
		ionic compound

The oxidation number is the formal charge that an atom would have in a compound if the electronic bond pair is considered wholly belonging to the most electronegative atom

The Periodic Table of the Elements reports the possible oxidation numbers for the different elements.

Rules for the assignment of the oxidation number (valence)

1. The oxidation number of an elementary substance is zero:

Ex. ox. n of Pb (s) = 0, ox. n of Li(s) = 0; ox. n of O in O_2 = 0

2. The sum of the oxidation numbers of all the atoms present in a neutral species is zero, in a polyatomic ion it is equal to the ion charge

Ex: PbO_2 ox.n. Pb=+4, ox.n. O=-2 1x(ox.n. Pb)+2x(ox.n. O) =4 + 2 x (-2) = 0

*PF_6^- hexaflorophosphate anion (charge=**-1**) ox.n. P=+5, ox.n. F=-1*
*1x(ox.n. P)+6x(ox.n. F) =5 + 6 x (-1) = **-1***

3. the oxidation number of an element in a monoatomic ion is equal to the ion charge

Es. $LiPF_6$ = $Li^+PF_6^-$ ox.n. of Li^+ is +1

4. Some elements have the same oxidation number in all (or almost all) of their compounds

element	number of oxidation
I group	+1
IIgroup	+2
Al	+3
O	-2 (oxides), -1 (peroxides)
H	+1 (except in hydride where is -1)
F	-1

Alogens nei composti metal-alogenides -1

Evaluation of the average oxidation state of tranistion metals in oxides

Most transition metals have multiple oxidation states and their oxides can feature the presence of the same metal in different oxidation states. Therefore, in these compound, the average oxidation state of the metal is taken as representative of the reactivity.

EX

To calculate the oxidation number of the elements in the following compounds

Possible oxidation numbers of Mn = +2, +3, +4, +6, +7

a) MnO_2 o.n. O = -2; o.n. Mn = x; x+2(-2)=0 x-4 =0 x=+4

but

b) $LiMn_2O_4$ (spinel) o.n. Li = +1; o.n. O = -2; o.n. Mn= x

1+2x+4(-2) = 0 2x-7 =0 x=+3,5!

In the spinel sutructure both Mn (IV) and Mn (III) are present

$LiMn_2O_4$ spinel structure

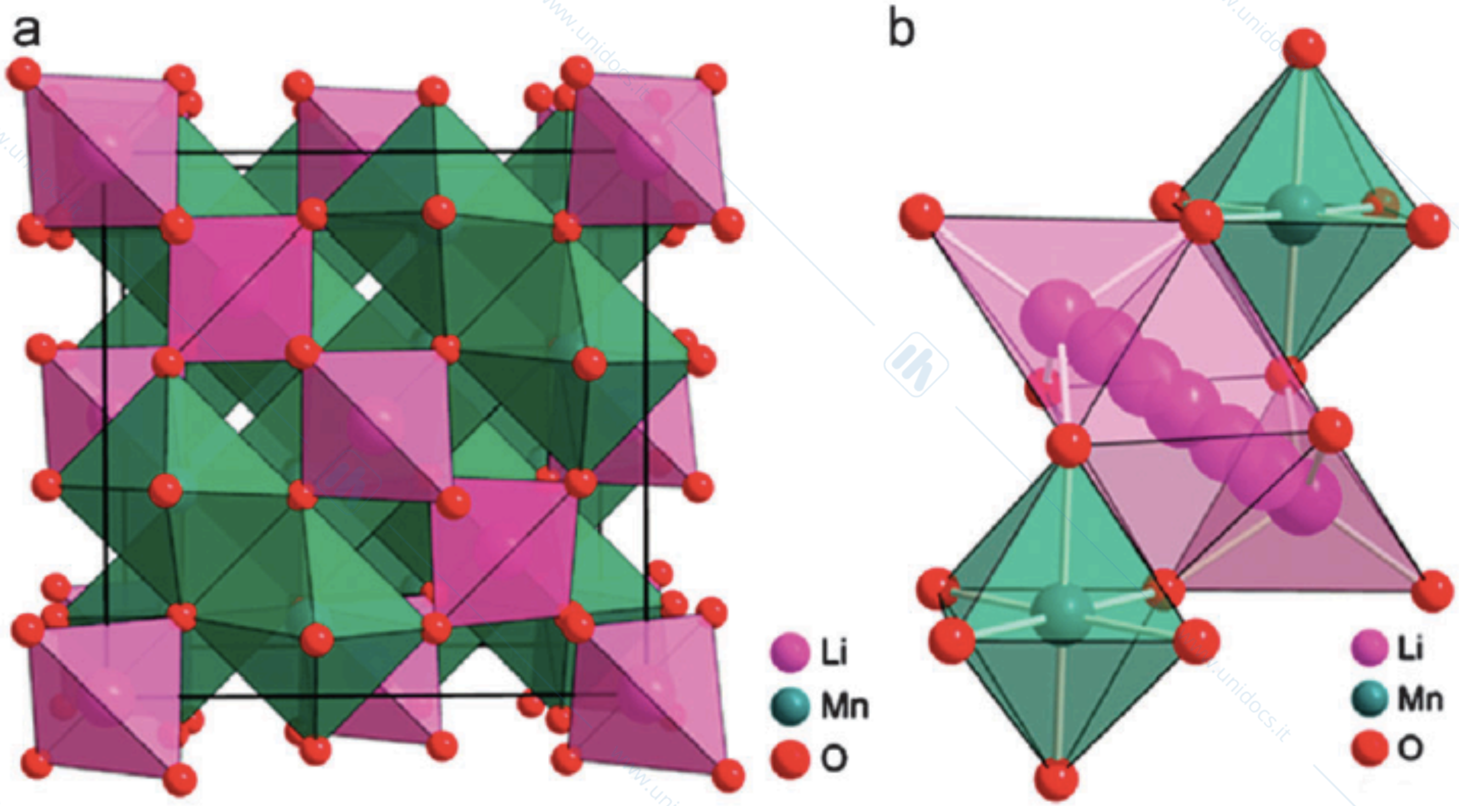


Fig. 12 (a) Crystalline structure of spinel $LiMn_2O_4$ and (b) its corresponding lithium diffusion pathways. Reprinted with permission from ref. 116. Copyright 2011 Royal Society of Chemistry.

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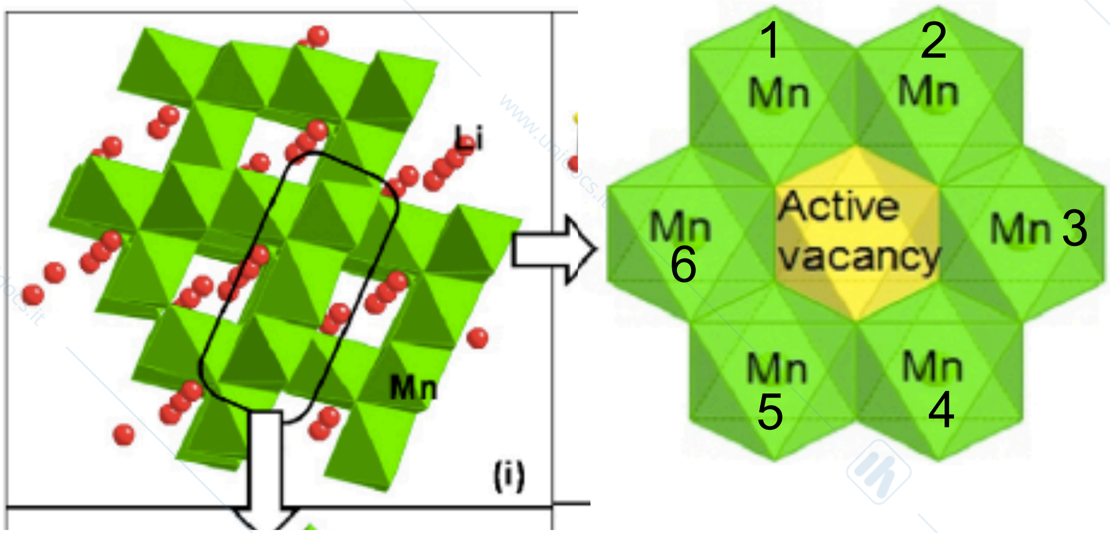

Three-dimensional lithium ion diffusion paths in $LiMn_2O_4$ through lattice vacancies.

Mn valence states in Mn-rings surrounding the diffusing Li^+ in the vacancy

# of Mn^{4+}	Label	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
5	a	4+	4+	4+	4+	4+	3+
4	b	4+	4+	3+	4+	4+	3+
	c	4+	4+	4+	3+	4+	3+
3	d	4+	3+	4+	3+	4+	3+
	e	4+	4+	3+	4+	3+	3+
2	f	4+	3+	3+	4+	3+	3+
1	g	4+	3+	3+	3+	3+	3+

Average valence = [22 (+4) + 20(+3)] = 3.52

B. Xu, S. Meng / Journal of Power Sources 195 (2010) 4971–4976

Excercises

1) Calculate the oxidation number of the different elements in the following compounds

- $LiCoO_2$ (lithium cobaltite, LCO, first Sony Lithium ion batteries)
- Graphite (C_6)
- $LiMnO_2$ (LMO, layered oxide)
- $LiFePO_4$ (Lithium iron phosphate, LPO, olivine)
- $Li(Ni_{0.5}Mn^{iv}_{0.5})O_2$ (Lithium Nickel Mnganese oxide, NMO)
- $Li_4Ti_5O_{12}$ (lithium titanate, LTO)
- $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC) ?????
- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA, Panasonic cells!) ????

In mixed metal transition oxides the oxidation number can be evaluated only by Chemical-physical methods: XRD, electrochemistry

REDOX REACTIONS

Reactions with electron transfer between atoms of different molecules, with consequent variation of the oxidation number of the atoms involved.

Example: Full redox reaction : $2\ H_2 + O_2 \rightarrow 2\ H_2O$

Semireactions:

- oxidation $H_2 \rightarrow 2\ H^+ + 2\ e^-$ (the oxidation number of H increases)
  o.n. H= 0 o.n. $H^+ = +1$

each H atom loses 1 electron. It is oxidized and is a reductant.

- reduction $O_2 + 4e^- + 4H^+ \rightarrow 2\ H_2O$ (the oxidation number of O decreases)
  o.n. O= 0 o.n. O in $H_2O = -2$

each O atom gets 2 electrons. It is reduced and is an oxidant

Redox reactions are balanced considering that the total number of electrons released by the reducing agent must be equal to the total number of electrons taken by the reduced species

2 x $(H_2 \rightarrow 2\ H^+ + 2\ e^-)$

1 x $(O_2 + 4e^- + 4H^+ \rightarrow 2\ H_2O)$

$$2\ H_2 \rightarrow 4\ H^+ + 4\ e^-$$
$$O_2 + 4e^- + 4H^+ \rightarrow 2\ H_2O$$
$$2\ H_2 + O_2 + \cancel{4}e^- + \cancel{4H^+} \rightarrow \cancel{4}H^+ + \cancel{4}\ e^- + 2\ H_2O$$

$$\boxed{2\ H_2 + O_2 \rightarrow 2\ H_2O}$$

The redox is the sum of the two combined half-reactions

Balancing redox reactions by the semireaction method

1. Identify the elements that change the oxidation number

2. Write the half-reactions and balance:
   a) the atoms that change the o.n. and the relative electrons
   b) the total charges (eventually by adding positive or negative ions)
   c) the mass

3. Combine and sum the two half-reactions, each one multiplied by the electron balancing factor

Balancing redox reactions in molecular form

1. Identify the elements that change the oxidation number

2. Balance the atoms that change the o.n. and the relative electrons

3. Multiply each semireaction by the electron balancing factor and complete the mass balance

Combustion reaction

It is a chemical reaction that involves the oxidation of a fuel (eg coal, methane, ...) by a comburent that is typically oxygen (which is reduced) with heat development.

Exemples.

<u>*Coal combustion:*</u> $C(g) + O_2(g) \rightarrow CO_2(g)$

$-4\ e^-$

$$C^0(g) + O_2^{\,0}(g) \rightarrow C^{+4}O_2^{\,-2}(g)$$

$+ 2\ e^- \times 2$ atoms $= +4e^-$

<u>*Methane combustion*</u> $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$-8\ e^-$

$$C^{-4}H_4^{\,+1} + 2O_2^{\,0} \rightarrow C^{+4}O_2^{\,0} + 2H_2O$$

$+ 2\ e^- \times 4$ O atoms $= +4e^-$

Ex.

1) Balance the following redox reactions (battery cell reactions) by the semireaction method

a) $PbO_2(s) + Pb(s) + H_2SO_4 \rightleftarrows PbSO_4(s) + H_2O$ Lead acid battery
b) $MH + NiO(OH) \rightleftarrows M + Ni(OH)_2$ Nickel metal hydride battery
c) $C + LiFePO_4 \rightleftarrows LiC_6 + FePO_4$
d) $C + LiCoO_2 \rightleftarrows LiC_6 + CoO_2 \rightleftarrows$ 90's Sony Li-ion battery
$(Li_xC_6 + Li_{1-x}CoO_2 \rightleftarrows C + LiCoO_2$
e) $Li(Ni_{0.5}Mn^{iv}_{0.5})O_2 + C \rightleftarrows LiC_6 + Ni_{0.5}Mn^{iv}_{0.5}O_2$
f) $Li_4Ti_5O_{12} + LiC_6 \rightleftarrows C + Li_9Ti_5O_{12}$
g) $Li + S_8 \rightleftarrows Li_2S$
a) $Li + O_2 \rightleftarrows Li_2O_2$

2) Individuate the oxidant and the reductant species in ex (1)

3) Evaluate the charge (in Coulomb,C, and Ah) that is exchanged between the reactants for mole and gram of each redox reactant species and for the overall reactants (consider the reaction complete)

1 Ah is the charge that is obtained when 1 A current flows over 1 hour

1 Ah = 1 C/s x 3600 s = 3600 C

4) Calculate the amount (moles) of Li^+ ions that are required to balance the semireactions of eq. 1c-h (excercise 1) for mole of reactant. If the source of Li^+ ions is the salt $LiPF_6$, which is the volume of LP30 electrolyte and the amount of salt (in gram) required for gram of reactant?

5) Which is the amount of Li(s) required for a complete reaction with 1 g of MnO_2 in eq 1e?

6) Write the oxidation reactions of the following lithium-ion battery cathode materials

Material	$LiFePO_4$	$LiMn_2O_4$	$LiCoO_2$	$LiNiO_2$	NMC
Crystal Structure	Olivine	Spinel	Layered	Layered	Layered
Discharge Voltage	3.4	4.0	3.9	3.8	3.8
Capacity	155 (170)	110-148	140-274	180-274	140-277