Measurements and Uncertainty

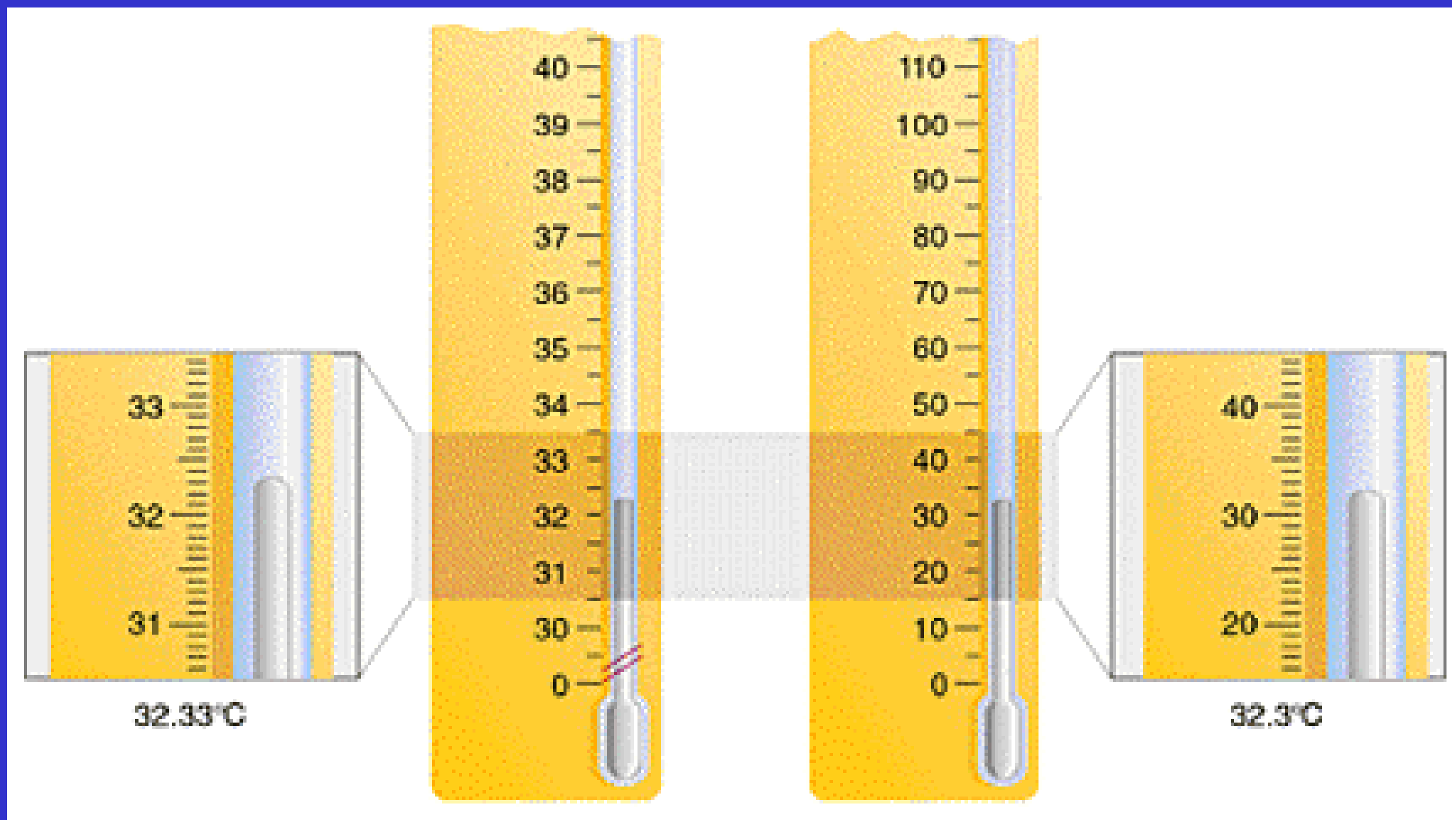
Measurement = comparing a value with a unit

Measurement = read between the scale division marks, estimate the measurement to the nearest one tenth of the space between scale divisions

Significant Figures = digits read from the scale + the last estimated digit

Measurement error = minimum ±1 of the last digit

Measurement

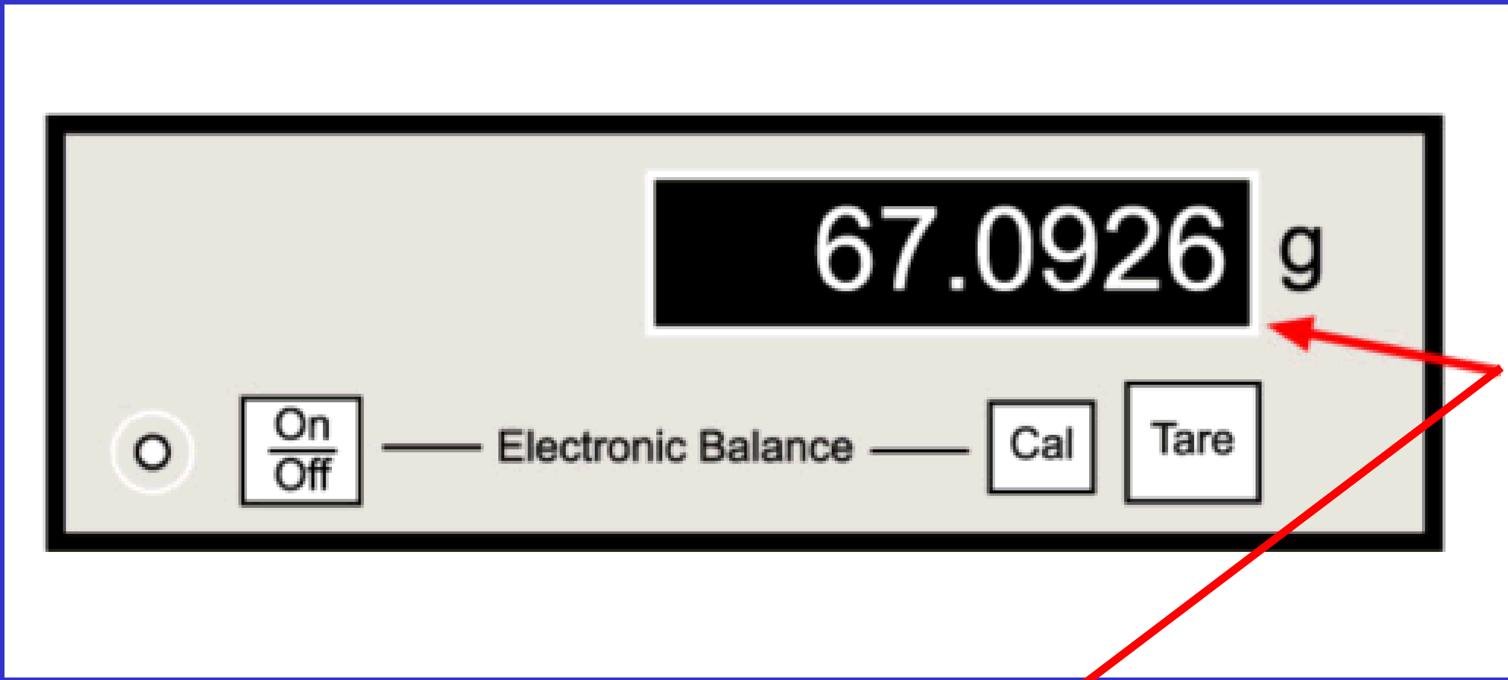


32.33 °C

What is the smallest scale division

32.3 °C

Reading from a digital display



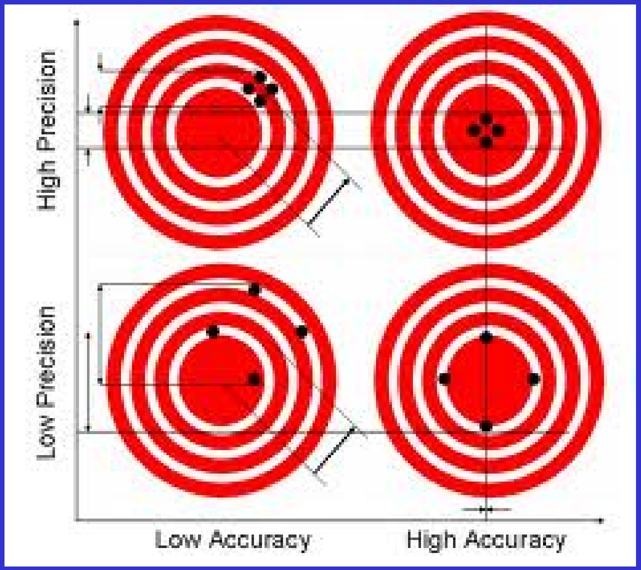
error = ±1 of the last digit

Accuracy and Precision

Every measurement has its error
Repeated measurements - error estimation

Precision = is the degree to which repeated measurements show the same results, depends on the abilities of experimentator

Accuracy = the agreement between experimental data and a known value, depends on instrument quality



Weighing

Number of significant figures is given by the instrument quality

Significant Figures

- All nonzero digits are significant **3.548**

- Zeroes between nonzero digits are significant **3.0005**

- Leading zeros to the left of the first nonzero digits are not significant 0.00**34**

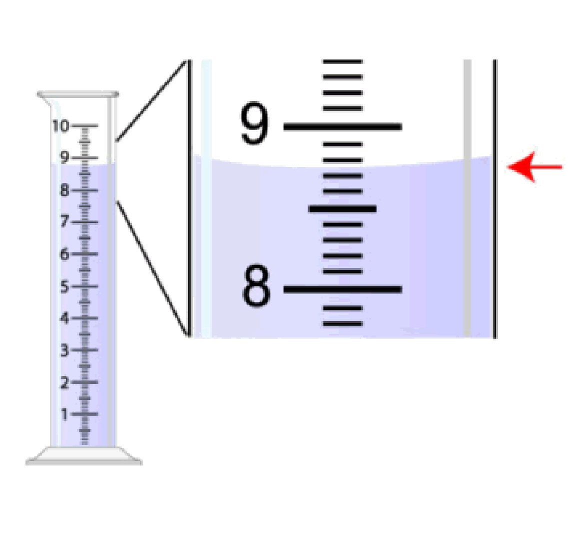
- Trailing zeroes that are also to the right of a decimal point in a number are significant 0.00**3400**

- When a number ends in zeroes that are not to the right of a decimal point, the zeroes are not necessarily significant 1200

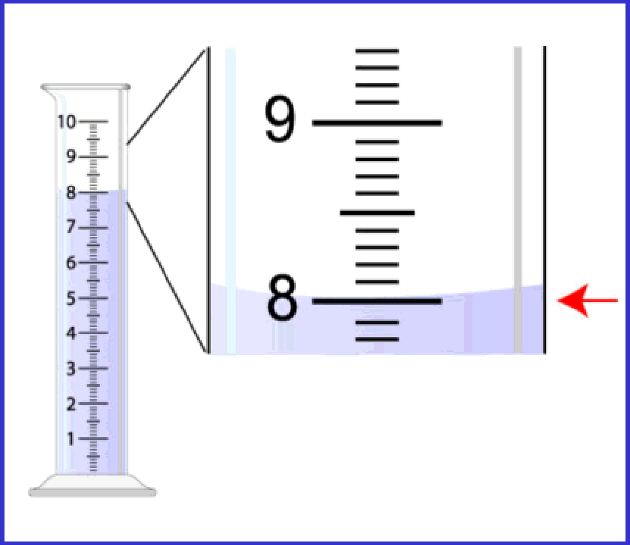
Ambiguity avoided by the use of standard exponential, or "scientific," notation: **1.2** 10^3 or **1.200** 10^3 depending on the number of significant figures

Significant Figures

Reading from a scale – number of significant figures is given by the instrument quality



8.75 cm^3



8.00 cm^3

Not 8 cm^3 !!!!

digits read from the scale + the last estimated digit

Significant Figures

Exact numbers = known with complete certainty, infinite number of significant figures

- Number of people, experiments, …

- conversion factors 1 week = 7 days 7.000000000
  1 inch = 2.54 cm

- definitions 0 °C = 273.15 K

can be ignored as a limiting factor in determining the number of significant figures in the result of a calculation

Rules for mathematical operations

Multiplication and Division, the result should be rounded off so as to have the same number of significant figures as in the component with the least number of significant figures.

p V = n R T

p = 748 Torr = 99.7 10^3 Pa

V = 1254 ml = 1.254 10^{-3} m^3

T = 298 K

R = 8.314 J K^{-1} mol^{-1}

$n = pV/RT$ = 5.0462226 10^{-2} mol = 5.05 10^{-2} mol

Rounding off numbers – in the final result of calculation

Rules for mathematical operations

Addition and Subtraction, the result is rounded off so that it has the same number of digits as the measurement having the fewest decimal places

Measured 2.5 cm with a ruler and 1.2 mm with a micrometer

add	2.5 cm	with uncertainty $\pm$0.1 cm
	+0.00012 cm	with uncertainty $\pm$0.00001 cm
The result is NOT		2.50012 cm
but		2.5 cm

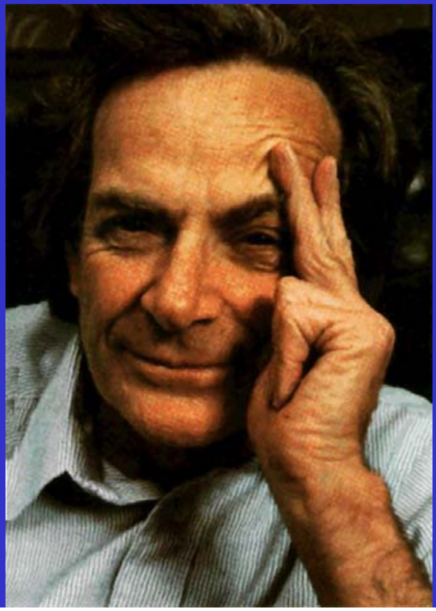
Because the error in the first number is 4 orders of magnitude bigger than the second number

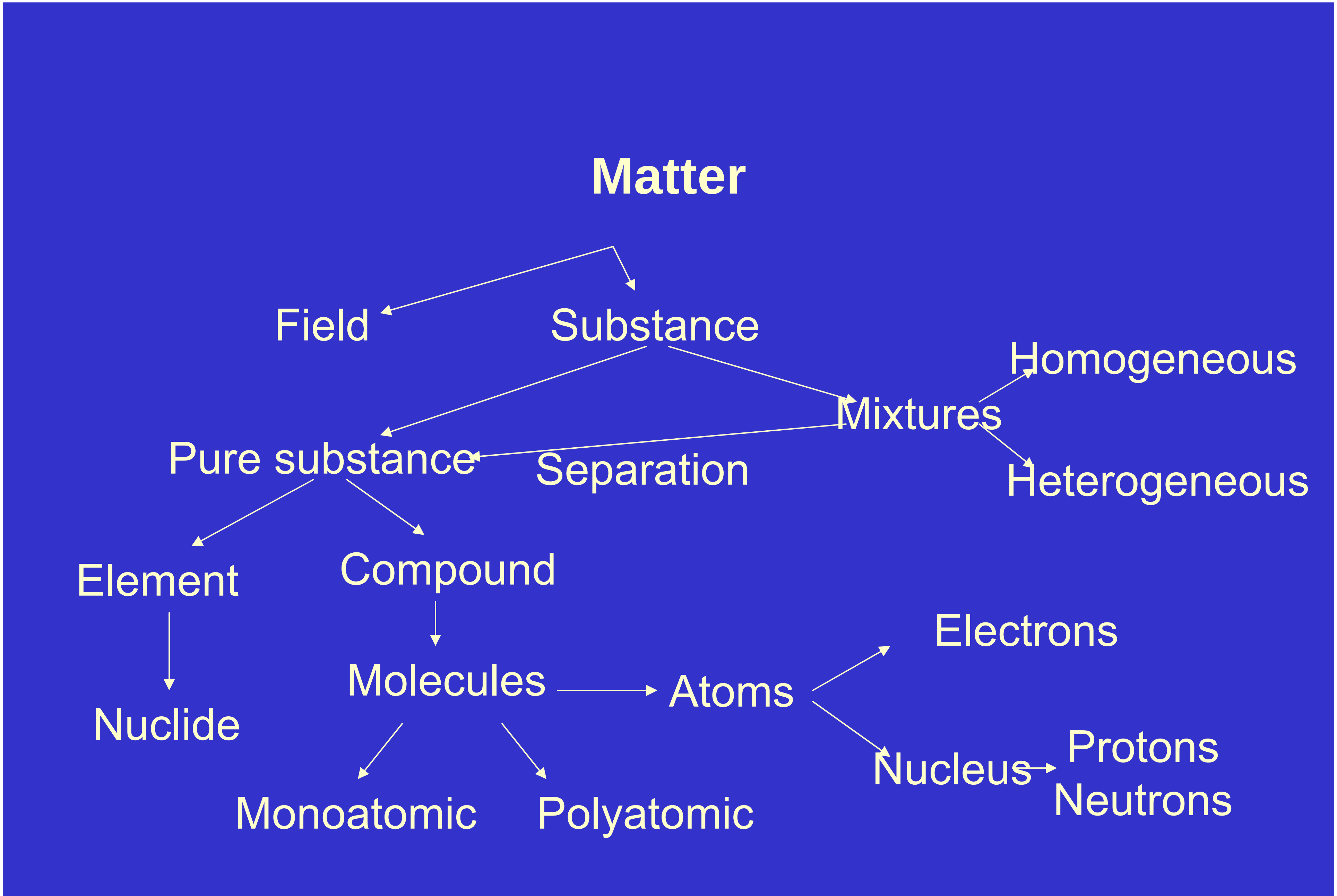
Matter

Matter is anything that occupies space, has rest mass, is composed of atoms, is convertible to energy

Matter is made of atoms - little articles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.

Richard P. Feynman
(1918 - 1988)
NP in Physics 1965



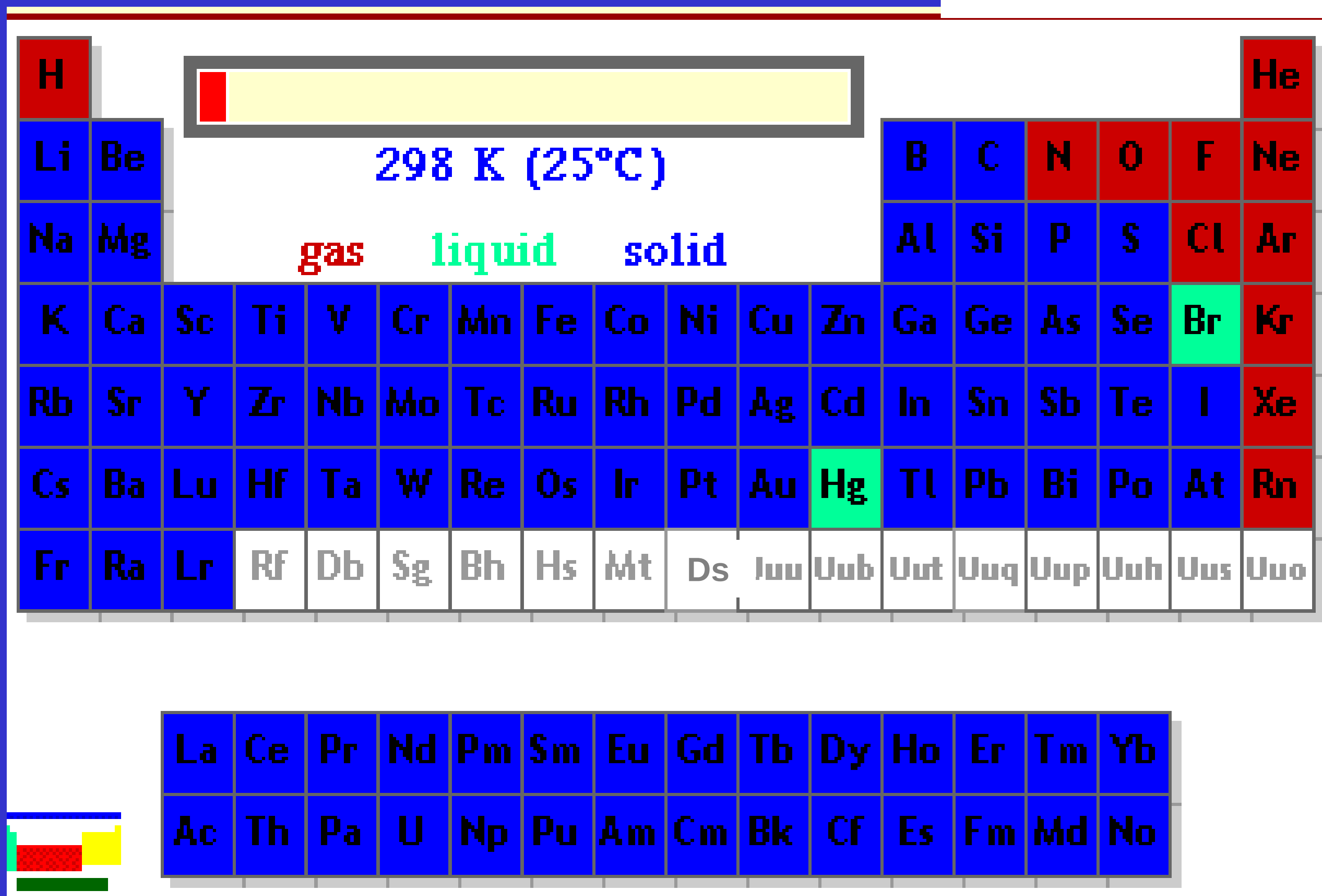

Matter
Field
Substance
Homogeneous
Mixtures
Pure substance
Separation
Heterogeneous
Element
Compound
Electrons
Molecules
Atoms
Nuclide
Protons
Nucleus
Neutrons
Monoatomic
Polyatomic

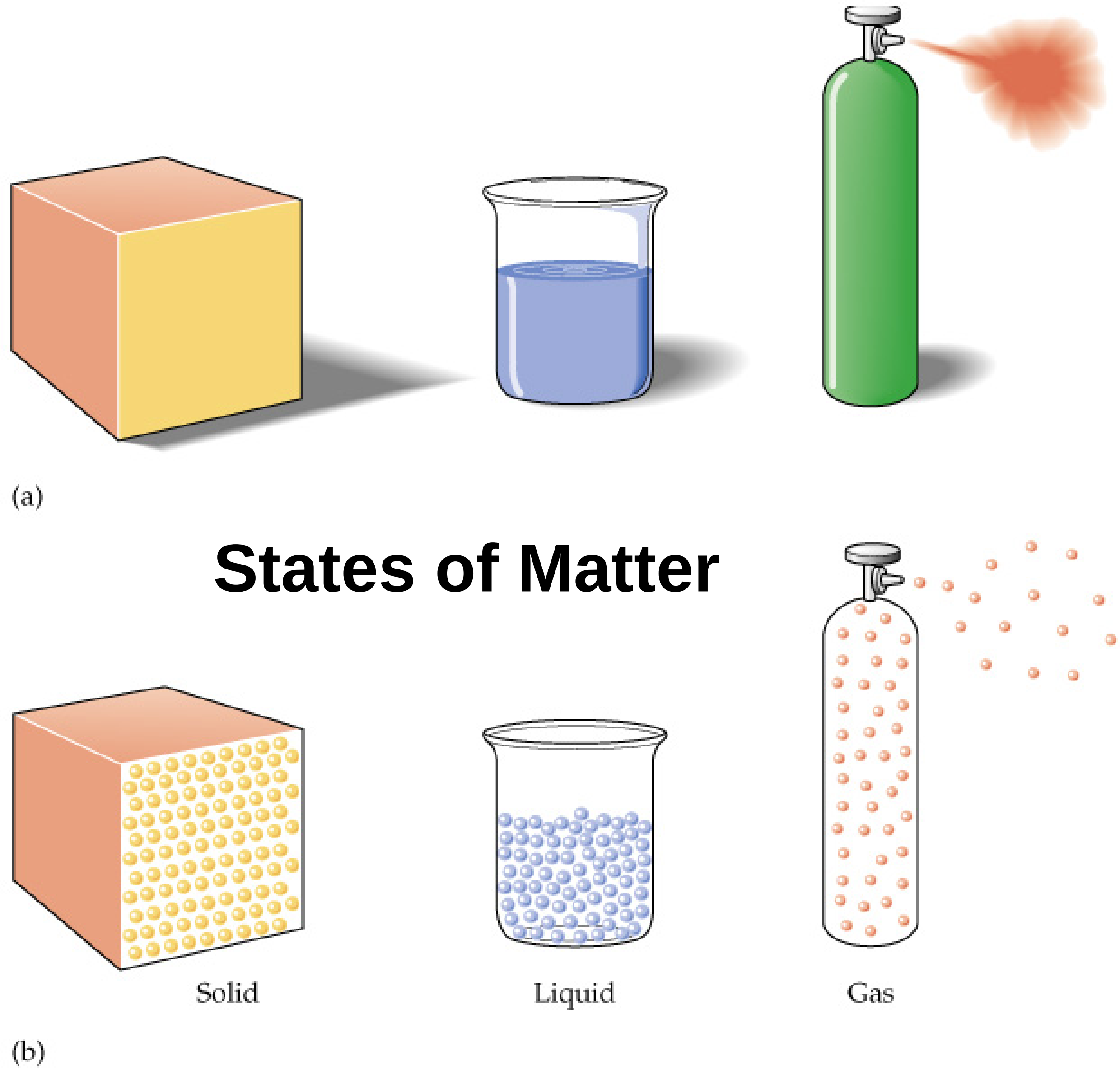
States of Matter

Gas

Liquid

Solid





States of Matter

Law of Conservation of Mass

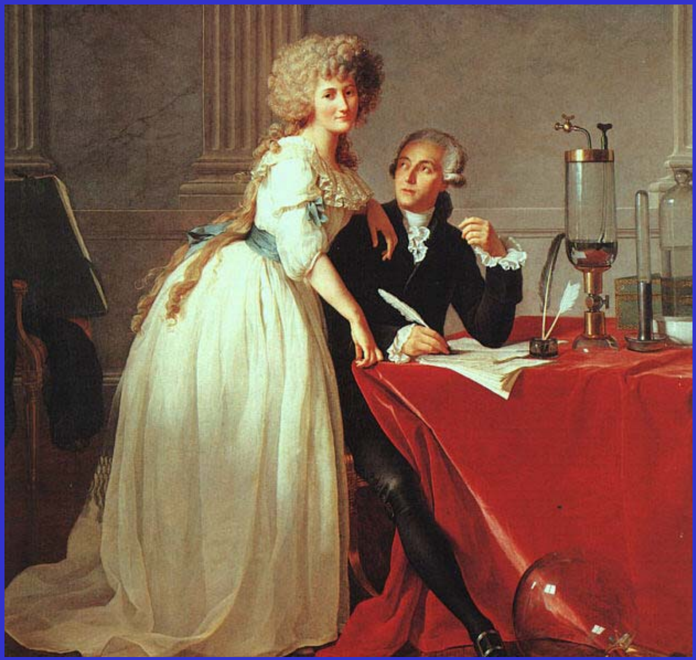
Lavoisier 1785

Matter can be neither created nor destroyed.

In a chemical reaction, the mass of the products equals the mass of the reactants.

The law is a result of precise weighing reactants and products

(conversely from weighing we obtain information about chemical reactions)



Antoine Lavoisier
1743 - 1794
(guilotined)

Law of Conservation of Energy

The first law of thermodynamics

Equivalence of mass and energy: $E = m\,c^2$
u = 1.66 10^{-27} kg = 931.4 MeV

System:
Isolated = Mass and energy is constant
Closed = Mass is constant, energy is exchanged with surroundings

Úbytek hmotnosti při uvolnění energie:
- Chemical reactions ng per mol
- Nuclear reactions mg per mol

Law of Definite Composition

Proust 1788 / 1799

Proved a constant composition of water.

There are SnO and SnO_2

$CuCO_3$ – a compound always contains the same relative masses of elements regardless of its origin.

Louis Joseph Proust
(1754 - 1826)

1.000 g of C will always react with 1.333 g of O_2 to CO

Law of Multiple Proportions

Dalton 1803

When elements combine, they do so in the ratio of small whole numbers. The mass of one element combines with a fixed mass (e.g. 1 g) of another element according to this ratio (N_2O, NO, N_2O_3, NO_2, N_2O_5).

Table of relative atomic masses
14 elements relative to H (=1)

John Dalton
(1766 - 1844)

Oxides of Chromium

$$r = \frac{m(O)Cr_xO_y}{m(O)CrO}$$

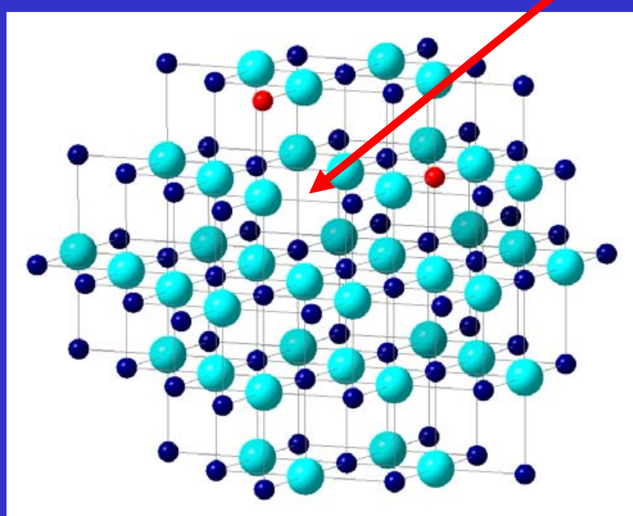
Compound	*m*(Cr) / g	*m*(O) / g	Ratio, *r*
CrO	1.000	0.3077	1.000
Cr_2O_3	1.000	0.4615	1.499
CrO_2	1.000	0.6154	2.000
CrO_3	1.000	0.9231	3.000

Non-stoichiometric compounds-bertholides

Compounds of a metal possessing several oxidation states - Oxides, sulfides, nitrides,...

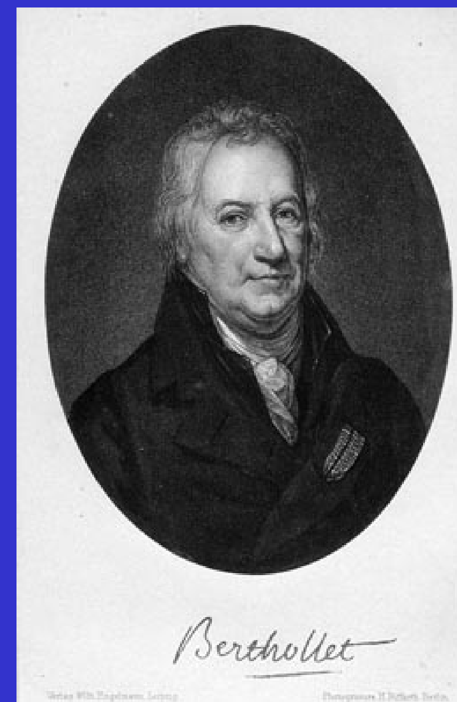
$Fe_{1-x}O$ $\quad x = 0.05 – 0.15$

$3\ Fe^{2+} = 2\ Fe^{3+} + 1$ vacancy (Fe)



Fe^{2+} = blue

Fe^{3+} = red



C. L. Berthollet
(1748 - 1822)

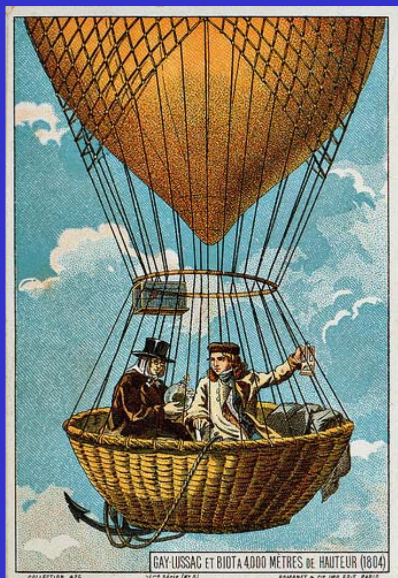
Vacancy = unoccupied position

Dalton's Atomic Theory

1805

- Matter consists of definite particles called atoms.
- Atoms are indestructable. They can rearrange in chemical reactions but they do not themselves break apart.
- Atoms of a particular element are indistinguishable from one another. They are all identical in mass, as well as other properties.
- Atoms of different elements (or types) differ in mass (and other properties).
- When atoms of different elements combine to form compounds, new and more complex particles (molecules) are formed. Their constituent atoms are always present in a definite numerical ratio.

Law - theory



Law of Constant Volumes

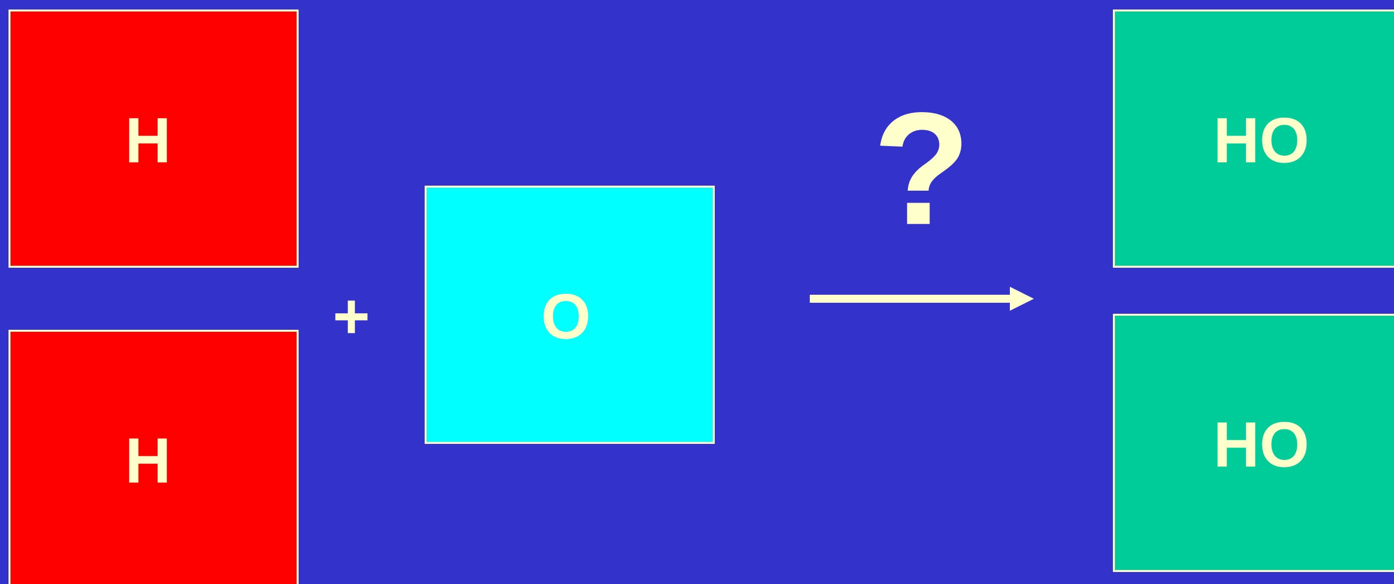
Gay-Lussac's law

Joseph Louis Gay-Lussac
(1778 - 1850)

1809 Gases combine together in volumes (measured at the same temperature and pressure) that bear a simple ratio to each other and to the gaseous products

2 volumes of H_2 + 1 volume of O_2 $\rightarrow$ 2 volumes water vapor

Law of Constant Volumes



2 volumes of H_2 + 1 volume of $O_2 \rightarrow$ 2 volumes water vapor

Avogadro's Hypothesis

1811 from Dalton **atomic** theory and Gay-Lussac Law derived:

Two equal volumes of gas, at the same temperature and pressure, contain the same number of molecules.

Gasses are diatomic molecules.

H_2, N_2, O_2

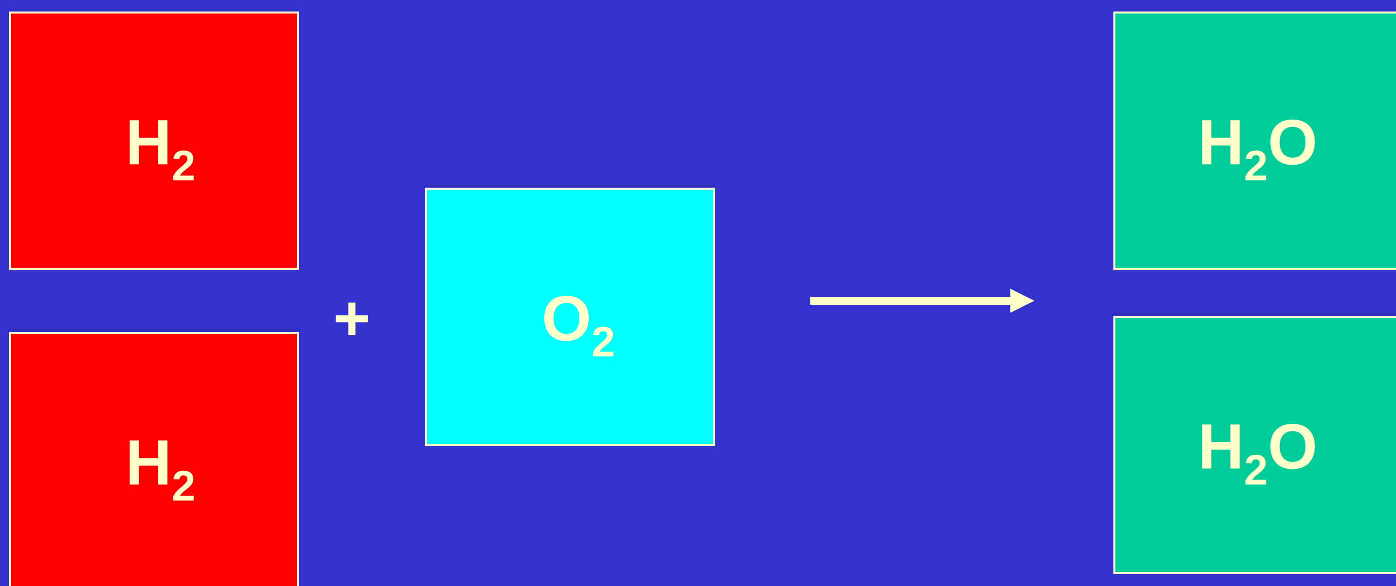
Volume of 1 mole of gas is 22.4 l at 0 °C and 101325 Pa

V_m = 22.4 l mol^{-1}

Amadeo Avogadro (1776 - 1856)

Avogadro's Law

At a constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of that gas.

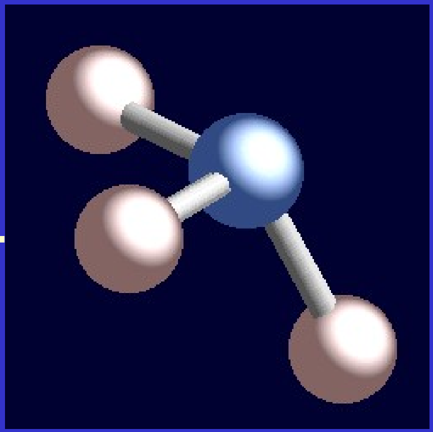


2 volumes of H_2 + 1 volume of $O_2 \rightarrow$ 2 volumes water vapor

Avogadro's Molecules

Molecules = smallest particles of matter capable of independent existence

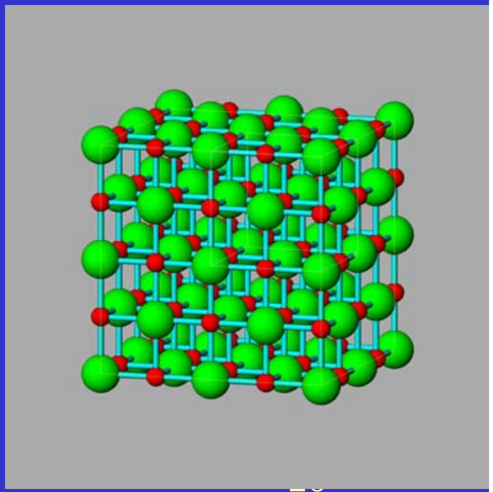
He, Ne, Ar, ...



N_2, P_4 (yellow), S_8, C_{60}, ...

BCl_3, CH_4, H_2O, NH_3......

Not molecules:
NaCl, SiO_2, BeF_2, C (graphite, diamond), ...



Mass – mol – Avogadro's constant

Elements combine in the constant ratios of small whole numbers:
NaCl = 23.0 g Na and 35.5 g chlorine

Scale of relative atomic masses:
H = 1.0, C = 12.0, O = 16.0

Definition of mole: 12.0 g C = 1 mol
then 23.0 g Na = 1 mol
1 mol of gas = 22.4 litre

Measure the number of particles in 1 mole (Loschmidt, Perrin,...)

$$N_A = 6.022\,140\,78(18)\ 10^{23}\ \mathrm{mol}^{-1}$$

Amount of Substance, n

1 mol = amount of substance that contains as many elementary entities (e.g., atoms, molecules, ions, electrons) as there are atoms in 12 g of pure ^{12}C

Avogadro's constant $N_A = 6.022\ 10^{23}\ mol^{-1}$

Chemical formulae Na_2SO_4

Stoichiometry in chemical equatins

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow 6\ CaSiO_3 + 10\ CO + P_4$$

Loschmidt's Number

Loschmidt's number = the number of molecules in a cubic centimetre of a gas under standard conditions.

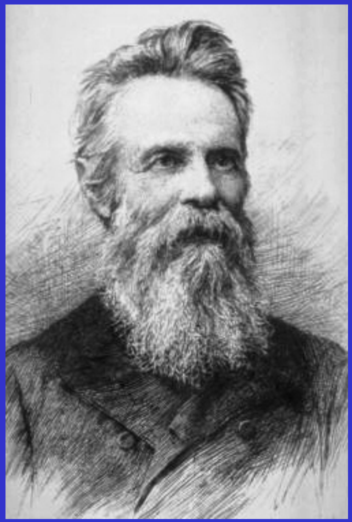
1865 from kinetic theory of gases calculated

n_0 = 2.6 10^{19} molecules cm^{-3}

Today's value: 2.686 7775 10^{25} m^{-3}

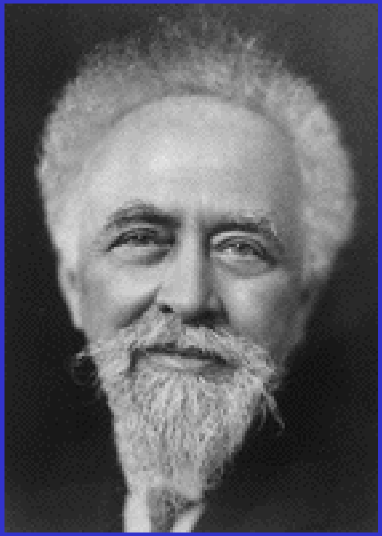
Avogadro's constant

N_A = 6.022 141 99 10^{23} mol^{-1}



Johann Josef Loschmidt
(1821 - 1895)
Počerny near Carlsbad

Avogadro's Constant



Brown motion of particles in a liquid
1908 Proof for the existence of molecules

Introduced term **Avogadro's constant** and experimentally measured

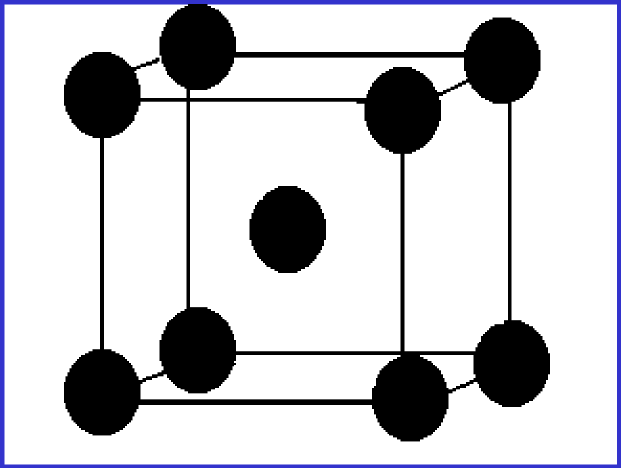
6.82 10^{23} molecules in 2 g of hydrogen

Jean Baptiste Perrin
(1870 - 1942)
NP in Physics 1926

Avogadro's Constant

From XRD structural analysis of single crystals of Ti

Ti = body centred cubic unit cell
Number of atoms in the unit cell $Z = 2$
Edge length $a = 330.6$ pm
Density Ti $\rho = 4.401$ g cm^{-3}
A(Ti) = 47.88 g mol^{-1}
2 Ti per 1 unit cell with volume $V = a^3$



$r\, a^3 = Z\, A(\mathrm{Ti}) / N_A$

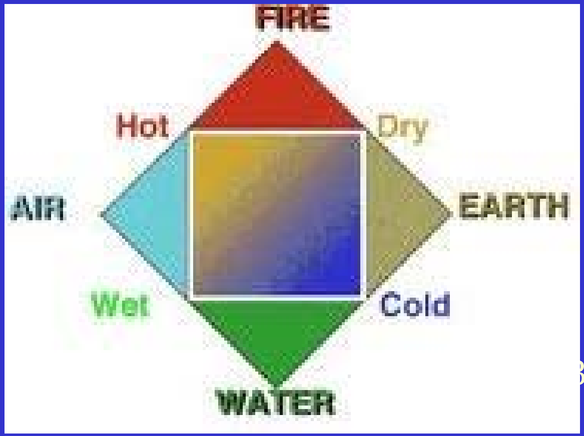
$N_A = Z\, A(\mathrm{Ti}) / V\, r$

Elements in the History of Chemistry

Empedocles (490 - 430 B. C.)
4 basic elements = fire, water, air, earth
and 2 basic forces: attraction and repulsion
(only in 1783 H. Cavendish proved that water is a compound of H and O)

Aristotle (384 - 322 B. C.) 4 basic elements + aether
an element is the source of properties

Combination of properties



Elements in the History of Chemistry

Alexandria: Greek theory + Egyptian practical "chemistry"

Arabic alchemy, transferred to Europe

Alchemist's elements : fire, water, air, earth and
Au, Ag, Hg, Fe, Sn, Cu, S, salt

Au	Sun
Ag	Moon
electrum (Sn amalgam)	Jupiter
Fe	Mars
Cu	Venus
Sn	Merkur
Pb	Saturn

Elements in the History of Chemistry

Philippus Aureolus Paracelsus (1493–1541)

3 elementary substances: Hg, S, and salt

Moravský Krumlov - Jan z Lipé

Hg = liquidity and metallic character

S = inflammability

Salt = inert element

Elements in the History of Chemistry

1661 Robert Boyle – scientific definition:
an element is any substance that cannot be decomposed into a simpler substance.

1789 Lavoisier - 21 elements

1808 Dalton - 36 elements – the first connection **atom/element concepts**
The same atoms have the same mass, multiples of H

1813-14 Berzelius - 47 elements

1869 Mendelejev table - 63 elements

2012 Periodic table - 118 elements (117 missing)

Elements names - 112

Concept of Atom

Leukippos (480-420 B. C.)
Is matter continuous or discontinuous?
World consists of matter and vacuum, indivisible particles.

Demokritos (470-380 B. C.) **Atom** (atomos = indivisible)
Everything is composed of atoms, which are indivisible; between atoms lies empty space; atoms are indestructible; have always been, and always will be, in motion; there are an infinite number of atoms, and kinds of atoms, which differ in shape, and size.

Next 2000 years rejected - till 1805 **Dalton**

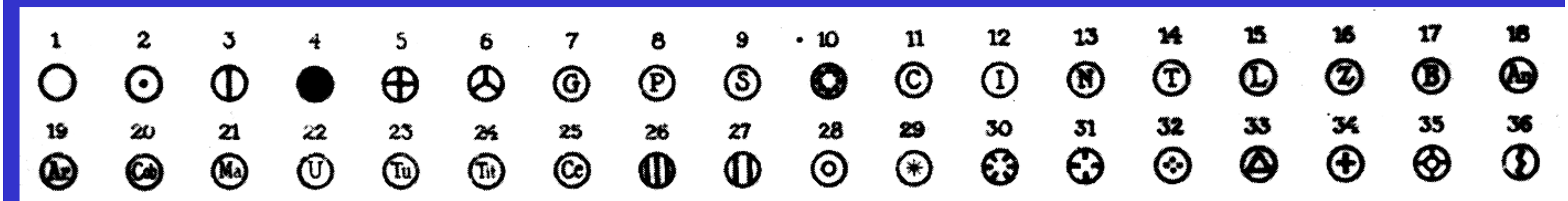
Dalton's Atomic Theory

1805

John Dalton
(1766 - 1844)

- Matter consists of definite particles called atoms.
- Atoms are indestructable. (not nuclear reactions)
- Atoms can rearrange in chemical reactions.
- Atoms of a particular element are indistinguishable from one another, identical in mass (not nuclides) and other properties.
- Atoms of different elements differ in mass (not isobars) and other properties.
- When atoms of different elements combine to form compounds, new and more complex particles (molecules) are formed.
- Their constituent atoms are always present in a definite numerical ratio.

Dalton's Symbols of Atoms/Elements



1. Oxygen.
2. Hydrogen.
3. Nitrogen.
4. Carbon.
5. Sulphur.
6. Phosphorus
7. Gold.
8. Platinum.
9. Silver.
10. Mercury.
11. Copper.
12. Iron.
13. Nickel.
14. Tin.
15. Lead.
16. Zinc.
17. Bismuth.
18. Antimony.
19. Arsenic.
20. Cobalt.
21. Manganese.
22. Uranium.
23. Tungsten.
24. Titanium.
25. Cerium.
26. Potassium.
27. Sodium.
28. Calcium.
29. Magnesium.
30. Barium.
31. Strontium.
32. Aluminium.
33. Silicon.
34. Yttrium.
35. Beryllium.
36. Zirconium.

Atomic Mass

J. Dalton H = 1

J. J. Berzelius O = 100

J. S. Stas   O = 16 (natural mixture of isotopes)
chemical scale

physical scale $^{16}O = 16$ Mess

1961
Atomic mass unit = 1/12 of mass of atom of nuclide ^{12}C

1 amu = 1 u = $1.6606\ 10^{-27}$ kg

Atomic Mass

1814 Table of relative atomic masses of 41 elements

O = 100

1811 Abbreviations as element symbols

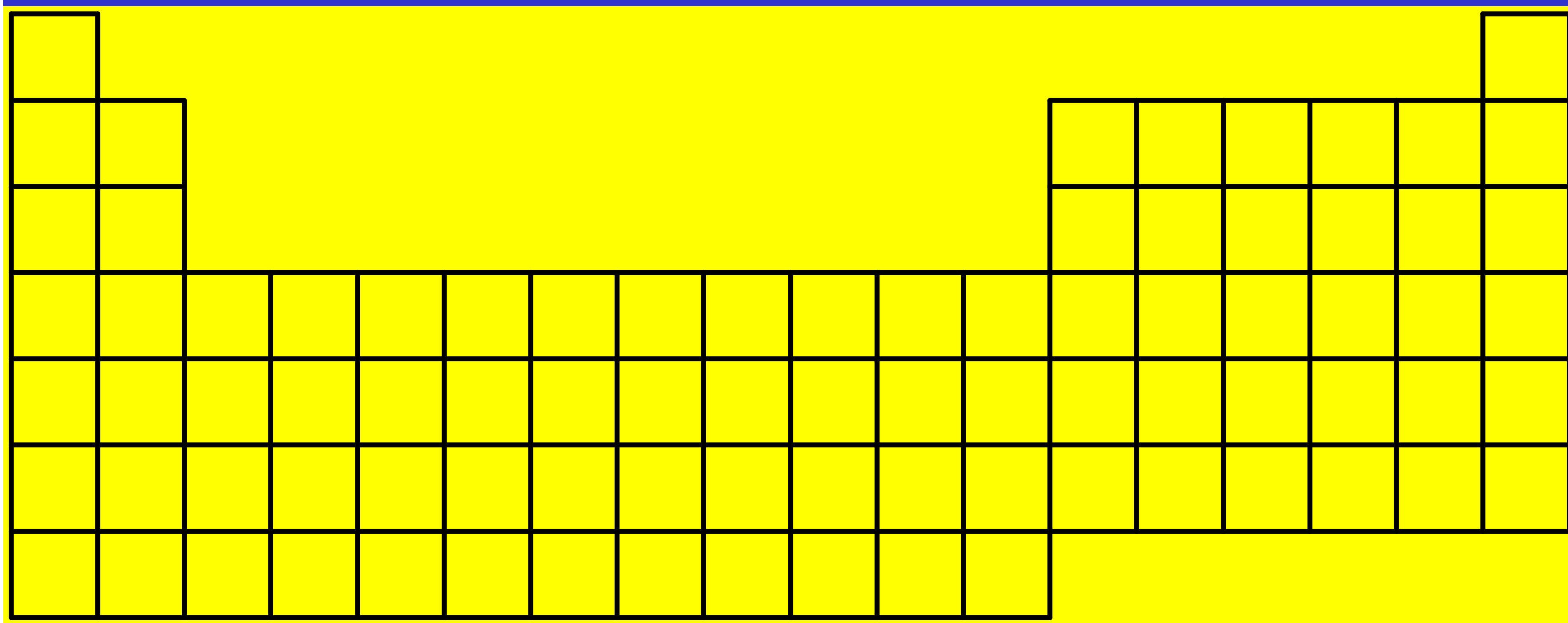
Li	**Lithium**	
Be	**Beryllium**	
Ga	**Gallium**	**(not Galium)**
Y	**Yttrium**	
Te	**Tellur**	
Tl	**Thallium**	
Ds	**Darmstadtium**	
(Cp)	**Copernicium**	

Jőns Jacob Berzelius
(1779 - 1848)

Compound formulae

Then H^2O, today H_2O

Periodic Table of Elements



Definition of an Element

A, Mass / Nucleon number → 19

Z, Atomic / Proton number → 9

$^{19}_{9}\mathrm{F}$

Nuclide = a set of atoms with identical A and Z

Element = a set of atoms with identical Z

Chemical Compounds - composition

Type of atoms A or B - elements

A and B or A and C - compounds

Relative number of atoms AB or AB_2

→ empirical formula (CO or CO_2)

Absolute number of atoms A_2B_2 or A_6B_6

→ molecular formula (C_2H_2 or C_6H_6)

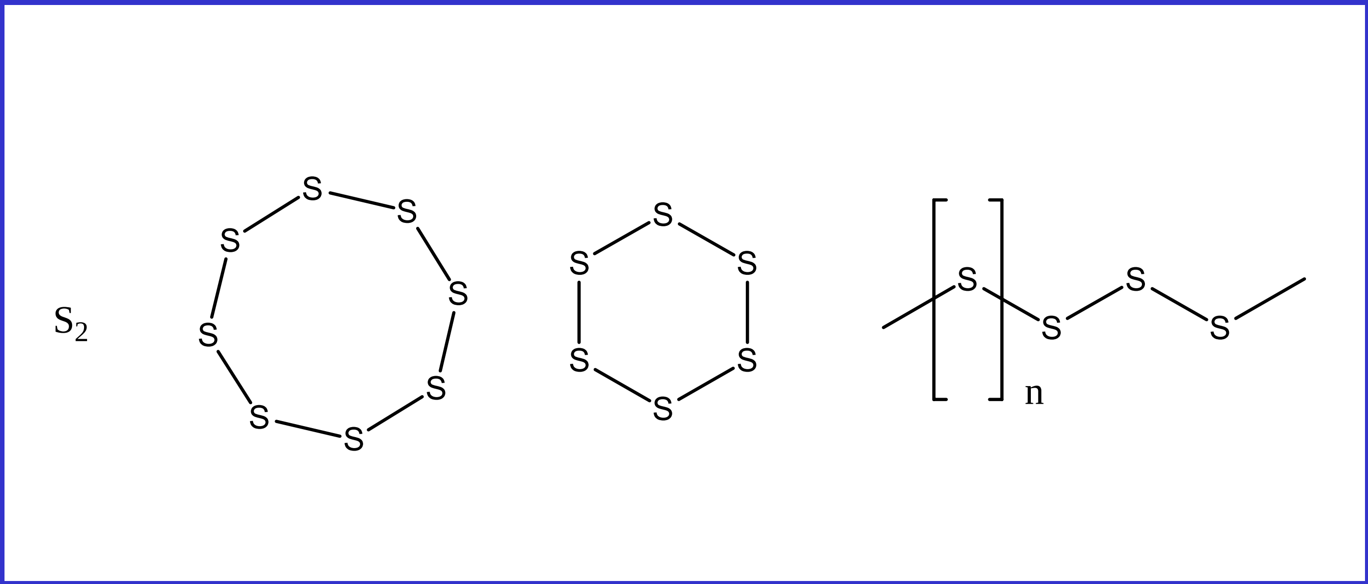
$[CoN_6H_{15}O_2]^{2+}$

Elements – Structure – Allotropy

Structure (bonds between atoms)

$\rightarrow$ structural formula

Bonding topology allotropy (elements): O_2, O_3



Compounds – Structure – Constitution

Bonding topology

$\rightarrow$ structural (constitutional) formula

topological (constitutional, bonding) isomerie (compounds)

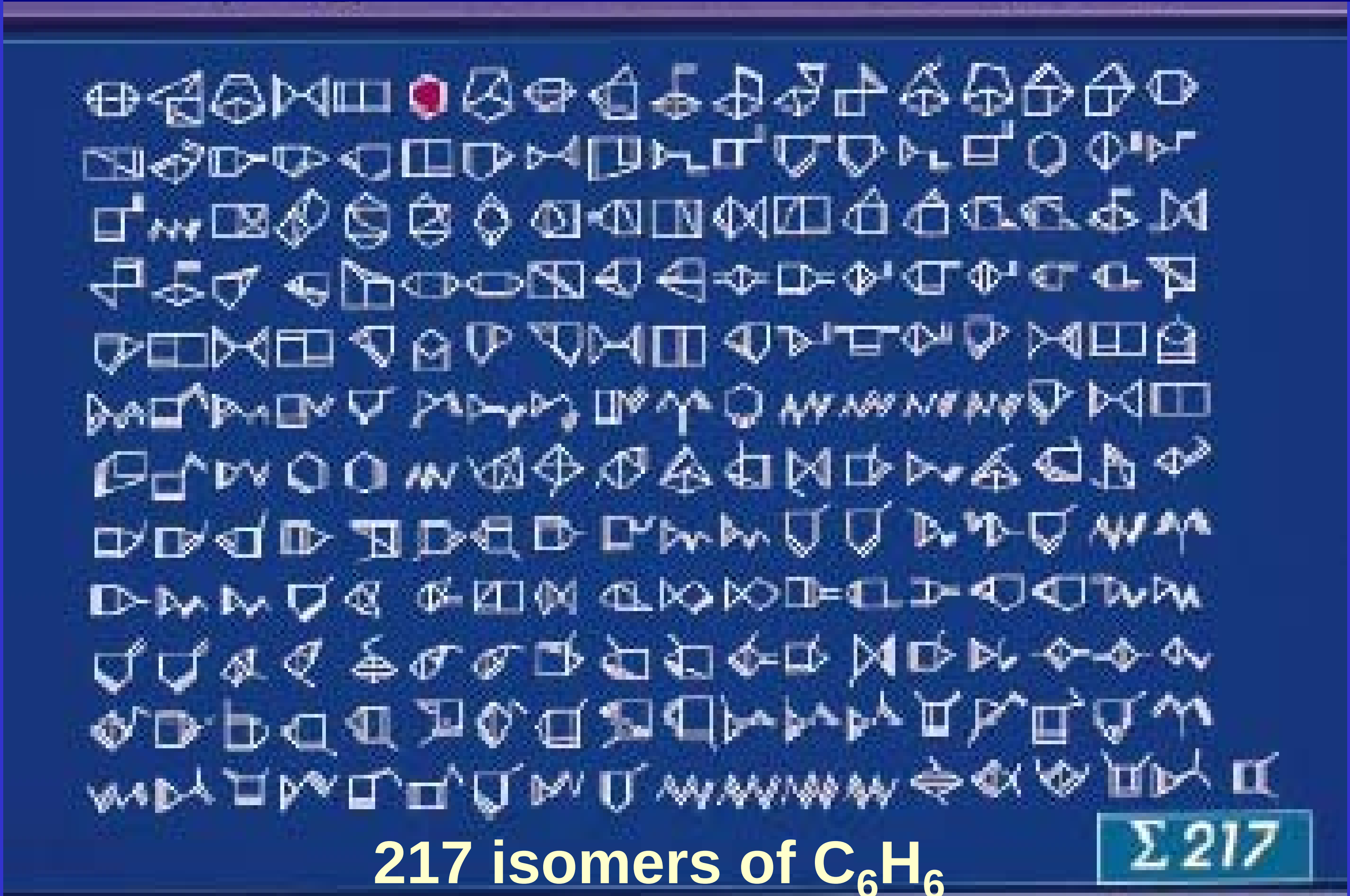
A-B-C or A-C-B

$C_5H_{10}O$

HOCN, HNCO, HONC

$[Co(NH_3)_5NO_2]^{2+}$ $[Co(NH_3)_5ONO]^{2+}$

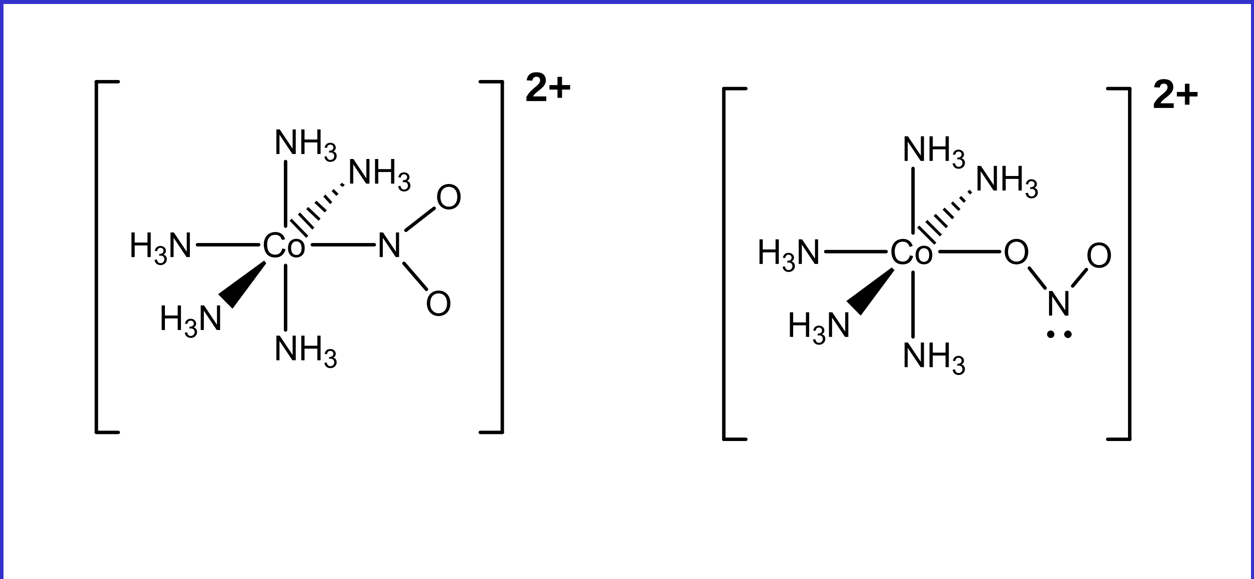
Topological (constitutional, bonding) Isomerie



217 isomers of C_6H_6

Molecular Shape

Molecular Shape → geometrical formula



bonding isomers of NO_2 groups

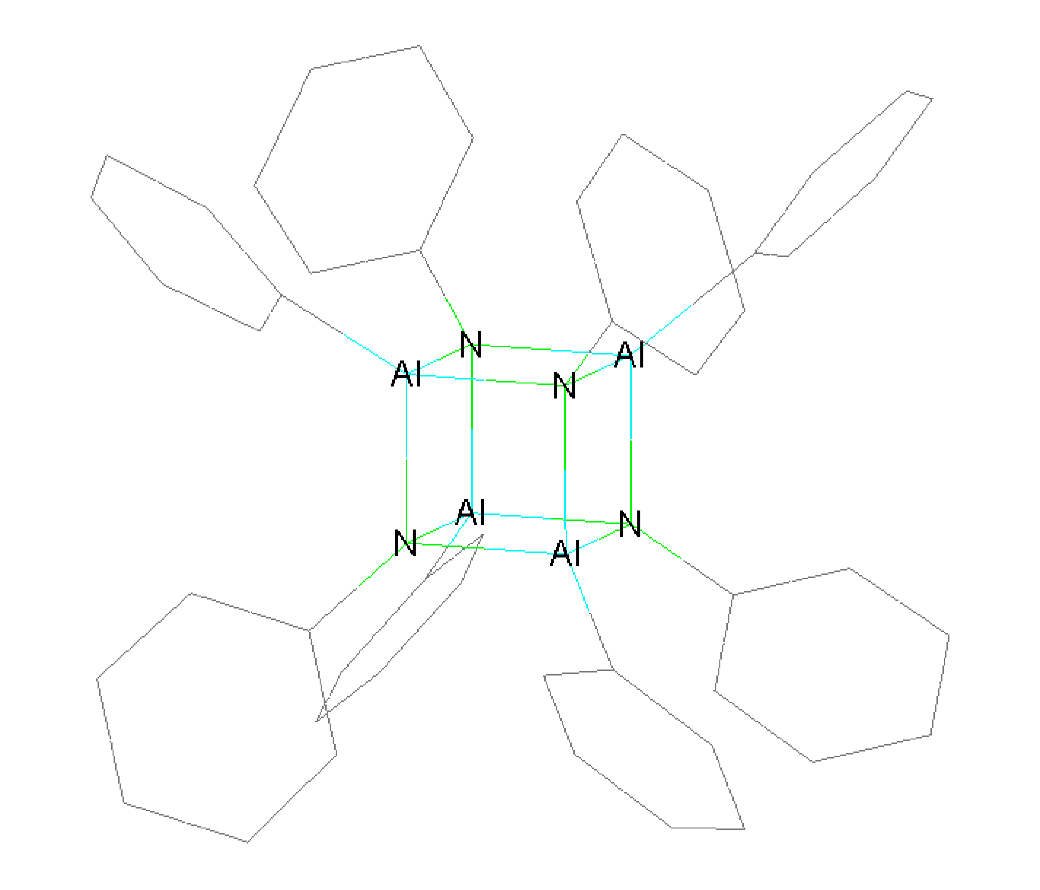
Compounds – Structure – Constitution

$AlNC_{12}H_{10}$

$Al_4N_4C_{48}H_{40}$

$Al_4N_4Ph_8$

$[PhAlNPh]_4$



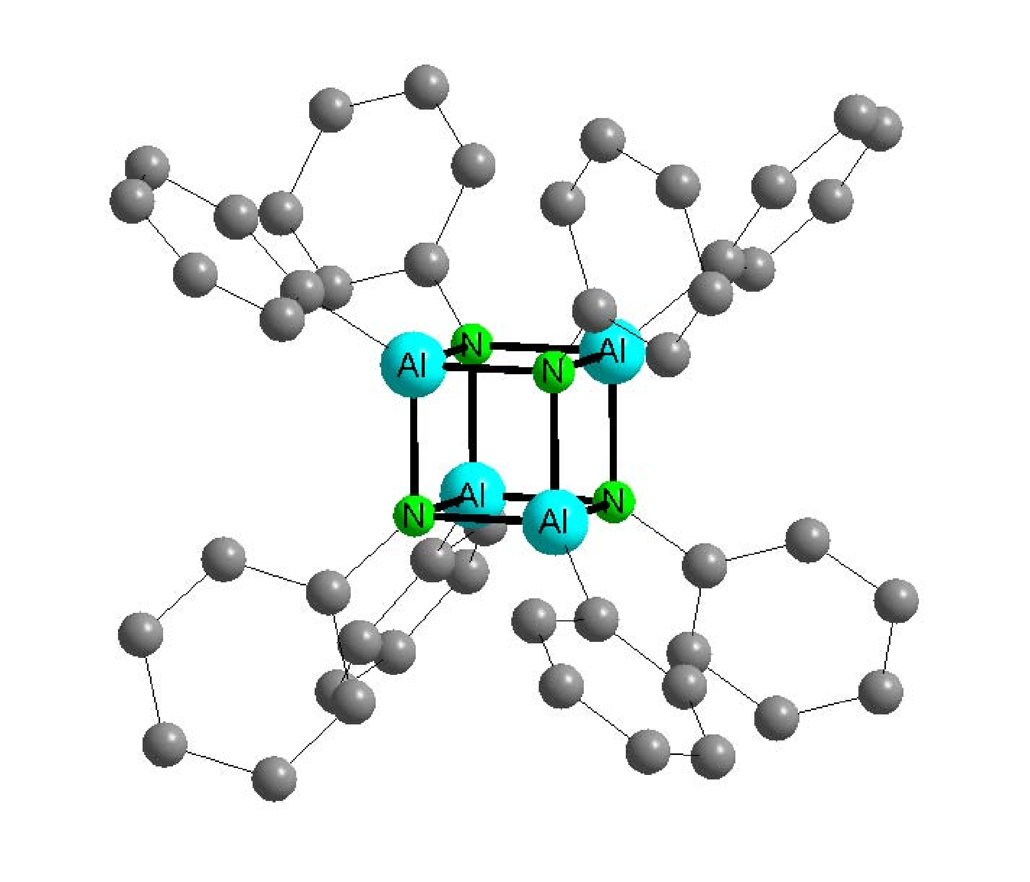
Compounds – Structure – Constitution

$AlNC_{12}H_{10}$

$Al_4N_4C_{48}H_{40}$

$Al_4N_4Ph_8$

$[PhAlNPh]_4$



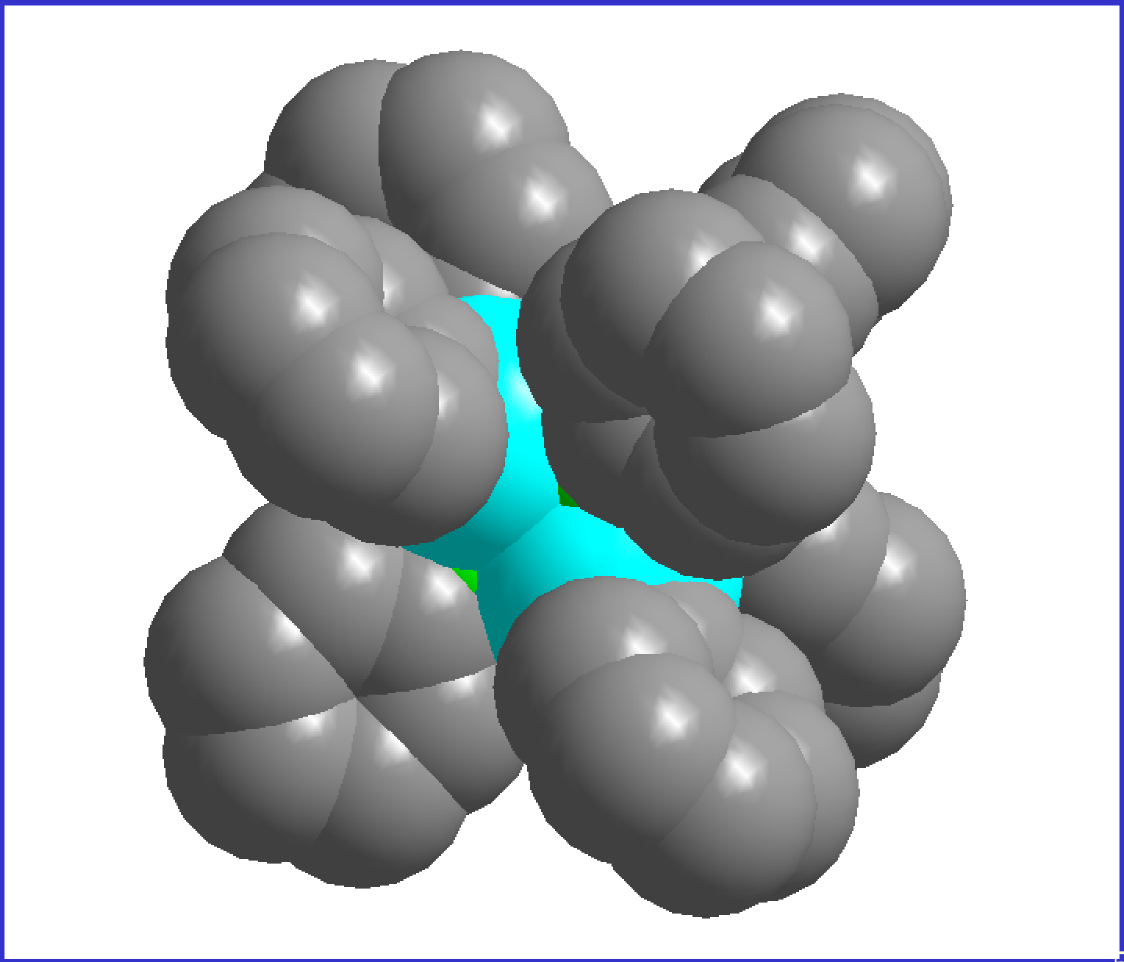
Compounds – Structure – Constitution

$AlNC_{12}H_{10}$

$Al_4N_4C_{48}H_{40}$

$Al_4N_4Ph_8$

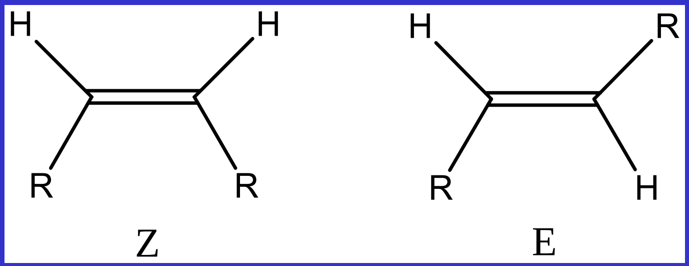
$[PhAlNPh]_4$

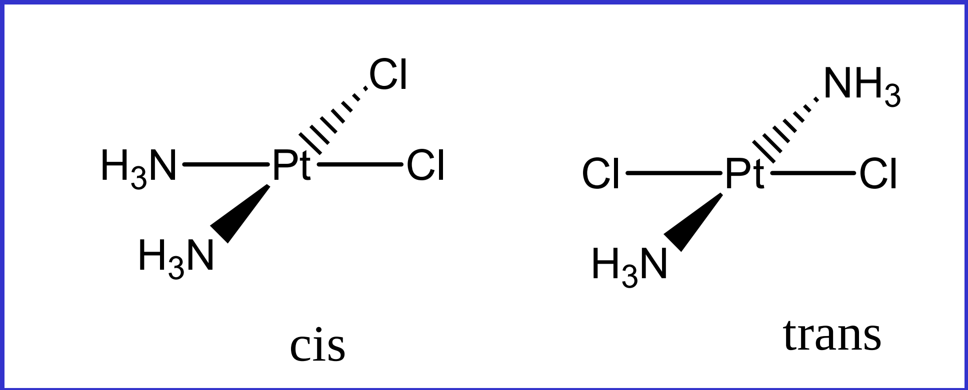


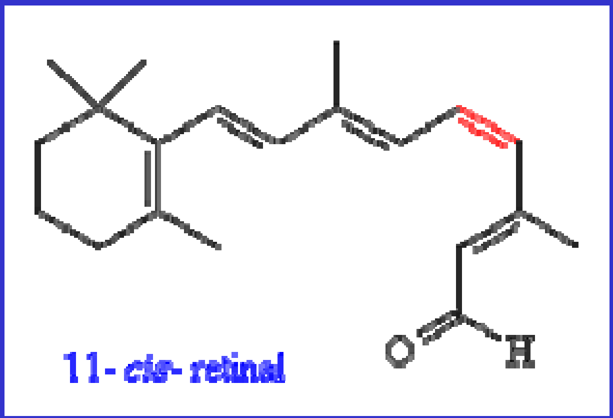
Molecular Shapes

Molecular Shapes geometrical formula

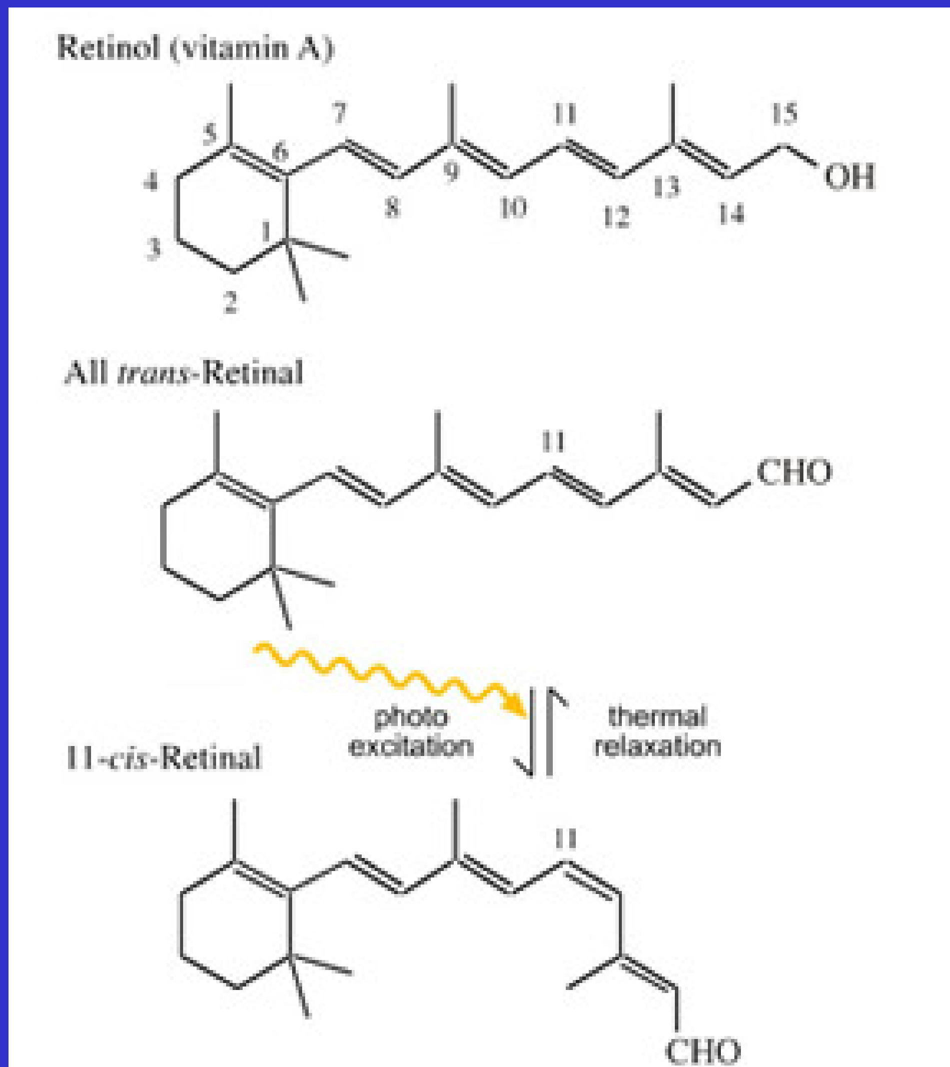
geometrical isomers







Molecular Shape
- physical properties
- chemical reactivity

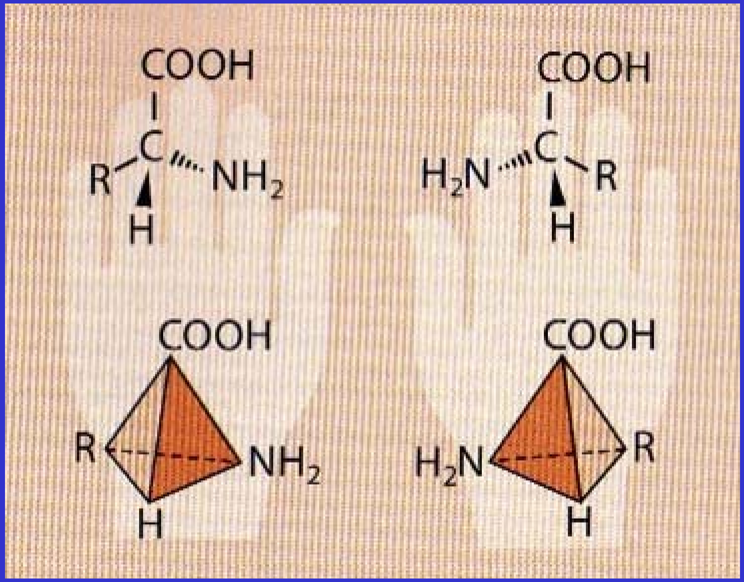

Retinol (vitamin A)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
OH
All trans-Retinal
11
CHO
photo
excitation
thermal
relaxation
11-cis-Retinal
11
CHO

Molecular Shapes

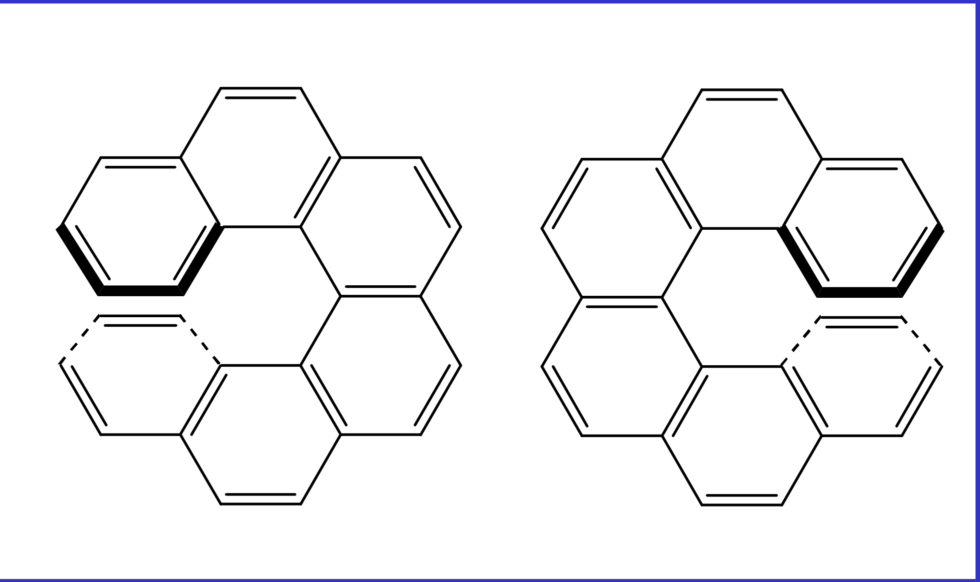
Molecular Shapes $\rightarrow$ geometrical formulae

Optical isomers – enantiomers

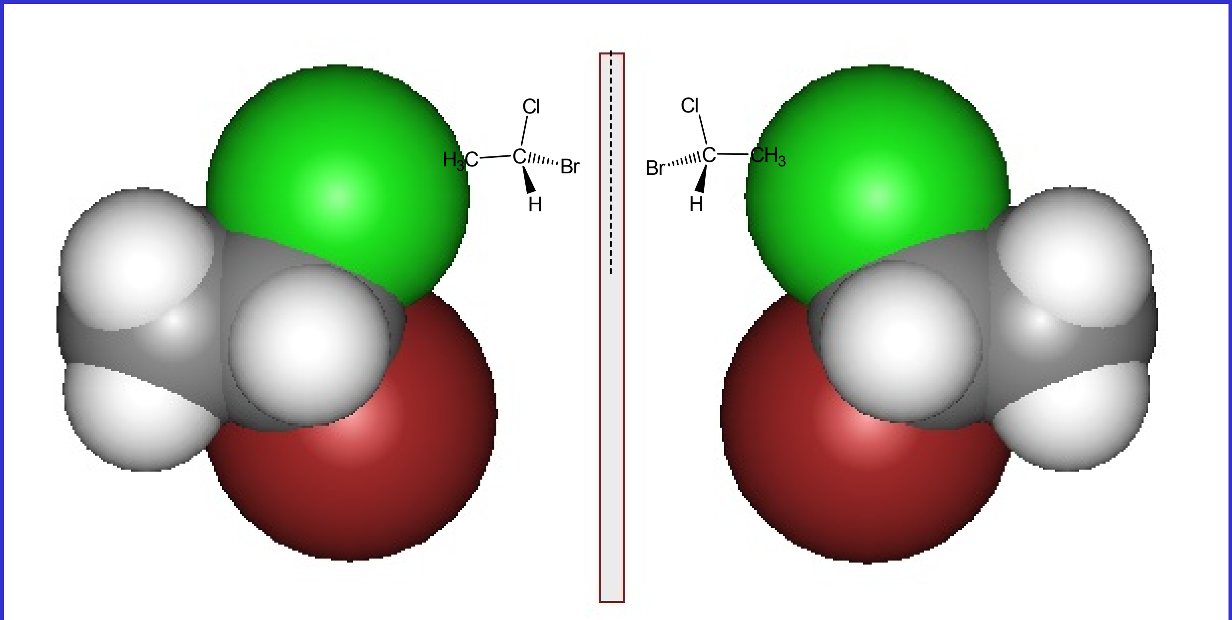
Dissymetry



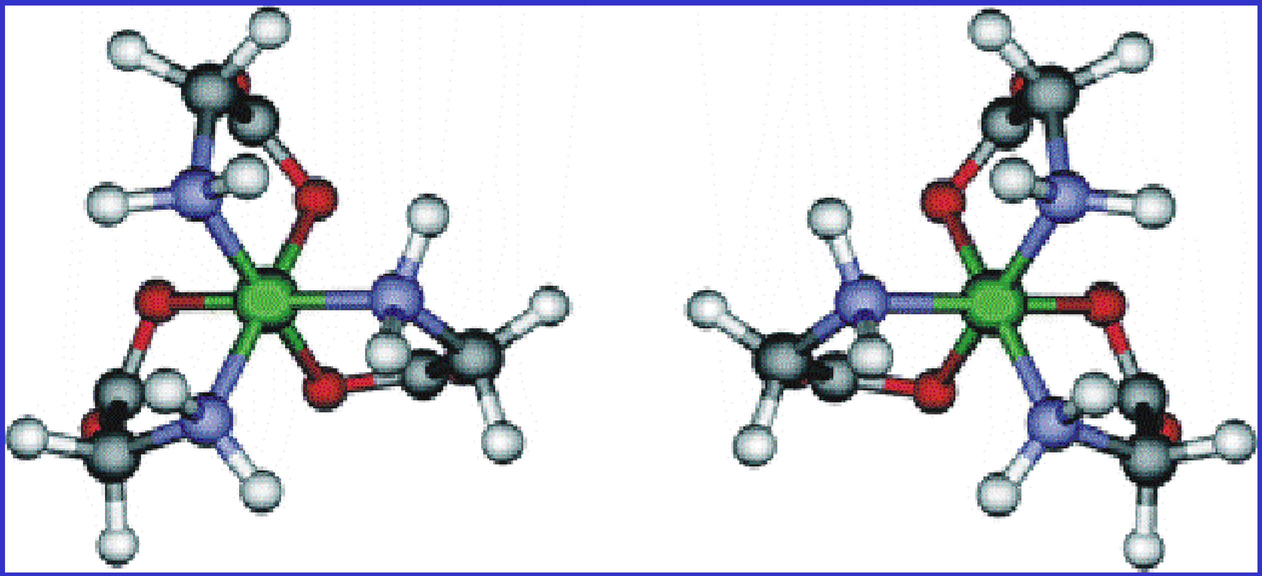
Asymetric atom



Optical isomers - enantiomers

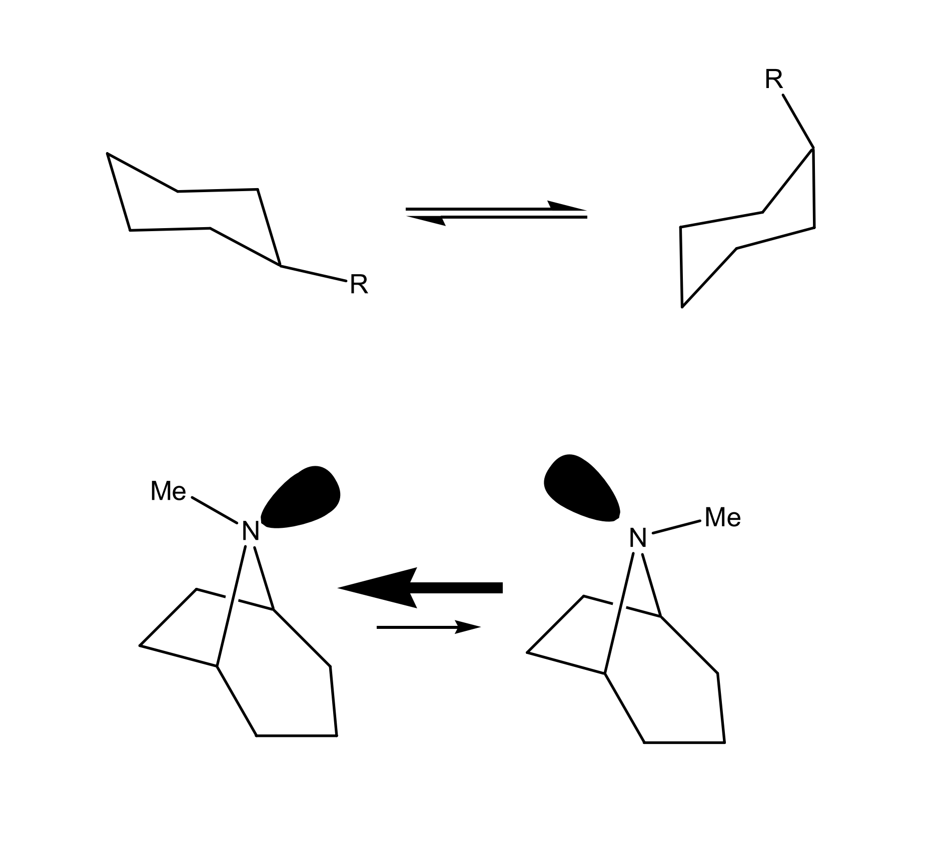


Optical isomers - enantiomers



Molecular Shapes

conformers

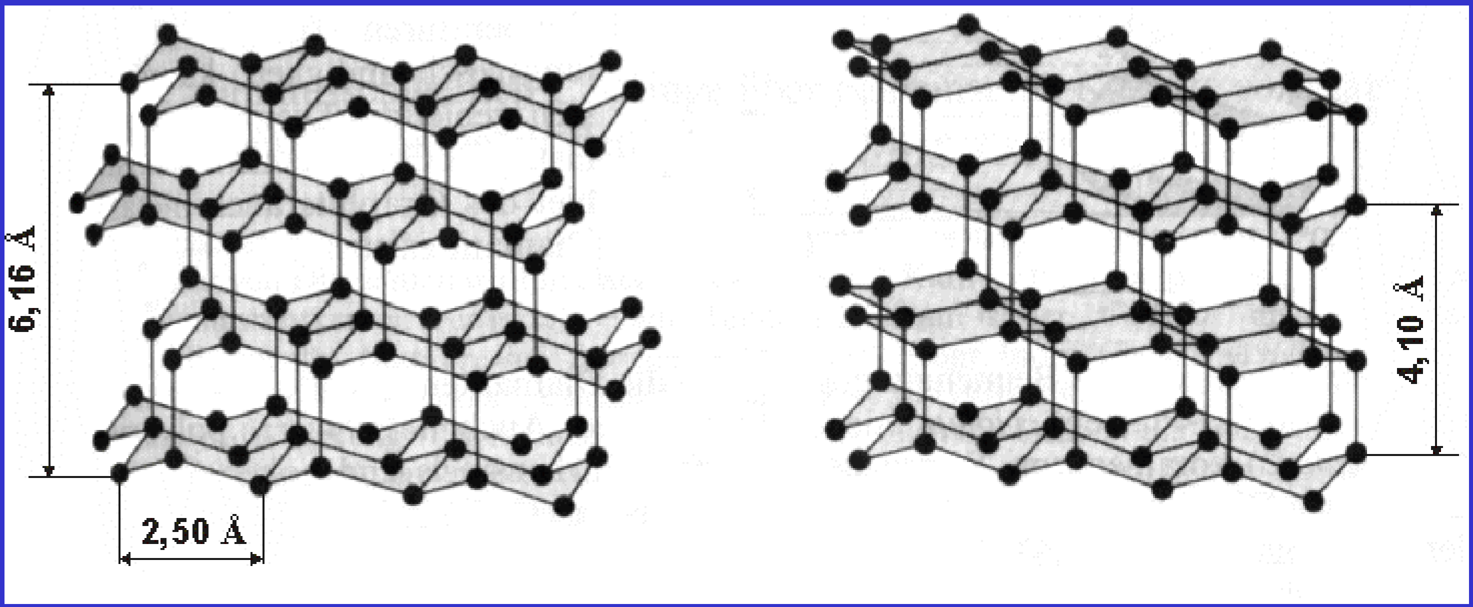


Crystal structures

Polymorphism – only for solids

Same building units (formula), same bonds, different arrangement in space

Cubic diamond Hexagonal diamond



Composition of Atoms

1807 Compounds are held together by electric forces

Prepared alkali metals from their melted salts

Electrolysis of K_2CO_3 melt $\rightarrow$ K

Electrolysis of NaCl melt $\rightarrow$ Na

Humphry Davy
(1778 - 1829)

$$m = \frac{MIt}{zF}$$

Faraday’s Law of Electrolysis

1833 The mass of a substance altered at an electrode is directly proportional to the quantity of electricity passed.
For a given quantity of electricity (electric charge), the mass of material altered at an electrode is directly proportional to its equivalent weight. The equivalent weight is its molar mass divided the number of electrons required to oxidize or reduce each unit of the substance

e = $1.602\ 10^{-19}$ C
Faraday Constant = F
Charge of 1 mol of e = 96500 C

1 mol M^{z+} ………….96500 C $\times$ z

n mol M^{z+} …………Q = I t

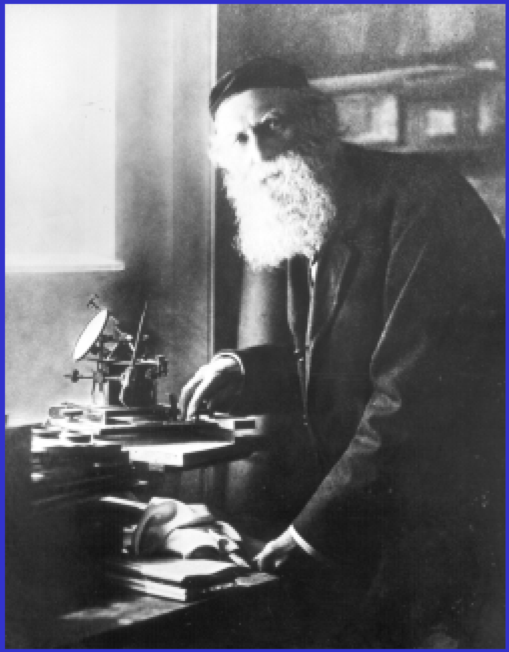
Michael Faraday
(1791 - 1867)

Composition of Atoms

1758
Two types of electricity: Robert Symmer – socks

1874
Electricity is formed by discreet negatively charged particles

1894   named **electron**



George J. Stoney
(1826 - 1911)

Composition of Atoms

Cathode Rays, 1898-1903

• A cathode ray tube - glass tube from which most of the air has been evacuated, electrodes placed at each end, a high-voltage current passed through the electrodes.

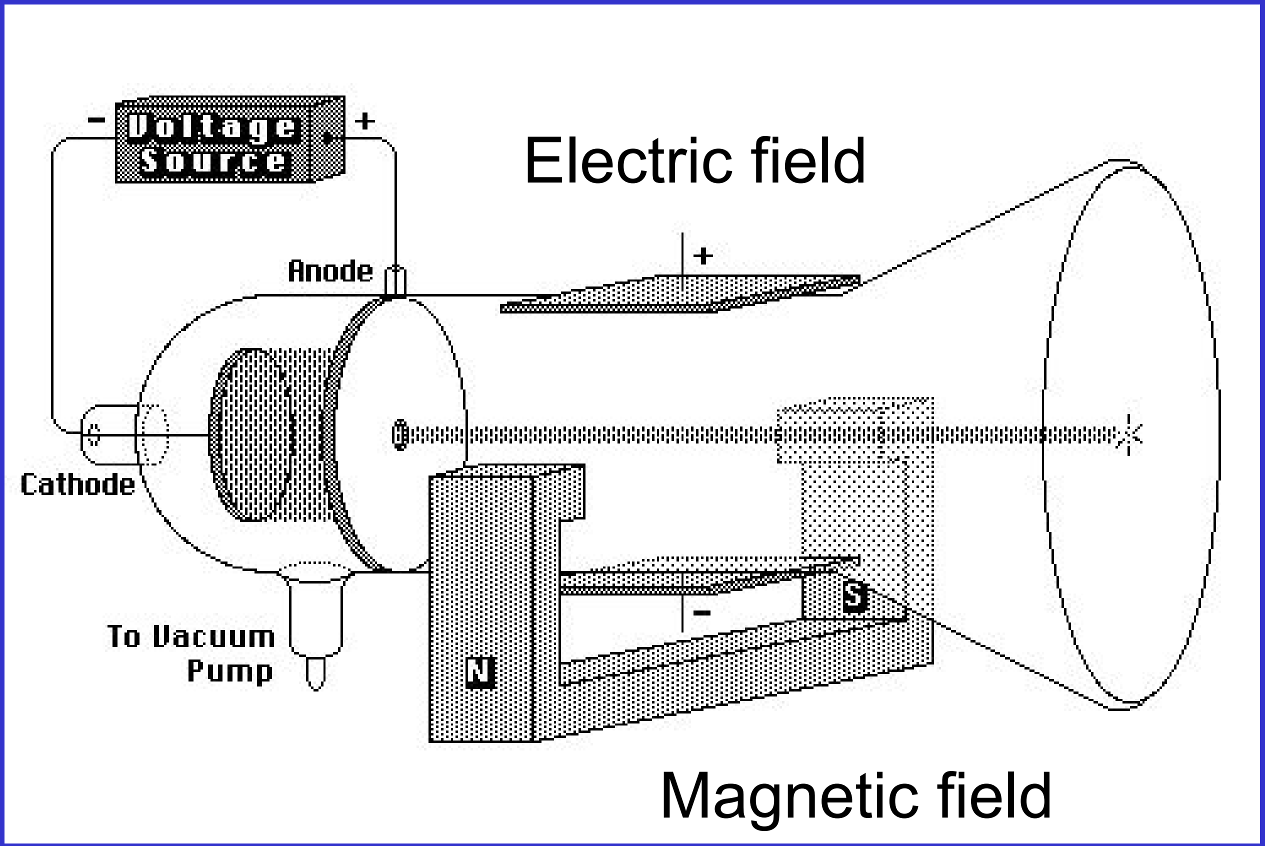
• A ray is produced at the cathode (negative pole) and travels to the anode (positive pole).

• The cathode ray responds to both magnetic and electric fields. Since the ray is attracted to a positive electric plate placed over the cathode ray tube (beam deflected toward the positive plate), the ray must be composed of negatively charged particles.

Experimental evidence for the existence of **electron**

Joseph John Thomson (1856 - 1940)

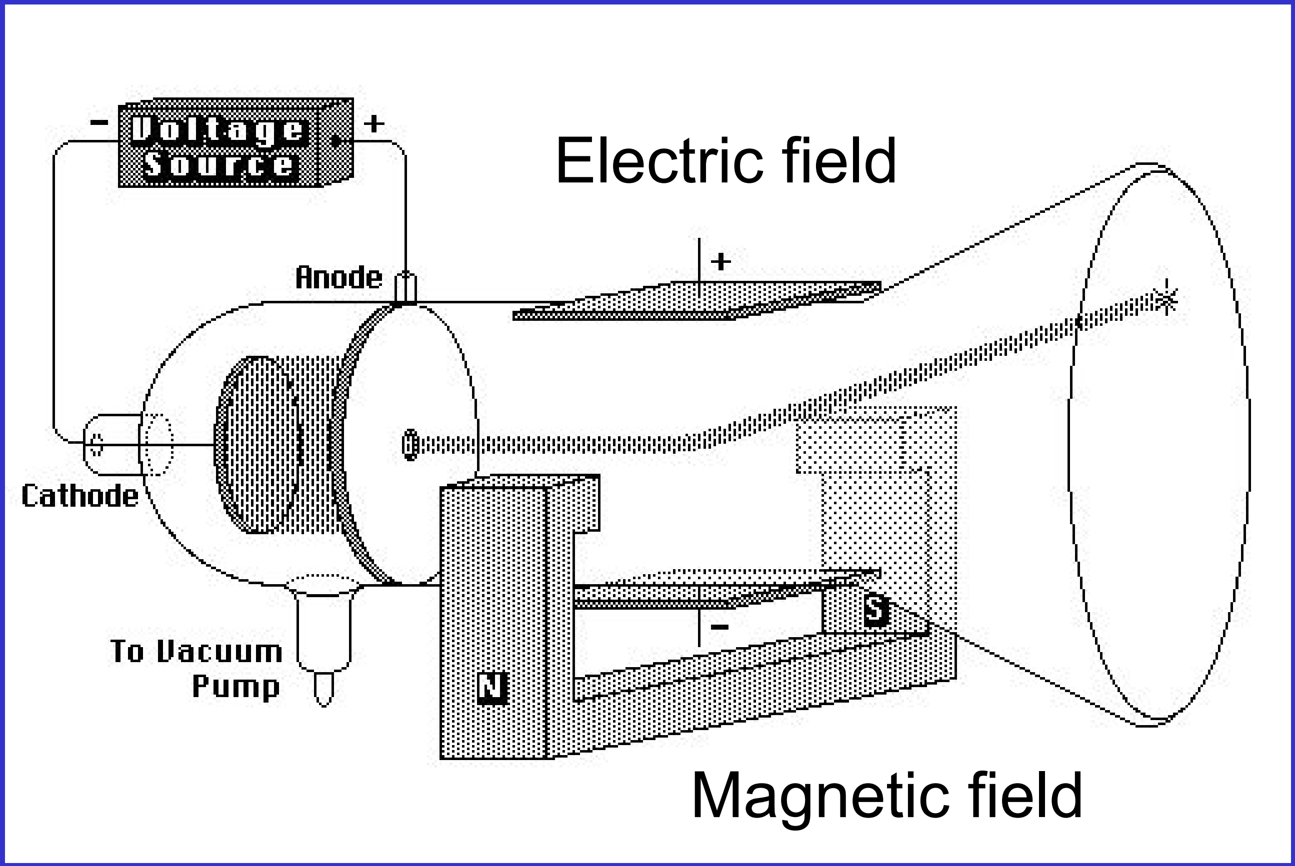
Cathode Rays



Specific charge

q/m_e **= –1.76 10⁸ C g⁻¹**

Cathode Rays

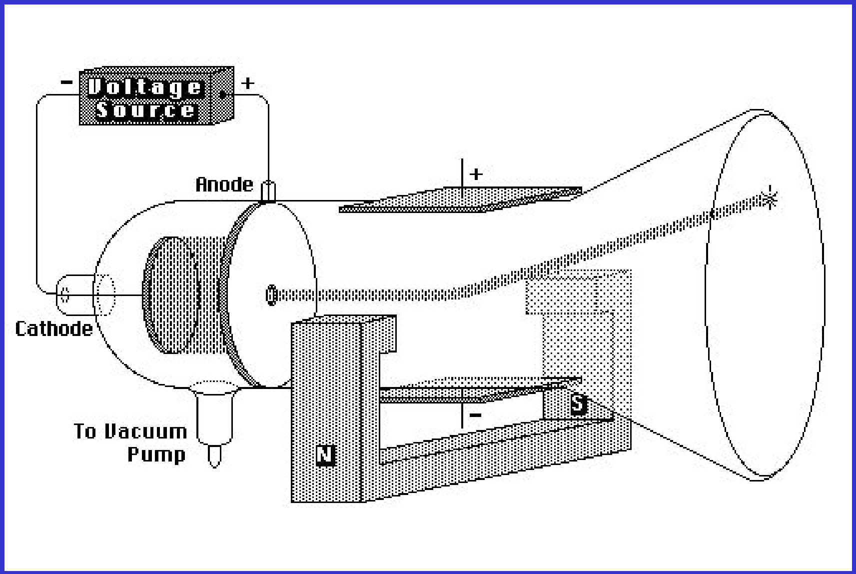


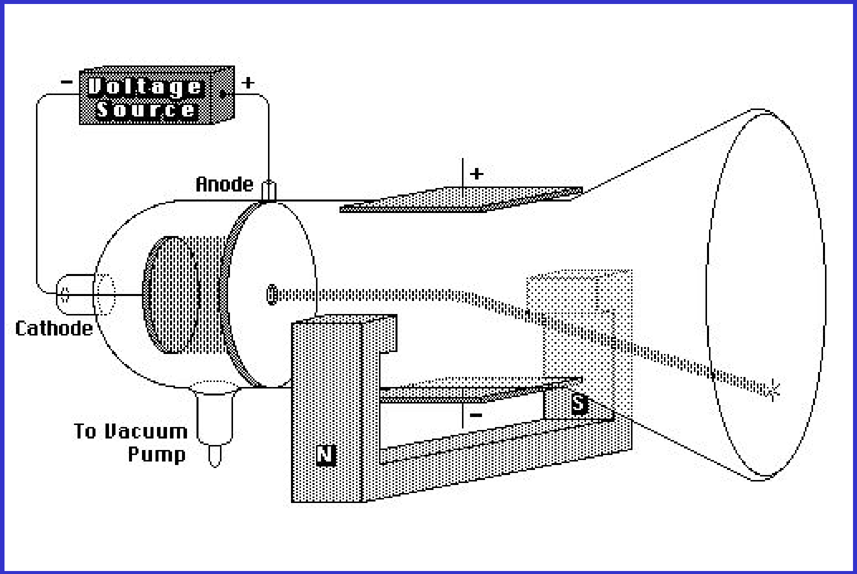
Specific charge

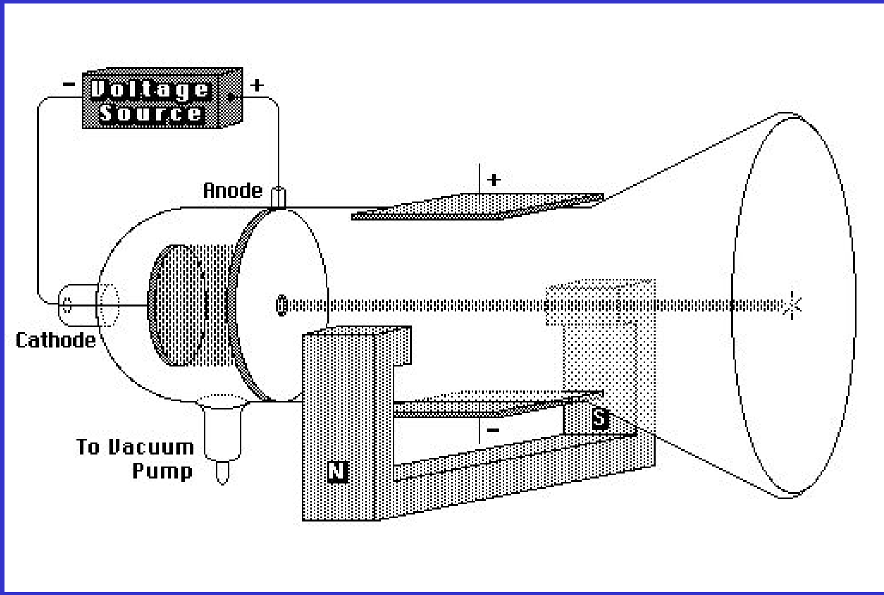
$q/m_e = -1.76\ 10^8\ \text{C g}^{-1}$

Electric field

Magnetic field

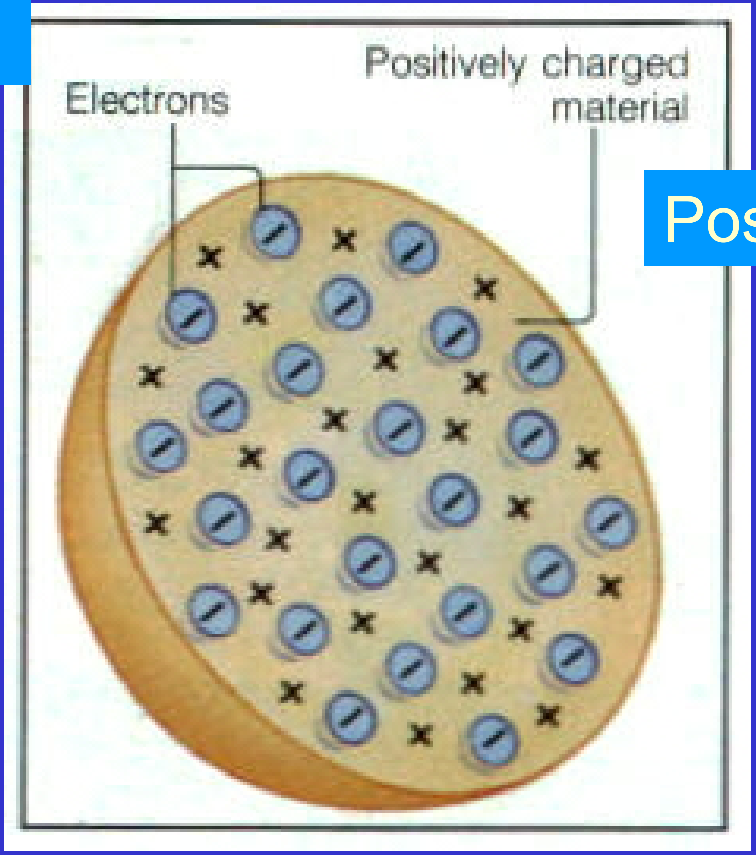






Thomson Atomic Model

Electrons



Positive charge diffuse