Selected Topics in General and Inorganic Chemistry

Lectures notes and interactive teaching by

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Table of topics:

Podmienky na absolvovanie predmetu (Grading policy):

There will be two running written tests examinations (maximum 20 points each) during the semester course. Final exam will consist of a 60-point test. Only those students will be admitted to final examination who achieve at least 60 % of the points from tests and 60 % of laboratory work evaluation. For grade A, it is necessary to obtain at least 92 %, for grade B at least 84 %, for grade C at least 76 %, for grade D at least 68 % and for grade E at least 60 % of all points. Credits will not be assigned to a student, who will not earn at least 60% from running tests, or who will not earn at least 60% from laboratory work and to student, who will not earn at least 60 % from final exam.

What is Chemistry?

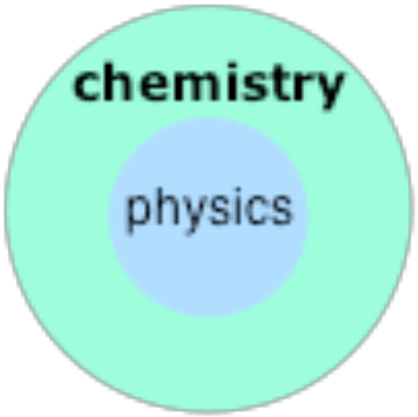
An introduction to chemical science

Chemistry is such a broad subject and one so full of detail that it is easy for a newcomer to find it somewhat overwhelming, if not intimidating. The best way around this is to look at Chemistry from a variety of viewpoints:

- How Chemistry relates to other sciences and to the world in general
- What are some of the fundamental concepts that extend throughout Chemistry?
- What are some of the major currents of modern-day Chemistry?

The scope of chemical science

physics might be considered more "fundamental"



Chemistry is too universal

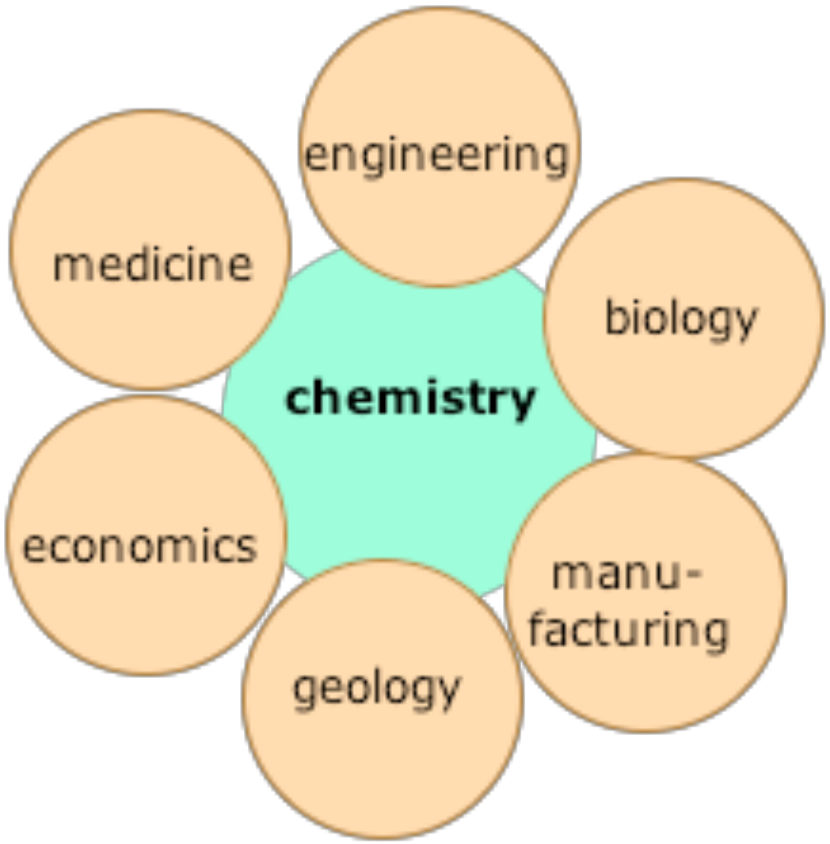
dynamically-changing

major focus:

the structure and properties of substances

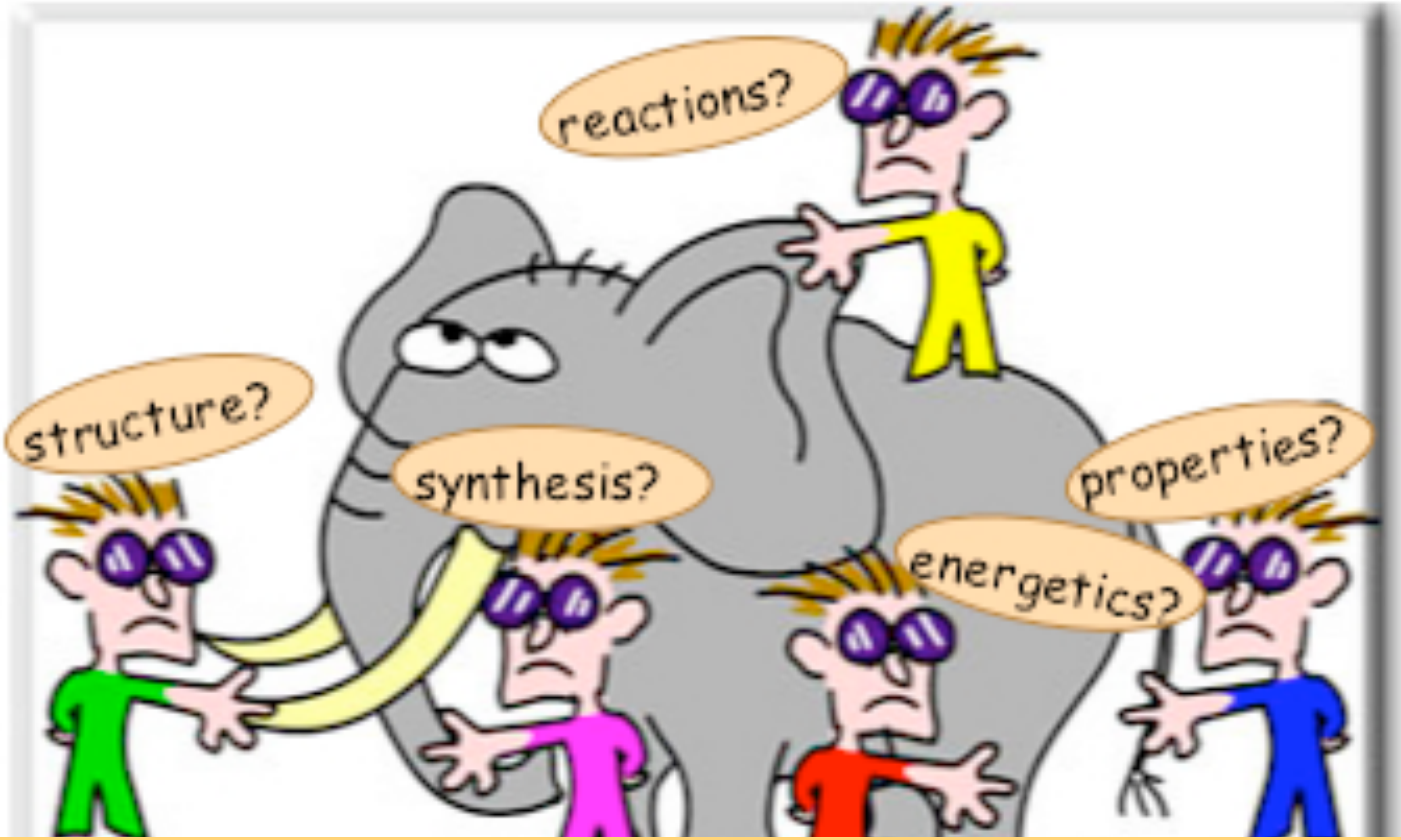
on the changes that they undergo

Chemistry: the central science



The real importance of Chemistry is that it serves as the interface to practically all of the other sciences

So just what is chemistry?



Chemistry can be approached in different ways, each yielding a different, valid, (and yet hopelessly incomplete) view of the subject.

Chemist's view

Mainly theoretical	to	Mainly practical
Why do particular combinations of atoms hold together, but not others?		What are the properties of a certain compound?
How can I predict the shape of a molecule?		How can I prepare a certain compound?
Why are some reactions slow, while others occur rapidly?		Does a certain reaction proceed to completion?
Is a certain reaction possible?		How can I determine the composition of an unknown substance?

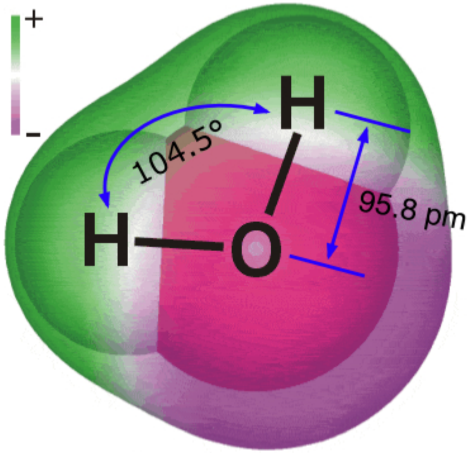
Chemistry is the study of *substances*; their properties, structure, and the changes they undergo.

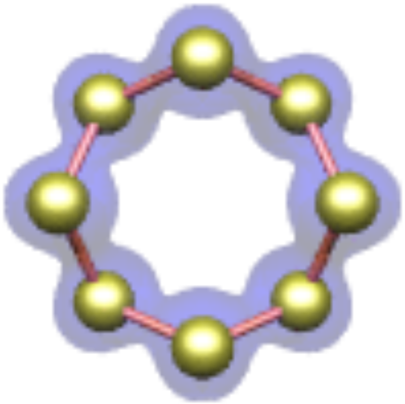
Observation:	**Direct**	**Indirect**
Realm:	Macroscopic	Microscopic

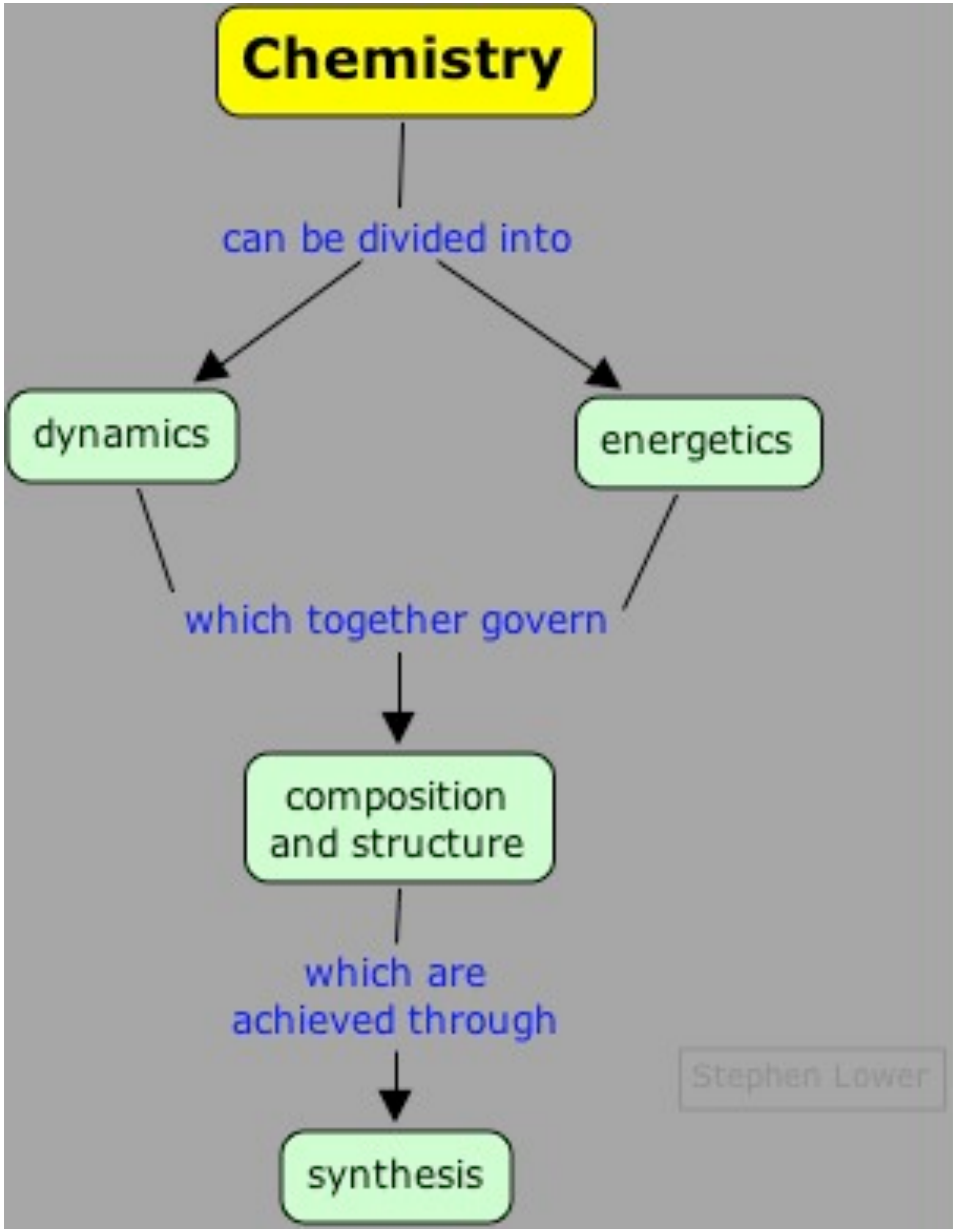
Composition	Stochiometric ratio, formulae, mixtures …	structures of solids, molecules, and atoms …
Changes (Energetics)	Thermal and other energetic effects, equilibria	statistics of energy distribution
Changes (dynamics)	Reaction rates	Mechanisms

Macroscopic

Microscopic







Dynamics refers to the details of that rearrangem-ents of atoms that occur during chemical change, and that affect the rate at which change occurs.

Energetics refers to the thermodynamics of che-mical change, relating to the uptake or release of heat.

HISTORY

Chemistry is a branch of science that has been around for a long time. In fact, chemistry is known to date back to as far as the prehistoric times. Due to the amount of time chemistry takes up on the timeline, the science is split into four general chronological categories.

The four categories are:

prehistoric times - beginning of the Christian era (black magic)

beginning of the Christian era - end of 17th century (alchemy)

end of 17th century - mid 19th century (traditional chemistry)

mid 19th century - present (modern chemistry)

Milestones in the history of Chemistry

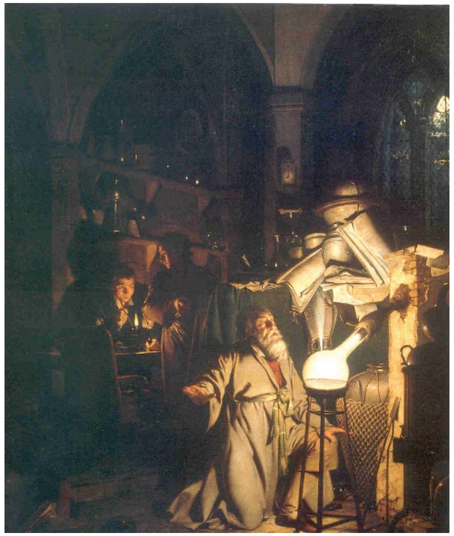
Prehistoric Times – Beginning of the Christian Era

Fire – Smoke – Ceramics

~3300 BC	**Bronze Age** (**alloy** consisting primarily of **copper**, with **tin** as the main additive)
1700 BC	6th Babylonian king Hammurabi's reign – known metals were recorded and listed in conjunction with heavenly bodies
~1300 BC	**Iron Age**
430 BC	**Democritus** proclaims the atom to be the simplest unit of matter
300 BC	**Aristotle** declares the existence of only four elements: fire, air, water and earth properties: hot, cold, dry and wet

History of Chemistry

~300 BC - End of 17th Century (Alchemy)



300 BC-300 AD the Advent of the Alchemists

attempt to transmute cheap metals to gold. The substance used for this conversion was called the Philosopher's Stone

13th-15th century intensive effort;
pope John XXII (1316-34) issued an edict against gold-making

Despite the alchemists' efforts, transmutation of cheap metals to gold never happened within this time period.

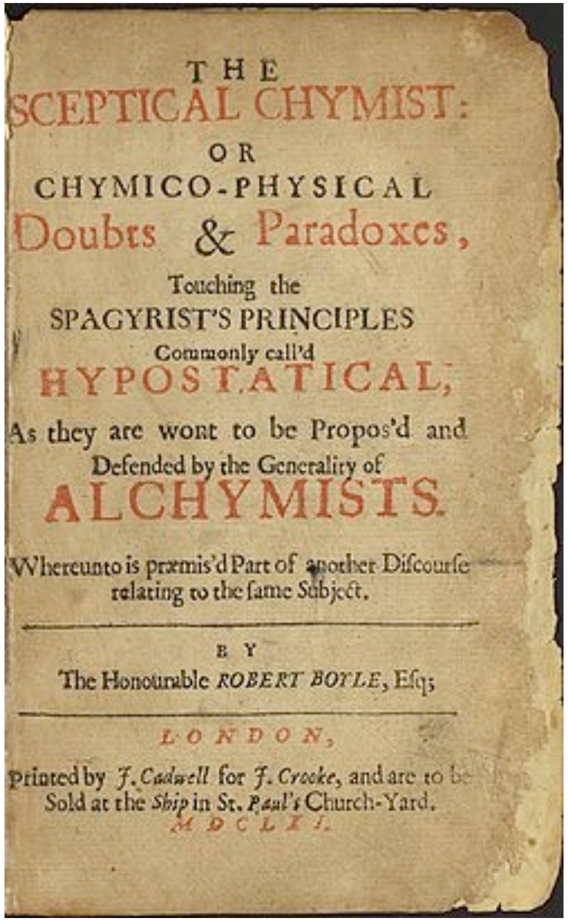
1493 – 1541 Paracelsus – (Philippus von Hohenheim)
Modern toxicology, pharmacology;
Three principles: salt (solidity, inertness),
sulfur (inflamability), mercury (fluidity, heaviness, metallicity)

16th century

Alchemists not only wanted to convert metals to gold, but they also wanted to find a chemical concoction that would enable people to live longer and cure all ailments. This elixir of life never happened either.

17th century – 1661 Robert Boyle

hypothesis that matter consisted of atoms and clusters of atoms in motion and that every phenomenon was the result of collisions of particles in motion



sometimes called

founder of modern chemistry

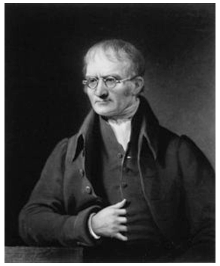
History of Chemistry ~1700 – ~1850 (Traditional Chemistry)

Johann Joachim Becher – 1667 **phlogiston theory**
postulated a fire-like element called *phlogiston*, contained within combustible bodies, that is released
during combustion (rusting).

1774 Joseph Priestly heated calx of mercury, collect-ed the colorless gas and burned different substances in this gas (discovery of oxygen)

Antoine Lavoisier – oxygen (1778); hydrogen (1783)
disproved the phlogiston theory; list of elements
law of mass conservation - Father of Modern Chemistry

John Dalton – 1803 Atomic Theory which states
that all matter is composed of atoms, which are small
and indivisible



History of Chemistry ~1850 - present (Modern Chemistry)

1854 Heinrich Geissler creates the first vacuum tube.

1879 William Crookes – plasma - ZnS fluorescence → **cathode rays**

1885 Eugen Goldstein - positive particles - **protons**

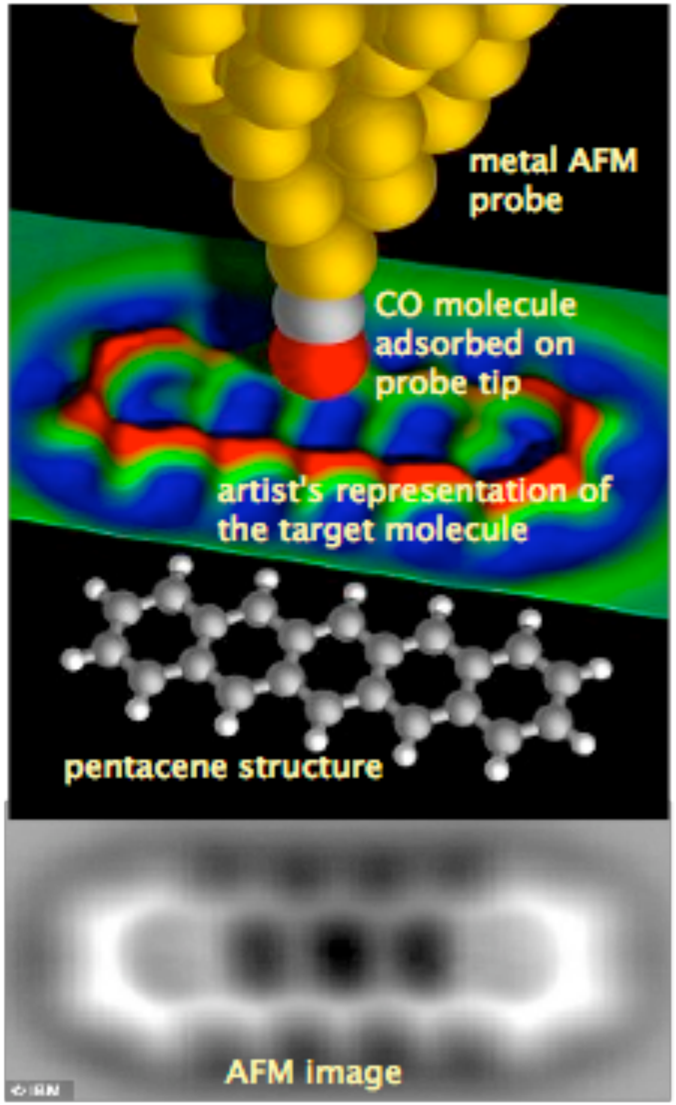
1895 Wilhelm Roentgen accidentally discovered **X-rays**

1896 Henri Becquerel - fluorescence of pitchblend – natural radioactivity – Nobel Prize in Physics1903 with Marie Skłodowska-Curie and Pierre Curie

1897 J.J. Thomson – discovery of the electron

2009, IBM scientists
in Switzerland

Imaging a real molecule!



AFM:
atomic force microscopy

atoms-thin metallic **probe** is drawn ever-so-slightly above the surface of an **immobilized** pentacene molecule **cooled** to nearly absolute zero.

Currents of modern Chemistry

few of the areas that have emerged as being especially important in modern chemistry

Synthesis

Separation science

Identification and assay

Materials, polymers, and nanotechnology

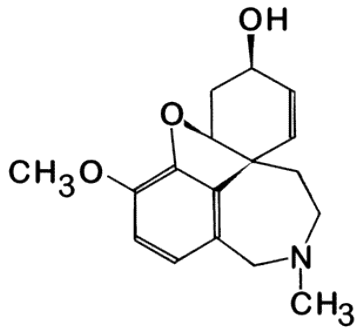
Biochemistry and Molecular biology

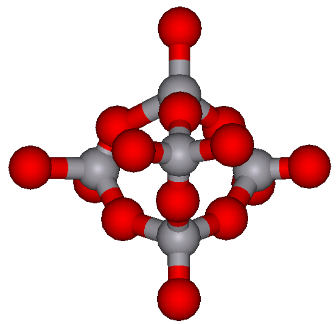
Theoretical and computational chemistry

Synthesis is both one of the oldest areas of chemistry and one of the most actively pursued:

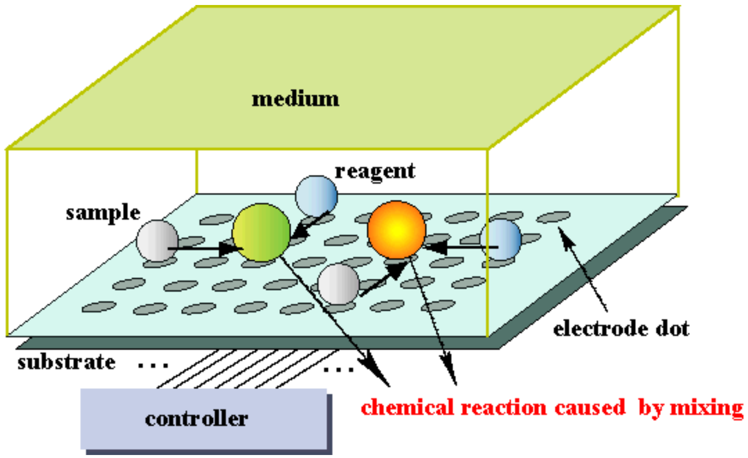
major threads

New-molecule synthesis - Chemists are always challenged to come up with molecules containing novel features such as new shapes or unusual types of bonds.

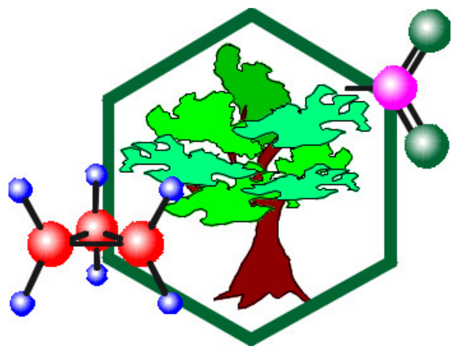




Combinatorial chemistry refers to a group of largely-automated techniques for generating tiny quantities of huge numbers of different molecules ("libraries") and then picking out those having certain desired properties. Although it is a major drug discovery technique, it also has many other applications.



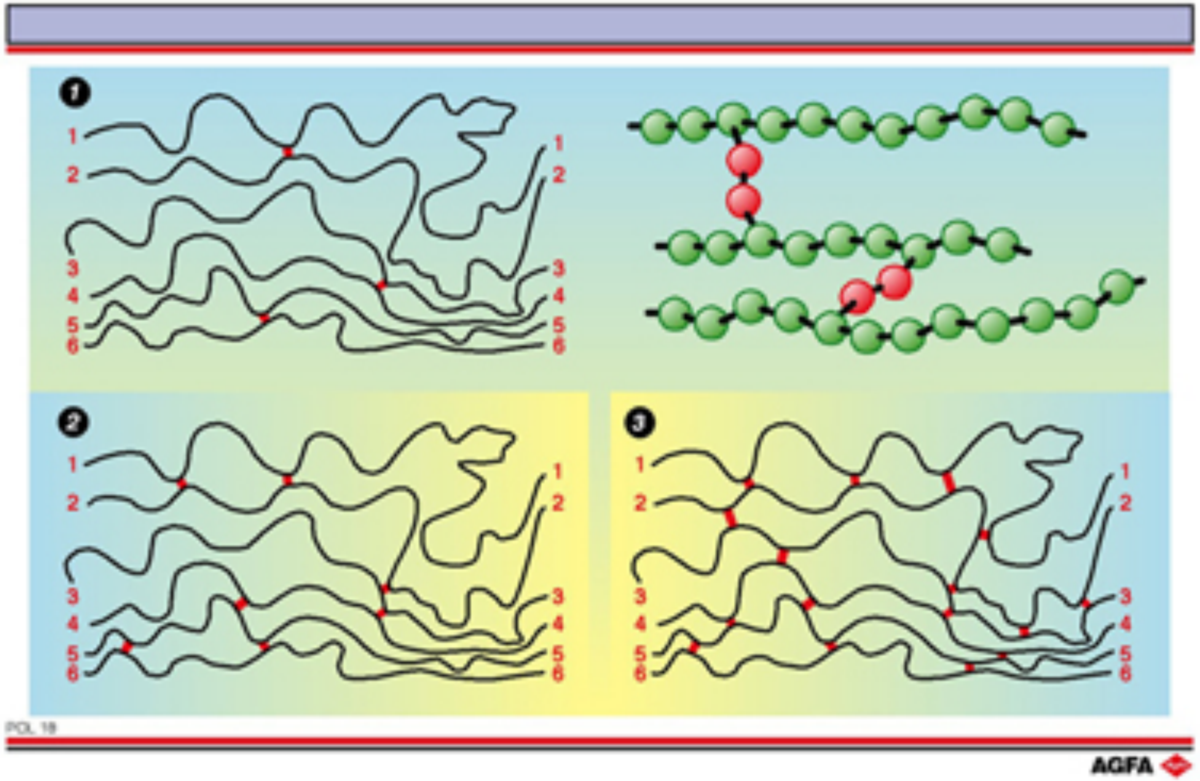
Green chemistry - synthetic methods that focus on reducing or eliminating the use or release of toxic or non-biodegradable chemicals or byproducts.



Materials, polymers, nanotechnologies

Materials science attempts to relate the physical properties and performance of engineering materials to their underlying chemical structure with the aim of developing improved materials for various applications.

Polymer chemistry



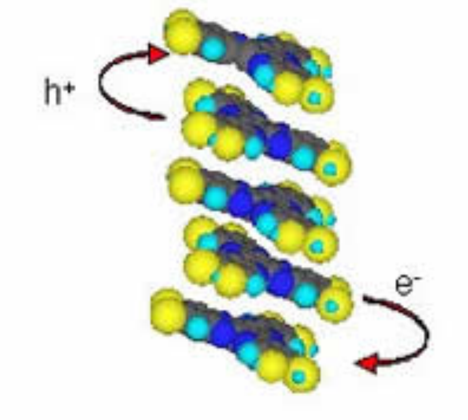
developing polymeric ("plastic") materials for industrial uses.

Connecting individual polymer **molecules by cross-links** (red) **increases** the strength of the material.

ordinary polyethylene is a **fairly soft** material with a low melting point, but the cross-linked form is **more rigid** and **resistant** to heat.

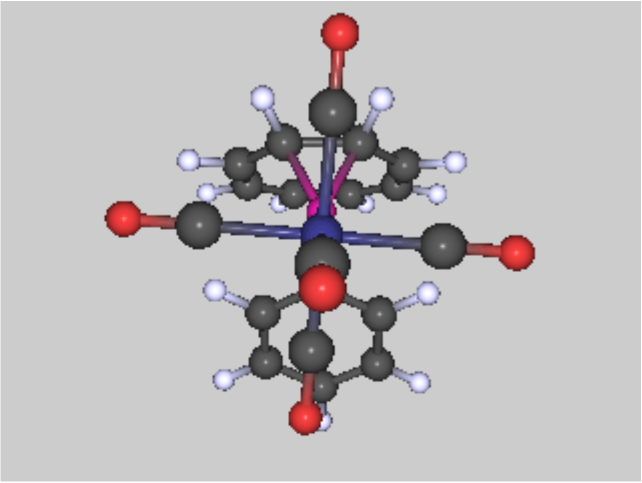
Organic semiconductors

number of potential advantages over conventional metalloid-based devices.



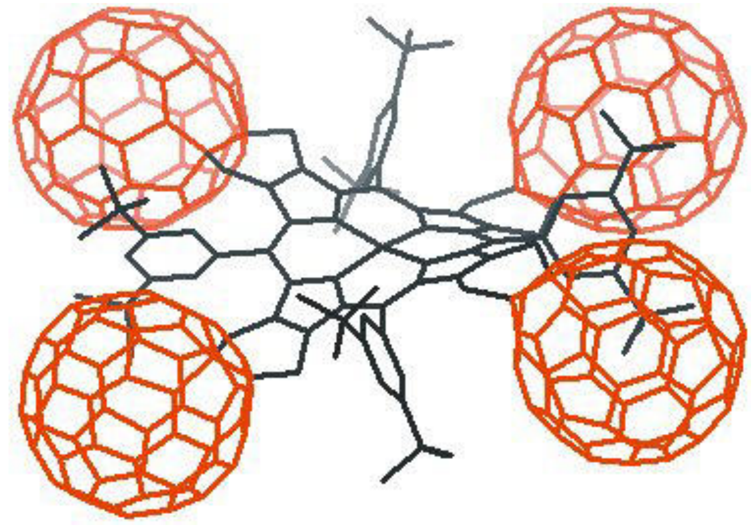
Nanodevice chemistry

constructing molecular-scale assemblies for specific tasks such as computing, producing motions, etc.



Fullerenes, nanotubes and nanowires, graphene

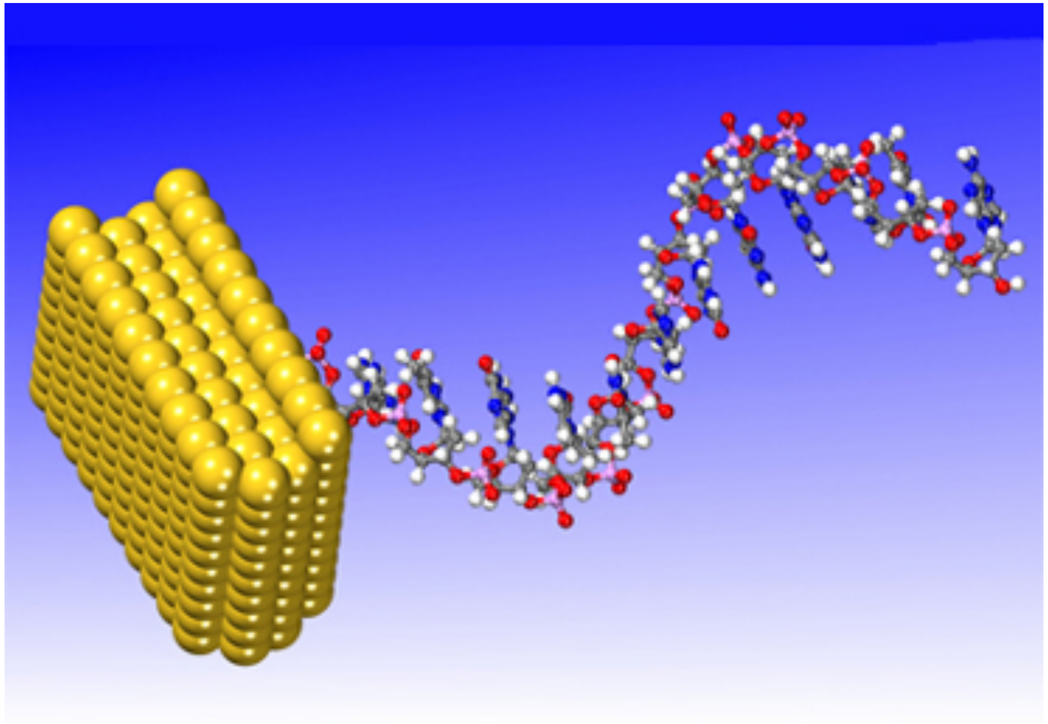
Fullerenes were first identified in 1985 as products of experiments in which graphite was vaporized using a laser



R. F. Curl, Jr., R. E. Smalley, and H. W. Kroto shared the 1996 Nobel Prize in Chemistry

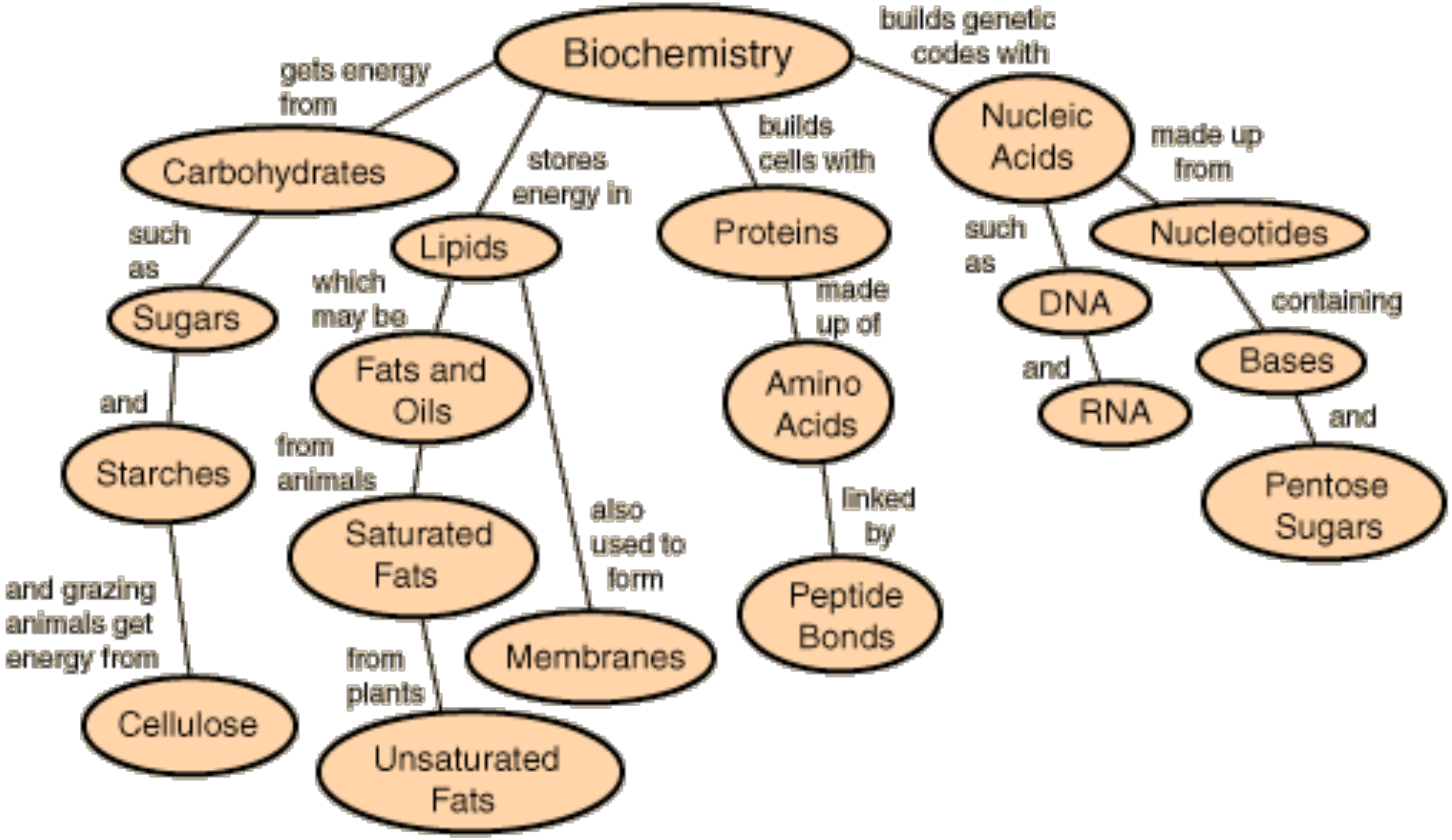
Fullerene research is expected to lead to new materials, lubricants, coatings, catalysts, electro-optical devices, and medical applications

Biosensors and biochips



the surfaces of metals and semiconductors "decorated" with biopolymers can serve as extremely sensitive detectors of biological substances and infectious agents

Biochemistry and Molecular biology

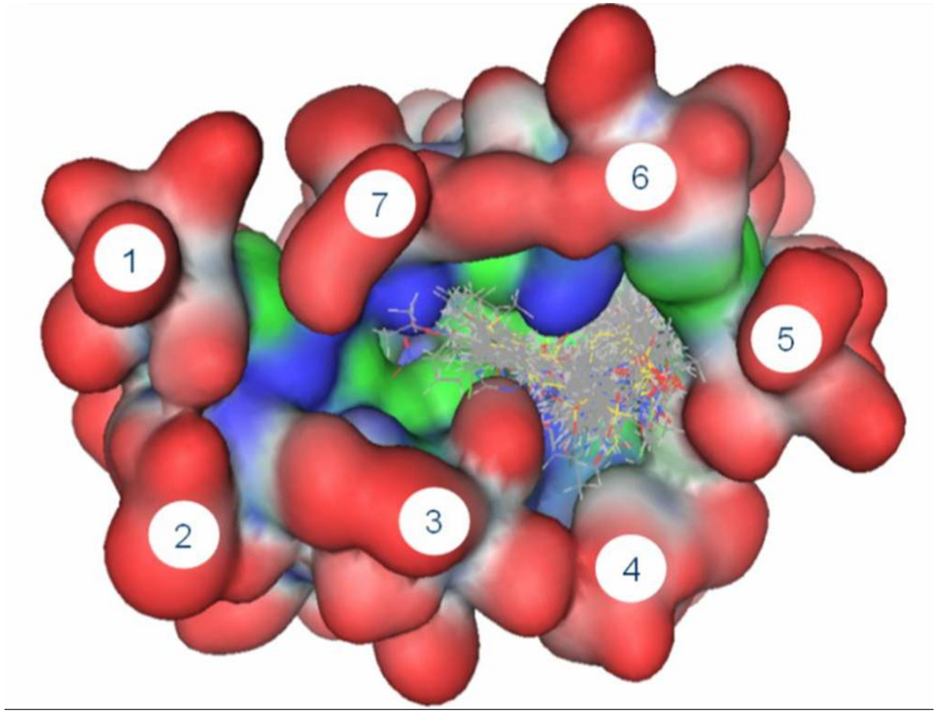


ranging from the fundamental chemistry of gene express-ion and enzyme-substrate interactions to drug design

Drug design

looks at interactions between enzymes and possible inhibitors

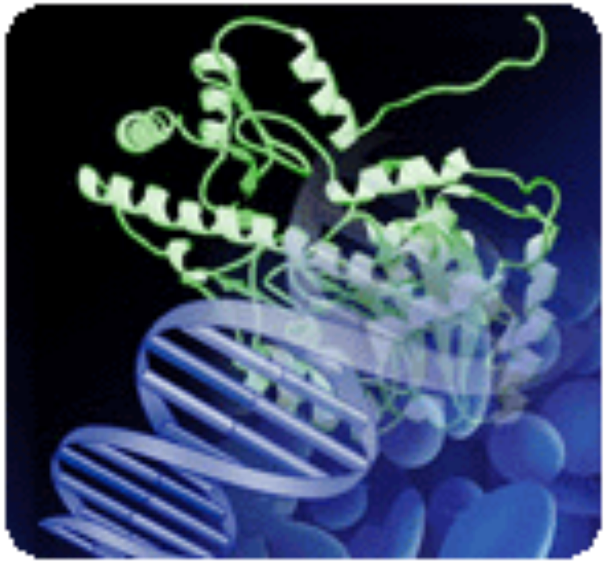
Computer-modeling is an essential tool in this work



Proteomics

This huge field focuses on the relations between structure and function of proteins

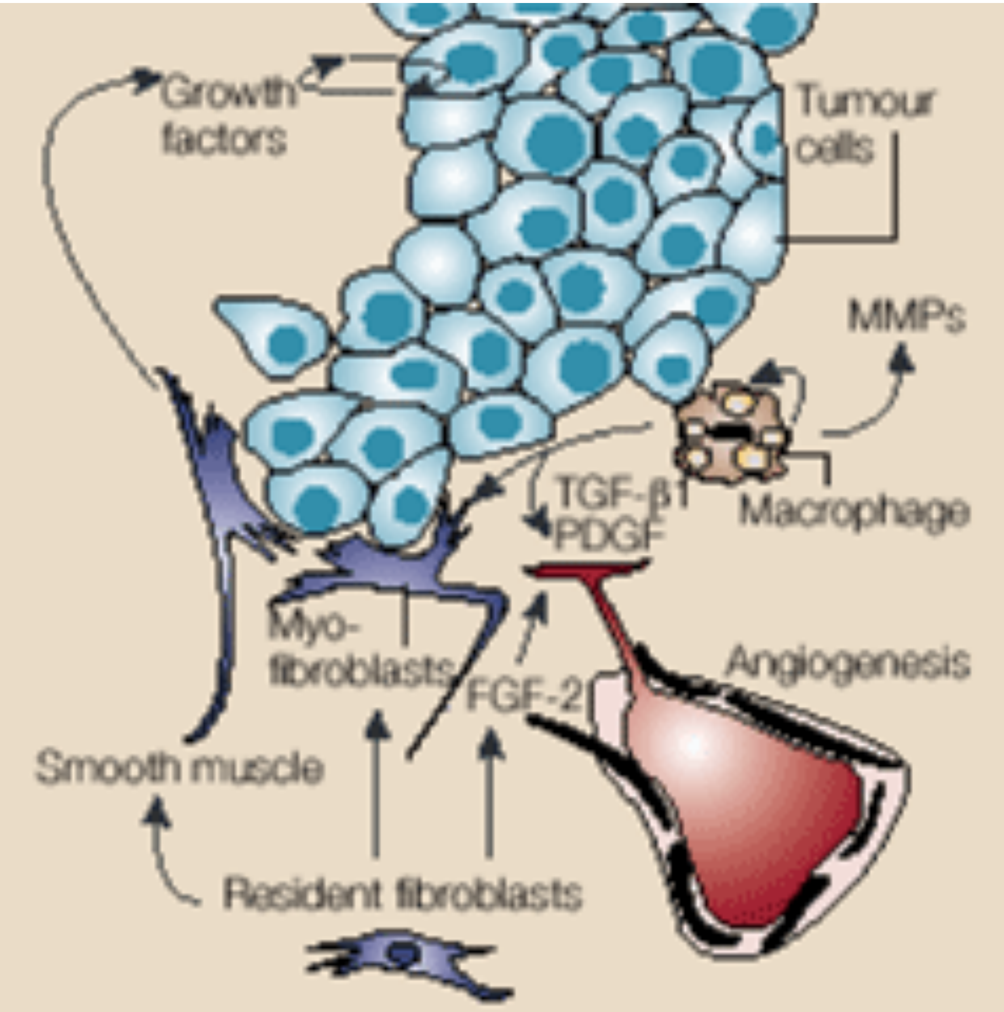
there are about 400,000 different kinds in humans.



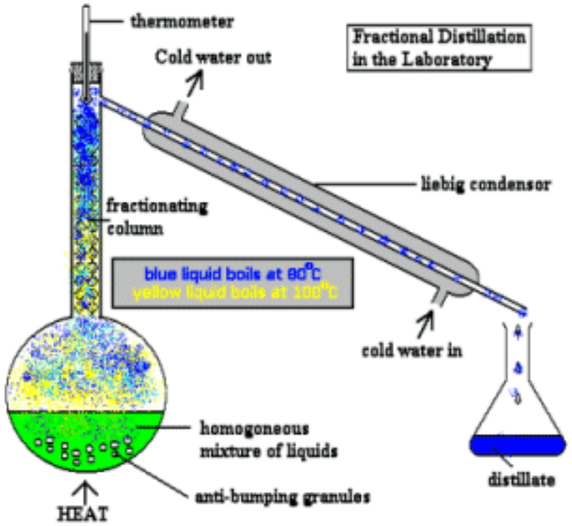
Proteomics is related to genetics in that the DNA sequences in genes get decoded into proteins which eventually define and regulate a particular organism.

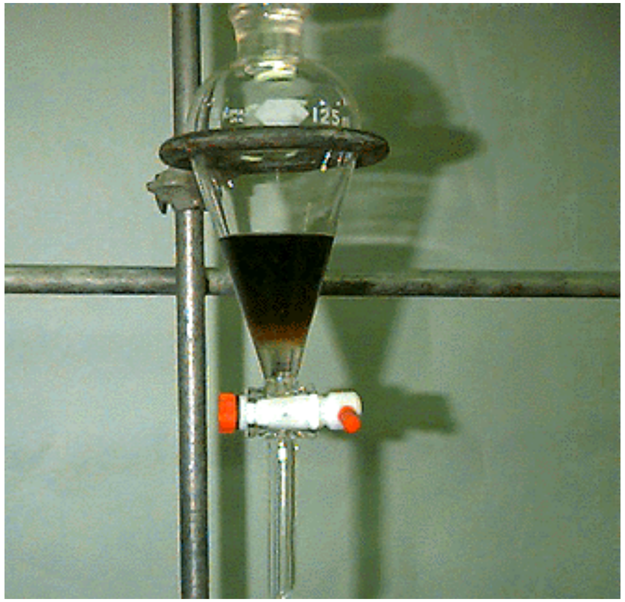
Chemical genomics

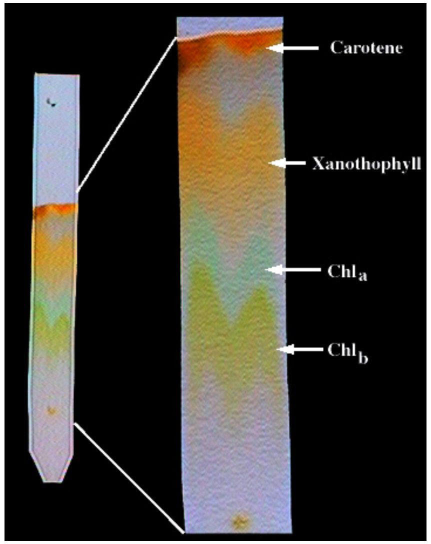
explores the chain of events in which signaling molecules regulate gene expression

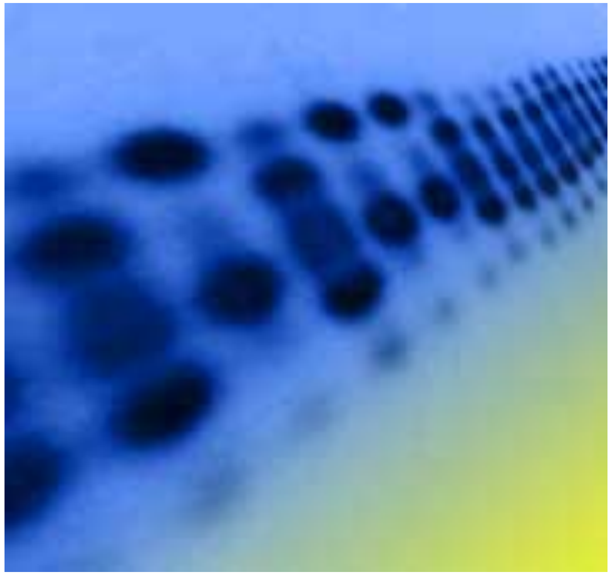


Separation methods:

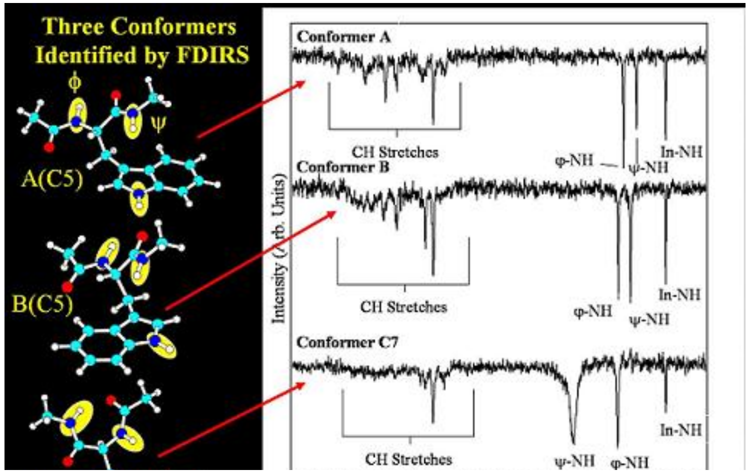


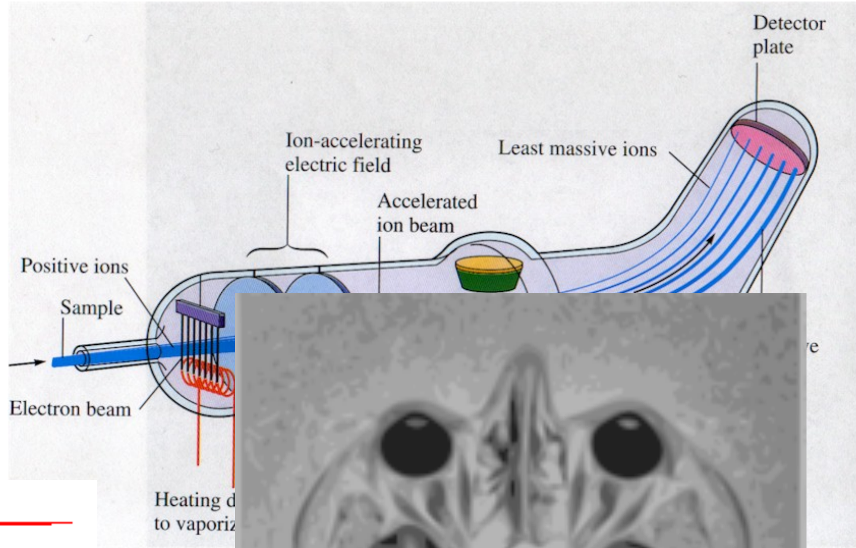


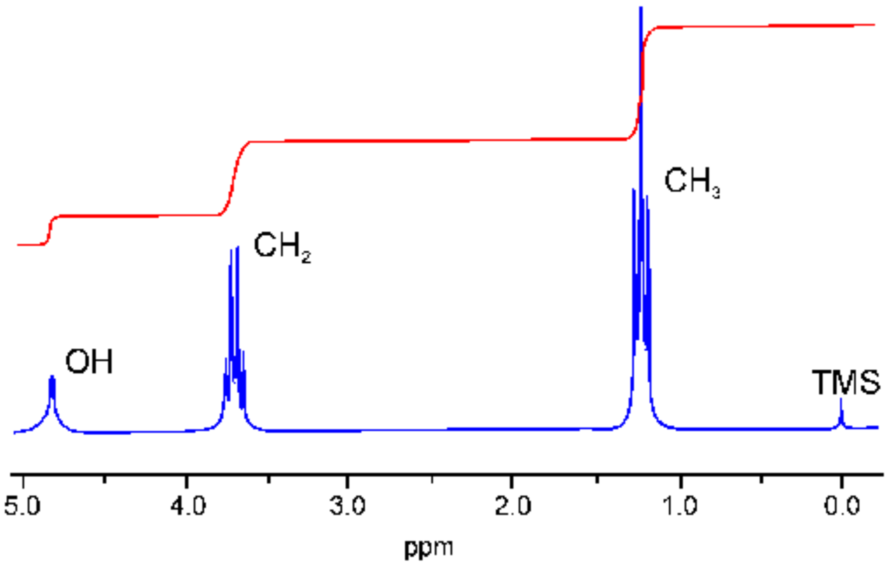




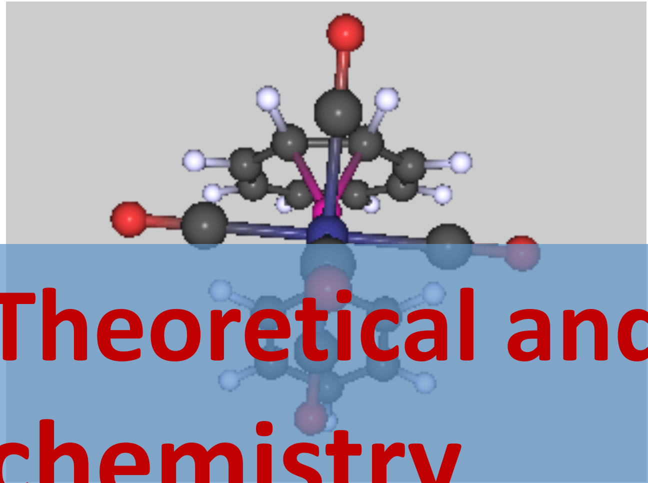
Identification tools:

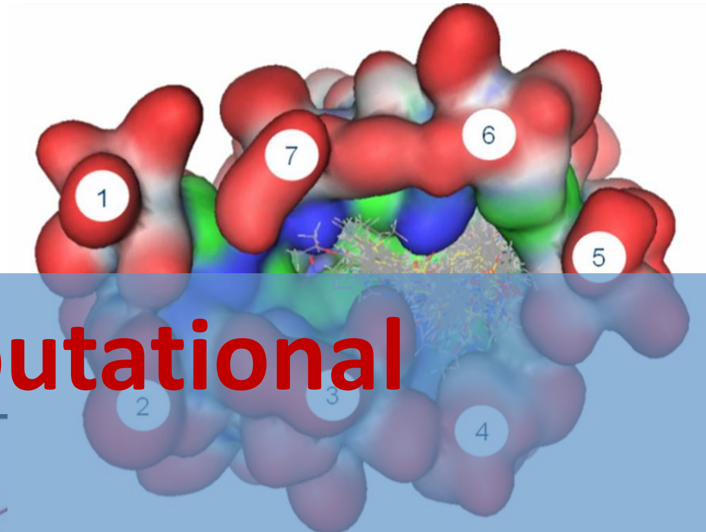


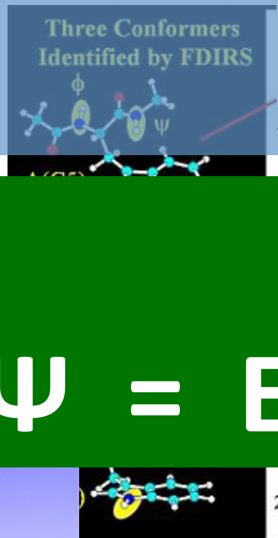


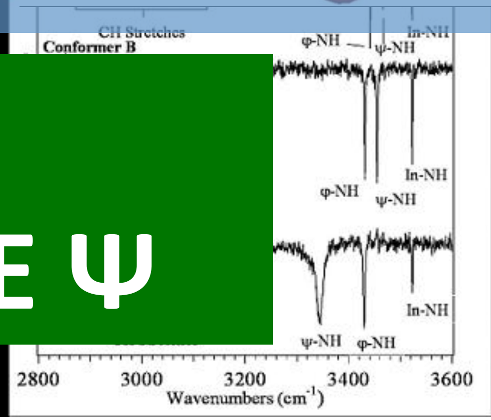


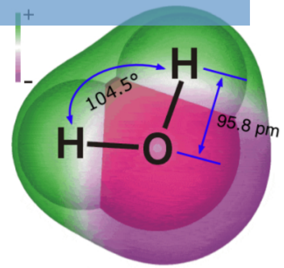
Theoretical and computational chemistry



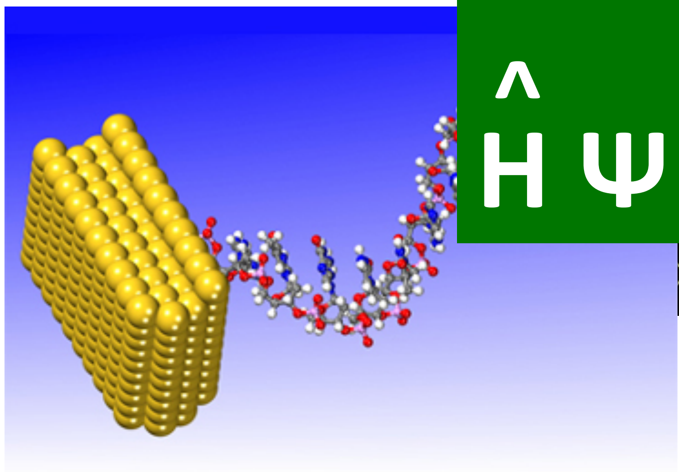


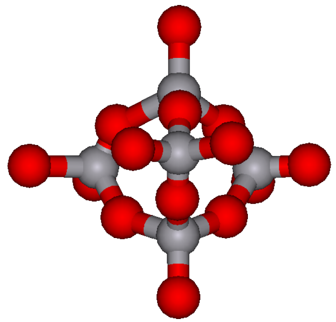






$$\hat{H}\Psi = E\Psi$$





Nature of the material world

Matter (Substance)

(Physical) Field

Internally discretized, particles with non-zero rest mass

Continuous internal structure,

What is a substance composed of?

(as related to Chemistry)

Elementary particles

... **leptons** **quarks** ...

electrons

composite particles

atoms ← **neutron, proton (baryons)**

Molecules – entities composed of atoms

entity – discrete unit with a defined unique structure and properties, able of an independent existence

... associates, crystals ... – condensed systems

Chemistry

Measures of the changes in material objects

Mass (SI: kg)

A measure of inertia of a body, (resistance to the motion changes);

$$m_{\mathrm{v}} = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

rest mass
velocity
light v.

The Law of Conservation of Mass

Σ *m* = const.

M. V. Lomonosov 1758
A. L. Lavoisier 1774-7

Energy (SI: J)

A quantitative measure of diverse forms of the motion; can be transferred to other objects; converted

$$E = mc^2$$

A. Einstein (1905)

and Energy

Σ *E* = const.

M. V. Lomonosov 1760

Atom (in a „nutshell“)

Nucleus

Protons (+)

nucleons

Neutrons (0)

surrounded by:

electrons (-)

Z – proton number

N – neutron number

A – nucleon number

$A = Z+N$

${}^{A}_{Z}E$ ${}^{23}_{11}Na$

Nuclide: atomic species characterized by a specific constitution of its nucleus.

Isotopes: same Z, different A

napr. ${}^{54}_{26}Fe$, ${}^{56}_{26}Fe$, ${}^{57}_{26}Fe$, ${}^{58}_{26}Fe$

Isobars: different elements, equal „A“

Atomic mass: ~ 10^{-27} - 10^{-25} kg

not practical ⟶ **relative atomic mass A_r**

Unified atomic mass unit (or constant):

$$m_u = \frac{1}{12} m({}^{12}_{6}C) = 1{,}660565 . 10^{-27} \text{ kg}$$

$$A_r({}^{A}_{Z}E) = m({}^{A}_{Z}E)/m_u$$

more isotopes → weighted average

Approval by: **IUPAC**

International **U**nion of **P**ure and **A**pplied **C**hemistry

Molecules – entities composed of atoms, with unambiguous structure and unique properties

Relative molecular mass M_r

$$M_r = m(X_aY_b) / m_u = a\,A_r(X) + b\,A_r(Y)$$

Amount of substance (Number of moles) (n) (SI): mol - number of N_A entities

N_A Avogadro's constant = number of atoms in 12g ^{12}C

$N_A = 6{,}022140.10^{23} mol^{-1}$

Molar mass: $M(A) = m(A)/n(A)$

Molar volume (V_m):

Avogadro's law – for an ideal gas

- equal volumes of all gases, at the same temperature and pressure, have the same number of molecules

equal n(A) → equal volume

standard: (T=273.1 K; p=101.32 kPa; V_m =22.41 $dm^3 mol^{-1}$)

otherwise: $V_m = V/n$

Amedeo Avogadro, 1776-1856, Italian

Physical properties of materials

Extensive

depend on the amount of a substance

mass, volume,
total energy content,
total electric resistance
total content of a given element, ...

Intensive

do not depend on the amount of a substance

density, colour,
boiling point,
electric conductivity,
concentration, ...

Used to characterize the substance

Dichotomy – a unique classification is not always possible

e. g. pressure – both dependent and independent

Classification of material systems

Homogeneous

uniform intensive properties
throughout its volume

A phase

Heterogeneous

two or more phases

Phase boundaries

colloids: no clear phase bondaries,
intesive properties vary within
the volume

Pure substances– Chemical individuals

Unique physical and chemical properties

Melting point (temperture), boiling p., spectral properties, ...

Production: from mixtures by separation methods

Destilation, crystalization, liquid extraction, chromatography ...

Are they really pure?

... pure → **For analysis** → **Chemically pure**

→ **Extra chemically pure substances**

special – 99,999 % Si - number of 9s

Pure substances

Chemical elements

isoatomic composition
same proton number

alotropic modification

O: O_2, O_3

C: graphite, diamond,
fulleren, amorfous carbon,
C-nanotubes, graphene, ...

Gr. *allos* , different *tropos* kind
Jöns Jakob Berzelius 1779-1848, Swedish

Compounds

heteroatomic
composition

Isomers – different modifications with equal composition.

Different molecular structures (locations of atoms in space)

Chemical formulae

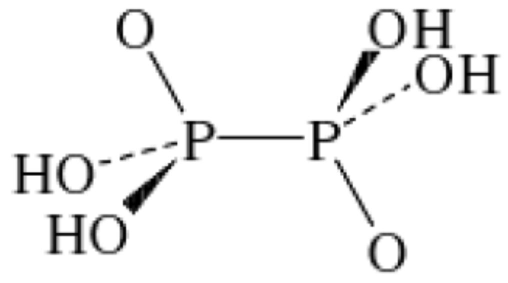
Stochiometric (empirical, summary)

H_2PO_3

Molecular $H_4P_2O_6$

Rational $(OH)_2OP\text{-}PO\,(OH)_2O$

Structural



Changes in the substances

Chemical change - reaction

Macroscopically:

process of creation of new compounds

Microscopically:

reorganisation of atoms in the space

$$A + B \rightarrow C + D$$

reactants **products**

$$A + B \rightleftarrows C + D$$

chemical equilibrium

Chemical equations, mass balance, charge balance

Empirical laws

Law of constant composition
(Law of definite proportions)

(Joseph Luis Proust – 1799, Francúz)
(John Dalton – 1803, Angličan)

A chemical compound always contains exactly the same proportion of elements by mass, irrespective of the way of preparation

$H_2 + Cl_2 \rightarrow 2\ HCl$

$3\ H_2O + PCl_3 \rightarrow 3\ HCl + H_3PO_3$

H:Cl = 2.76%:97.24%

daltonides

bertholides – non-stochiometric

Claude Louis Berthollet
1748-1822 Francúz

Empirical laws

Law of multiple proportions

(John Dalton – 1803)

If two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small integer numbers.

MnO, MnO_2

$Mn = 1$

$O(MnO): O(MnO_2) = 1:2$

Empirical laws

Law of combining volumes

(Joseph Luis Gay-Lussac – 1808, Francúz)

The ratio between the volumes of the reactant gases and the products can be expressed in simple whole numbers.

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

1 l   1 l   2 l