

General chemistry

Course notes

Lorentz Jäntschi



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1.1 The place and role of chemistry

1.1.1 Introduction

Engineering education is built around fundamental scientific concepts through the transfer of knowledge guided by the principle of developing products and processes that contribute to economic growth, advances in medical care, improved national security systems, ecological resource management, and many other beneficial areas.

A classification could include physics, chemistry, and biology as natural sciences, while logic, mathematics, and computer science as exact sciences, while geology and geography as earth sciences, but there are no strict demarcations.

The study of the structure of matter and the processes within it is done with tools specific to several fundamental sciences. Thus, physics and chemistry are closely related, and some authors consider analyses to belong to physical chemistry, because they use tools and notions specific to both physics and chemistry [5].

1.1.2 Quantities

A quantity is the result of a measurement performed on an observable in order to collect the value of a property.

The observation process is an activity of collecting knowledge using the senses or instruments. It assumes the existence of an observer and an observable. The observation process transfers an abstract form of knowledge from the observable to the observer (for example, in the form of numbers or images).

Measurement comprises two serialized operations: observation (defined previously) and recording the results of the observation. Measurement depends on the nature of the observed object (material) or phenomena (immaterial), the measurement method and the way of recording the results of the observation [6].

In the information space, the result of a measurement is recorded by a number and always has a meaning (of the quantity subject to measurement) and a unit of measurement attached to it. Conventionally, if the quantity counts pieces or represents a relative quantity then the unit of measurement is no longer expressed.

On the one hand, because the numbers represented in the information space use a defined (and finite) representation method and on the other hand, because the resolution of the measurements is limited (and finite), the representation is often degenerate (degeneration is the representation

by means of the same numerical value of the result of the observation of two different, distinct elements).

Most of the time, however, the degeneracy is intrinsic (i.e. there are actually two distinct objects in the observational space that possess the same value for a certain measured property). The rule is that the measurement scale must be carefully chosen so as to reflect the observed phenomenon as well as possible. From the point of view of structure, measurement scales¹ are classified as in Tab. 1.1.

Scale	Туре	Operatio	onStructure	Statistics	Examples
Nominal	Discret	"="	Standard	Mode,	Blood types,
			set	Chi squared	Chemical elements
Binary	Logic	"=",	Boolean	Mode,	Sides of a coin
		"!"	algebra	Fisher Exact	(element) Present/Absent
Ordinal	Discrete	"=",	Commutativ	veMedian,	Numberof atoms
		"<"	algebra	Rank	Atomic number Z
Interval	Discrete	"≤",	Affine	Average,	Likert scale
	or	"_"	space	StDev,	Date (year, month, day)
	Continuous		(1D)	ANOVA,	Direction (in $^{\circ}$) relative to
				Correlation,	North
				Regression	Pauling electronegativity
Ratio	Continuous	"≤",	Vector	GeoMean,	Distance, Time, Mass,
		"-",	space	HarMean,	Energy, Temperature (in K),
		"*"	(1D)	CV,	Mass, pH, Concentration,
				Logarithm	Sweetness relative to su-
					crose

Table	1.1:	Measurement	scales
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The binary scale is a special case (n = 2) of the nominal scale with *n* elements

1.1.3 Study of chemistry

Chemistry focuses on the material species contained within substances (Fig. 1.1).

Fig. 1.1: Observing space

Structure	Property
–Universe	Entire space of observation
-Radiant energy	Speed comparable to that of light
-Radiations such as $β$, $γ$	Differentiated by properties
– <mark>Matter</mark>	Entire non-relativistic space of observation
Body	Speed much lower than that of light
Materials ensemble	Variable and discontinuous (chemical) composition
-Materials	Variable and continuous (chemical) composition
-Substances mixture	Well-defined (chemical) composition
+ Heterogeneous substance	Variable (chemical) composition
- Solution	Well-defined state of aggregation
+Alloy	Mixture of metals in liquid or solid state
Homogenous substance	Constant (chemical) composition
+Chemical compound	Well-defined and unique chemical structure

¹see also http://en.wikipedia.org/wiki/Level_of_measurement

Among substances, an important place is occupied by the concept of a chemical compound (unitary and well-defined), formed from atoms. A special place in chemistry is occupied by the study of atoms and their combinations, molecules, ions, solutions and crystals.

From the perspective of chemistry, atoms are (complex) structures formed by electrons and nucleons (which are classified into protons and neutrons). It should be noted that on the one hand, the subatomic structure and the processes that occur at the subatomic level constitute the subject of study of a branch of physics - atomic and nuclear physics, and on the other hand, complex and large molecules can perform biological functions, becoming the subject of study of biology and the interdisciplinary field of biochemistry (Tab. 1.2).

Table 1.2: Positioning	chemistry	among t	he sciences
------------------------	-----------	---------	-------------

Chemistry	Biochemistry	Biology
Physical chemistry	Mathematical chemistry	Mathematical biology
Physics	Mathematical physics	Mathematics

The volume of information in chemistry means that formally, several disciplines cover the field of knowledge of chemistry (Tab. 1.3), including organic chemistry (which deals with the study of carbon compounds) and inorganic chemistry (encompassing the study of the rest of the compounds), the study being led towards the characterization and classification of compounds within descriptive chemistry and respectively towards the characterization and classification of processes within synthetic chemistry [7], the specialized areas of chemistry being broader (Tab. 1.4).

Table 1.3: Area of chemistry

Chemistry	Organic chemistry	Biochemistry
Inorganic chemistry	General chemistry	Agrochemistry
Metals chemistry	Organometallic chemistry	Enzymology

Table 1.4: Specialized areas of chemist	ry
---	----

Chemistry	Physical chemistry	Mathematical chemistry
Analytical Chemistry	Chemometrics	Instrumental Analysis
Computational Chemistry	Chemoinformatics	Structure-Property Relationships

The large number of facts and observations in nature accumulated under all aspects constitutes the permanent and invariable treasury of the natural sciences.

In a number of cases, the study is reduced to the observation of phenomena without the possibility of intervening in their development - observational studies. In other cases, experience is used to accumulate new knowledge - phenomena are caused in the simplest possible conditions by avoiding accessory, non-essential aspects. An observation has scientific value when it leads to true conclusions and outside the particular case observed in time and space. It has been highlighted that any phenomenon is preceded or followed by other phenomena - and hence the concept of effects. A relationship that quantitatively establishes effects is called a law. Due to the multitude of phenomena and methods of observation, their systematization - classification (the one in Fig. 1.1) has become necessary.

The various trades with a chemical substrate - metallurgy, ceramics, extraction and processing of soil or plant or animal matter - have their origins far back in history, and the techniques with which these trades operate have evolved over time, as a necessity imposed by problems of production, efficiency, or environmental conservation.

Returning to Fig. 1.1, the Universe is composed of matter. In this sense attributed to the word matter, it can exist in two forms:

- substances, which move through the universe at a speed lower than the speed of light;
- radiant energy, which moves through the universe at the speed of light.

A body can be defined as an assembly of materials. What distinguishes bodies from materials is that materials can have a variable but not discontinuous composition, while bodies can have a discontinuous composition and the surfaces of discontinuity also define the separation surfaces between the different materials that form the body. Furthermore, substances are defined by a constant chemical composition (homogeneous materials). The term heterogeneous materials (sometimes substances) is used for materials whose composition is variable but not discontinuous or for mixtures of substances in which the mixing ratio varies. For mixtures of substances there are two more frequently used notions: that of alloy, which defines a mixture of metals in the solid state and that of solution which is used for mixtures of substances in both solid and liquid states. Later, the notion of alloy expanded its concept so that today solid solutions of metals with small amounts of metal carbides and metal oxides are also called alloys. The chemical study of a substance provides solutions for the composition of substances, their physical and chemical properties and for the reactions of substances. Materials (both homogeneous and heterogeneous) are in turn made up of even smaller parts, called chemical elements. A chemical element is defined as the smallest part of a substance that can be detected by ordinary physical and chemical methods. Nuclear processes such as fusion and fission are an exception to ordinary physical and chemical methods. Several chemical elements (of the same kind or different) can combine to form sets of elements between which chemical bonds are established. When a set of elements cannot be detected by ordinary physical methods, it is a chemical molecule (chemical compound). In nature, elements are found in a variety of chemical states (in the form of combinations, in the native state, or in the ionized state) and physical states (solid, liquid, gaseous, or plasma).

If a substance contains the same type of elements then it is called a simple substance. Simple substances actually represent the natural state in which elements can exist at a certain temperature. From a structural point of view, elements can exist in the following forms in simple substances:

- in monoelemental form (the case of monatomic gases);
- in molecular form (a set of molecules formed from a finite and small number of elements of the same kind);
- in reticular form (a set in solid state formed from a large number of elements of the same kind).

Allotropy is a phenomenon characteristic of simple substances by which an element can exist in different crystalline forms (form allotropy) or in different molecular forms (structures) (position allotropy). Allotropy is determined by the type of chemical bonds and molecular and crystalline structures that the atoms of an element can achieve.

A classification of chemical elements can be made into metals, nonmetals and inert elements (noble gases):

- Metals have crystalline structures and form mainly metallic covalent bonds, commonly called metallic bonds;
- Nonmetals form mainly covalent bonds;
- Noble gases are almost always present in monatomic form, because the outer layer is completely occupied with electrons and they can form chemical bonds very difficultly.

According to the electron octet rule, the structures of nonmetals derive from the $8 - N_g$ (N_g = group number) covalent bonds that their atoms can form between them. The form of existence of these elements is as diatomic molecules (nitrogen and oxygen), rings or linear macromolecules, in which each atom is covalently bonded to two neighboring atoms, tetraatomic molecules or networks of two double layers of atoms, in which each atom is covalently bonded to three others, or three-dimensional networks.

1.2 Amount of substance. Mole

The chemical composition of a multicomponent system is expressed in several ways. The composition parameter is usually given in mole fractions, molarities, molalities, or percent concentrations. The mole is the amount of substance that contains as many species (atoms, molecules, ions, formula units, electrons, or other specified entities) as there are atoms in 12 g of the ¹²C isotope of the carbon atom, i.e. $N_A \approx 6.023 \cdot 10^{23}$ electrons/mol, N_A being called Avogadro's number [8]. The number of moles, denoted by *n*, is given by the relation 1.1:

$$n = N/N_{\rm A} \tag{1.1}$$

and represents the amount of substance containing N specified entities.

1.3 Intensive and extensive properties

Properties are classified as extensive (depend on the size of the sample; examples: mass and volume) and intensive (independent of the size of the sample; examples: temperature, density, pressure).

What is the difference between them?

Molar properties are intensive quantities and are calculated based on extensive properties with the formula 1.2:

$$X_m = X/n, \tag{1.2}$$

where X is an extensive property and n is the number of moles in the sample and X_m is the molar property (example: V_m , molar volume) associated with the extensive property X. The following quantities are examples of molar (and therefore intensive) quantities:

- The molar mass *M* is the mass of the sample (*m*) divided by the amount of substance (*n*) contained (*M* = *m*/*n*, [*M*] = g ⋅ mol⁻¹);
- The molar concentration or molarity c of a solvate which represents the number of moles of substance (n_d) dissolved in one liter of solution (V the volume of the solution): c = n/V, [c] = mol · l⁻¹ = M;
- The molal concentration or molality *b* which is the number of moles of solute relative to the mass of solvent used to prepare the solution: $b = n_d/m$, $[b] = \text{mol} \cdot \text{kg}^{-1}$.

For a mixture the following quantities are examples of extensive quantities:

- mass of each component and of the mixture;
- volume of each component and of the mixture;
- number of entities in each component and of the mixture;
- quantity of each component and of the mixture;

1.3.1 Density is an intensive quantity

The density of a mixture with J components is given by Eq. 1.3.

$$\rho = \frac{\sum_j m_j}{\sum_j V_j} \tag{1.3}$$

Problem: prove that density is an intensive quantity.

Solution: according to the definition of density in Eq. 1.3, explaining the masses, we obtain:

$$\rho = \frac{\sum_j n_j M_j}{\sum_j V_j} = \frac{\sum_j n \cdot x_j M_j}{\sum_j V_j} = \frac{\sum_j x_j M_j}{\sum_j V_j / n} = \frac{\sum_j x_j M_j}{V_m}$$

Since the molar volume (V_m) is an intensive quantity and the other quantities $(x_j \text{ and } M_j)$ are also intensive quantities, the expression that composes them (in this case ρ) defines an intensive quantity in turn.

1.4 Dimensional analysis

Dimensional analysis² is the analysis of the relationships between various physical quantities by identifying their basic quantities (such as length, mass, time, and electric current) and units of measurement (such as meters and grams) and keeping track of these dimensions as calculations or comparisons are made.

In general, in science we operate with quantities and units of measurement, and a dimensional analysis can be conducted by choosing a reduced set of quantities and units in terms of which all others can be expressed. The problem does not have a single solution, but some solutions are preferred, one of which is expression in units from the international system of units.

In the dimensional analysis of physical quantities and relationships, length, mass, time, and electric charge are preferred as basic quantities. Even here, however, a remark can be made, namely that using the constant of the speed of light in a vacuum, a dependency relationship between length and time can be expressed, and as for electric charge, its definition uses length, mass, and time.

An important element of dimensional analysis is the choice of the set of basic quantities. For example, in kinematics a set of basic quantities is (mass, distance, time) or (M, L, T). Based on it, the dimensionality of velocity ($V = LT^{-1}$), acceleration ($A = LT^{-2}$), momentum ($I = MLT^{-1}$) and force ($F = MLT^{-2}$ can be expressed. The set of quantities (distance, velocity, time) is not a basic set for kinematics because mass cannot be expressed based on it and also the three are not independent ($V = LT^{-1}$).

With the help of dimensional analysis, the correctness of an equation can be established from the point of view of dimensional homogeneity and in the case where a series of different quantities are involved in a simple expression, the form of the equation from dimensional analysis can even be established.

The three systems of measurement units, MKS (meter, kilogram, second), CGS (centimeter, gram, second), FPS (foot, pound, second) differ from each other only by the choice of measurement units, the measured quantities being the same (distance, mass, time).

The international system of units recognizes 7 quantities as basic (Tab. 1.5, [9]).

Size	Dimension	Symbol	Unit	Abbreviation
mass	М	m	kilogram	kg
amount of substance	N	n	mol	mol
thermodynamic temperature	Θ	Т	kelvin	K
time	Т	t	second	S
length	L	l, x, r	meter	m
electric current	Ι	I, i	ampere	А
luminous intensity	J	Iv	candle	cd

Table 1.5: SI base units and quantities

Molecules are made up of atoms between which chemical bonds are established (based on electrical forces). The principle of formation of molecules is a mechanistic one: they collide and at the moment of contact the chemical bonds between the atoms can break and form others (Fig. 1.2).

Fig. 1.2: Kinetics of a chemical reaction (AB + CD \rightarrow AC + BD)

²see also http://en.wikipedia.org/wiki/Dimensional_analysis

Temperature is an intensive quantity that measures the disordered energy that is stored in a system [10], usually in the form of kinetic energy (mechanical movement: vibrations, rotations and/or translations) and sometimes in the form of potential energy (electronic excitation). In chemistry, temperature (measured in Kelvin, degrees Celsius, or Fahrenheit, see Fig. 1.3) is extremely important.



Fig. 1.3: Four temperature scales

Increasing temperature increases (on average) the speed of molecules participating in a reaction. If more molecules move faster, the number of molecules moving fast enough to react increases, which leads to the (faster) formation of other molecules (Fig. 1.2).

Temperature is a statistical measure ([11], a value of the central tendency of the system) so that in the case of very rarefied systems (such as outer space) it loses its meaning ([12]; in regions of space where there is no matter or radiation at all, temperature as defined can neither be calculated nor measured).



2.1 Distribution of chemical elements

When observing the surrounding nature, we can relate to what is on the earth (inside it or above its surface) or in outer space (Fig. 2.1).

Reference system in the study	Characteristic
Universe	All space
Galaxy	Ensable of solar systems
-Solar system	The Sun together with the ensemble of planets
– Planet	Subsoil and atmosphere
Subsoil	Liquid or solid, $\leq 0 \text{ km}$
+Oceans, sees, other water	sSubstances in water, ≥ -10 km
+Vegetal soil	Composition given by interaction with organisms, ≥ 20 m
+Crust	Planetary layer accessible for mineral extraction, ≥ -35 km
+Manta	In solid state, ≥ -2900 km
+Core	In liquid state, < −2900 km, ≥ −6400 km
Atmosphere	In gaseous state, > 0 km
+Planetary boundary layer	Composition given by interaction with organisms, $\leq 2 \text{ km}$
+Troposphere	$\leq 20 \text{ km}$
+Stratosphere	≤ 51 km
+Mesosphere	≤ 82 km
+Thermosphere	≤ 800 km
+Exosphere	≤ 100000 km
+Organisms (alive)	Carbon-based composition

Fig.	2.1:	Metric	space
8.			opace.

The siderosphere or magmasphere (from 2900 to 6370 km) is the deepest zone and is formed by a melt of iron and nickel, the calcosphere (from 1200 to 2900 km) is the intermediate zone and is formed by sulfides and oxides of heavy metals and the lithosphere (from 0 to 1200 km) is the outer zone which is in turn formed by two layers: the lower layer (from 120 to 1200 km) which is composed of magnesium-rich silicates and the outer layer (from 0 to 1200 km) which is called and the Earth's crust and is made up of oxygenated compounds, silicates, aluminosilicates, etc. The most accessible area of the planet for humans is the Earth's crust (Fig. 2.2, [13]).

The atmosphere¹ is the gaseous zone that surrounds the Earth and together with it forms the Earth's ecosystem (Fig. 2.1). The chemical composition of the atmosphere is relatively constant up to 57 km from the Earth's surface. Determinations of the chemical composition of the atmosphere have shown that in volume percentages it contains 78% nitrogen, 20.95% oxygen, 0.93% argon, 0.03% carbon dioxide, and in smaller quantities other chemical compounds (Fig. 2.3).





Fig. 2.3: Composition of the Atmosphere with Altitude in Logarithmic Representation



¹see also http://en.wikipedia.org/wiki/Atmosphere_of_Earth

The lower region is called the troposphere (from 0 to 10 km) and it is in it that meteorological phenomena occur. Next comes the stratosphere (from 10 to 60 km), in which the temperature increases vertically. In the mesosphere the temperature decreases again, and in the upper region of the atmosphere, in the thermosphere (over 100 km), the temperature increases again due to the dissociation and recombination of atoms, by absorption of light energy [14]. In the ionosphere, at very high altitudes, photoionizations occur, due to X-rays and ultraviolet radiation emitted by the sun. Reaction mechanism studies have shown that in the ionosphere transformations of oxygen (O_2) into ozone (O_3) and vice versa take place.

At temperatures of tens of thousands of degrees, all elements are in the form of ions; at thousands of degrees they are in the form of free atoms. On Earth, the normal state of elements is that of combination (chemical) and only rare gases (He, Ne, Ar, Kr, Xe, Rn) exist in atomic form.

The abundance of heavy elements (other than H and He) in the galaxy does not exceed 1% per element and decreases with atomic number (Fig. 2.4).



Fig. 2.4: Element abundance in the Galaxy from spectroscopic measurements [1]

Elements with even numbers of protons and neutrons are better represented, but the abundance of elements in the Galaxy decreases very rapidly with atomic number Z, which suggests that heavy elements are synthesized in stars through a chain of successive reactions, from simple (e.g.: H) to complex (e.g.: Fe).

At temperatures of tens of thousands of degrees, all elements are in the form of ions and at thousands of degrees they are in the form of free atoms. On Earth, the normal state of the elements is that of chemical combination (Fig. 2.5, 2.6 and 2.7) and in atomic form there are only rare gases (He, Ne, Ar, Kr, Xe, Rn). In the solid state $(M_n, n \rightarrow \infty)$ there is carbon (coal, graphite, and diamond), and some transitional elements (Au, Ag, Pt) and in the gaseous state nitrogen (N₂) and oxygen (O, O₂, and O₃).

The composition of the topsoil² includes approximately half fluids (of which approximately half are liquids), and half solids (of which up to approximately organic matter and the rest minerals). The organic part of the topsoil contains an impressive number of living organisms (Fig. 2.5). Typical minerals in soil are silicates (magnesium, manganese, aluminosilicates (sodium, potassium), and their hydroxy forms (Fig. 2.5).

The subsoil contains a lot of oxygen, followed by silicon, aluminum, and hydrogen (together representing 89% by number of atoms). Which chemical compound best reflects this distribution? The distribution in Fig. 2.6 explains the abundance of silicates ($M^{IV}SiO_3$), aluminosilicates ($M^{IA}ISiO_3$), and water (H_2O).

Most likely the distribution of elements in the crust and upper mantle is logarithmic ($X_{at}(x) = \frac{-b a^x}{x \ln(1-a)}$, $a = 0.64 \pm 0.03$, $b = -95 \pm 3$, $r_{adj}^2 > 99.6\%$). It is more than a coincidence that the

²see also http://en.wikipedia.org/wiki/Soil

5	45		30 20							
	<u></u>									
30)	20	20	30						
Orga	inic	Mineral	Air	Water						
Organ	ics for 1	g of soil:	Typical minerals of soil:							
Bacteria:	$[3.10^{6},$	5.10^{8}]	SiO ₂ , CaCO ₃							
Actinomy	vcetes: [$10^6, 2.10^7$]	MAlSi $_{3}O_{8}$, M = Na, K, Ca							
Fungi: [5	$\cdot 10^3$, 10	6]	KAlSi ₃ O ₁₀ (OH) ₂							
Yeast: [1	$0^3, 10^6$]		K(Mg,Fe)3AlSi3O10(OH)2							
Protozoa	$[10^3, 5]$	·10 ⁵]	$MSiO_3$, $M = Mg$, Mn							
Algae: [1	$0^3, 5.10$	5]	(Mg,Fe) ₂ SiO ₄							
Nematod	es: [10 ¹ ,	$5 \cdot 10^{3}$	Ca2Mg5Si8O22(OH)2							

Fig. 2.5: Typical composition of topsoil

Fig. 2.6: Typical basement composition

Eleme	nts in cru	ist + upp	er mant	le (mola	ar fracti	ons, X _{at}	[%])	
Element	0	Si	Al	Н	Na	Ca	Fe	
Xat [%]	59.4778	20.4663	6.2294	2.8963	2.5455	1.8774	1.8471	
ΣX _{at} [%]	59.48	79.94	86.17	89.07	91.62	93.49	95.34	
Element	Mg	K	Ti	C	F	Р	Mn	
Xat [%]	1.8016	1.3739	0.1896	0.1724	0.0871	0.0801	0.0376	
$\Sigma X_{\rm at}$ [%]	97.14	98.52	98.70	98.88	98.96 N 0.0074	99.04 Sr	99.08 Li	
Element	S	Cl	V	Ba				
Xat [%]	0.0323	0.0291	0.0077	0.0076		0.0071	0.0059	
ΣX _{at} [%]	99.11	99.14	99.15	99.16	99.17	99.17	99.18	
Element	Cr	Zr	Ni	Zn	Cu	В	Ce	
Xat [%]	0.0056	0.0045	0.0032	0.0025	0.0023	0.0019	0.0009	
$\Sigma X_{\rm at}$ [%]	99.18	99.19	99.19	99.19	99.20	99.20	99.20	

logarithmic distribution also appears in biology in the number of individuals of animal species [15].



Fig. 2.7: Typical composition of some soils and organisms

Fig. 2.7 shows associations between the element content of different soils (marine sediments, crust and topsoil). The highest concordance (see Gamma qualitative correlation in [16]) is between the values of element concentrations in marine sediments and topsoil (90%), followed by that between marine sediments and crust (80%) and that between crust and topsoil (75%).

The Moon contains rocks on its surface similar to those on Earth (silicates). Mercury cannot

retain gases in its atmosphere, being a celestial body without an atmosphere. Venus has approximately the same density as Earth and is made up of CO_2 and sulfurous gases. The Sun's atmosphere contains hydrogen, helium, carbon, nitrogen, oxygen in larger quantities and sodium, potassium, magnesium, calcium, aluminum, silicon, sulfur, selenium, and even transitional elements.

2.2 Chemical Systems

The observations accumulated regarding nature and society necessarily lead to a series of conclusions of maximum generality. One of these is the systemic organization of the world (both in nature and in society the relationships between certain objects, processes, parts, determine their organization into systems).

We call a system a set of elements (objects, beings, particles, processes, laws, concepts, symbols) between which specific relationships can be established, which give the whole set certain characteristics (a certain individuality). Examples are:

- The relationships that are established in the organism of a mammal, between its component parts are different from the organism environment relationships; these provide the organism with specific properties (individuality);
- The relationships that exist within an enterprise (between people, between people and machines, the relationships between departments or between technological lines) different from the enterprise society relationships, provide the relative individuality of the enterprise; this can be considered as a system.

The properties of a system are not reduced to the sum of the properties of the system's component elements. Using an analogy, a clock is a system formed by an assembly of parts, but this set of parts will not measure time unless they are linked in a strictly determined way. Therefore, the composition of the assembly leads to the emergence of new properties. In many cases, the elements of a system can in turn be systems at another level of organization [17]. The representation of a chemical system and its environment can take different forms (see the water molecule in Fig. 2.8).

Fig. 2.8: Water molecule: graph, structural formula and plane projection



Currently, the totality of connections, mutual dependencies and interactions between objects and phenomena are included in the concept of relationship. By interaction we understand a particular case of the relationship, characterized by the fact that between two bodies A and B binding forces are established or exist. The concept of relationship has a much broader meaning and includes, for example, the spatial relationships between the two bodies (e.g., body A is located 1 cm from body B). When the concept of relationship refers to phenomena, it describes the causal dependencies between them or the temporal relationships. Regarding chemical systems, based on numerous examples, the following principles have been established in chemistry:

- The principle of interaction. The stability of chemical systems, as well as their ability to transform, is due to the interactions between the component elements, respectively between the chemical system considered and other systems (including the environment);
- The principle of minimum energy. Any chemical system is stable if it is in a state of minimum energy; a system removed from its stable state tends, under given conditions, through interactions with systems in its vicinity, to evolve towards a state of minimum energy (identical or different from the initial state).

2.3 Classification of chemical elements

The classification of chemical elements was made both based on their observed properties and on the structure of the electron shell. After 1869, when Mendeleev proposed organizing the elements in the form of the periodic system³, various authors proposed improved models for representing and classifying the elements [18].

A form of its representation is shown in Fig. 2.9.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Н	He																
2	Li	Be											в	U	N	0	F	Ne
3	Na	Mg											Al	Si	Ρ	S	Cl	Ar
4	к	Ca	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	\mathtt{Br}	Kr
5	Rb	\mathtt{Sr}	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
6	Cs	Ва	Lu	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ро	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	$\mathbf{B}\mathbf{h}$	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		4f	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb		
		5f	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Fig. 2.9: Organization of the elements in the periodic table

In Fig. 2.9 on a background with red shades the alkali and alkaline-earth elements (with a high tendency to form positively charged ions, carriers of a single positive charge, denoted M^{1+} and respectively carriers of two positive charges, denoted M^{2+}) were represented, with blue shades the halogens and chalcogens (with a high tendency to form negatively charged ions, carriers of a single negative charge, denoted X^{1-} and respectively carriers of two negative charges, denoted A^{2-}), with a blue shade purple the noble gases (with a tendency to form molecules made up of a single atom, A^{0}), followed by the transition metals (on a green background, with a tendency to form ions with several values of positive and negative charges) and the chemical elements with additional f-type orbitals (also metals, also in yellow, with a general tendency to form ions M^{3+}). Three groups of elements (13, 14 and 15) represent a special group of elements, with a tendency to form bonds in which the electric charge is delocalized.

Positively charged ions (M^{1+} , M^{2+} , M^{3+}) are called cations (the notation M^{x+} , with x = 1, 2, 3 comes from M = Metal, metals forming the vast majority of elements with this tendency). Negatively charged ions (A^{1-} , A^{2-} , A^{3-}) are called anions (the notation A^{x-} , with x = 1, 2, 3 comes from A = Anion).

Two atomic properties are very important in characterizing elements: the atomic mass (which is given by the sum of the number of protons and neutrons in the atomic nucleus, denoted by A or M) and the atomic number (which is given by the number of protons and is denoted by Z).

From a historical perspective, Mendeleev (the one who proposed the systematic organization of chemical elements in the periodic system) considered that atomic mass is the basic property that determines the other properties of the elements [19], while subsequent research by Moosley showed that the properties of chemical elements are periodic functions of the atomic number [20]. In Fig. 2.10 a modified version of the spiral-shaped periodic table is shown, which also illustrates the sequence of atomic numbers.

2.4 Properties and trends

Elements have a series of properties (atomic properties) that can have the following characteristics:

³see also https://en.wikipedia.org/wiki/Periodic_table



Fig. 2.10: Spiral succession of chemical elements

- Ascending trend: atomic number (Z), atomic mass (denoted A or M), based on which the elements can be arranged in an ascending row;
- Periodic trend, such as oxidation state and electrode potential (chemical properties), spectra, ionization energies (physical properties), atomic and ionic radii, atomic and ionic volumes (geometric properties), density, melting and boiling points, etc. that allow similar elements to be grouped in a table.

In the periodic table, a group is a series of elements with the same number of electrons in their outermost shell, and a period is a series of elements with the same number of electron shells.

The physical properties of the elements, with a periodic trend, include: densities, atomic and ionic radii, atomic and ionic volumes, melting and boiling points, ionization energies, thermal and electrical conductivity, and optical spectra [21]:

- Atomic and ionic radii are expressed in ångströms (Å) or pm (1 Å = 100 pm), with the vast majority of values oscillating in the range 1 3 Å. The exact values of atomic and ionic radii depend on the method of determination or estimation and in the case of ionic radii they also depend on the electric charge of the ion. However, the trends are as follows: Atomic radii decrease in periods, in the order: alkali metals, rare gases, alkaline earth metals, halogens, group 16 elements, etc. In groups, atomic radii increase from top to bottom, due to the increase in the number of electron shells and the atomic number Z. In order to form a metal cation, it must lose electrons, which results in lower values of the ionic radius than the atomic radius. The radii of cations, in periods, decrease from left to right. In the case of the formation of anions, they have a surplus of electrons, and the radii of the anions are larger than their atomic radii. In groups, the radii of cations and anions increase from top to bottom.
- Atomic volume is defined as the ratio of atomic mass to density. Atomic volume is the volume of a gram atom of an element. Atomic volumes have a periodicity close to that of atomic radii. Fig. 2.11 represents atomic volumes.
- The density of elements in the solid phase (Fig. 2.12) is a measure of the crowding. It increases in groups from top to bottom, with increasing atomic numbers *Z*, and in periods, it increases from the extremities towards the center of the periodic table (group 9). Metals are classified into light metals, i.e. with densities up to 5 g/cm³, and heavy metals with $\rho > 5$ g/cm³. The element with the lowest density is Li (0.53 g/cm³), and the heaviest metal is Ir (22.65 g/cm³);
- The melting point (Fig. 2.13, the temperature at which substances change from a solid to a liquid state) and the boiling point (Fig. 2.14 the temperature at which substances change from a liquid to a gaseous state) vary periodically.

The values of these temperatures provide qualitative information about the amount of thermal



Fig. 2.11: Atomic volumes on a logarithmic scale

Fig. 2.12: Solid State Density of Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H	S	olio	d st	ate	den	sity	v of	che	emi	cal	eleı	ner	nts [kg	m ⁻³]	He
2	Li	Be											B	С	N	0	F	Ne
3	Na	Mg											Al	Si	P	S	C1	Ar
4	968 K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	2030 Br	Kr
5	856 Rb	1550 Sr	2985 Y	4507 Zr	6110 Nb	7140 Mo	7470 Tc	7874 Ru	8900 Rh	8908 Pd	8920 Ag	7140 Cd	5904 In	5323 Sn	5727 Sb	4819 Te	4050 I	2155 Xe
6	1532 Cs	2630 Ba	4472 Lu	6511 Hf	8570 Ta	10280 W	11500 Re	12370 Os	12450 Ir	12023 Pt	10490 Au	8650 Hg	7310 Tl	7310 Pb	6697 Bi	6240 Po	4940 At	3640 Rn
7	1879 Fr	3510 Ra	9841 Lr	13310 Rf	16650 Db	19250 Sg	21020 Bh	22610 Hs	22650 Mt	21090 Ds	19300 Rg	14190 Cn	11850 Nh	11340 Fl	9780 Mc	9196 Lv	6400 Ts	4400 Og
<i>'</i>	2900	5000	9840	17000	21600	23200	27200	28600	28200	27400	24400	16800	16000	11400	13500	12900	7170	7200
$\left \right $			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb		
			6146 A.c	6689 Th	6640 Pa	6800 U	7264 Np	7353 Pu	5244	7901 Cm	8219 Bk	8551 Cf	8795 Fs	9066 Fm	9321 Md	6570 No		
			10070	11724	15370	19050	20450	19816	13780	13510	14780	15100	13500	8840	10300	9940		

energy required to overcome the forces between atoms established in the solid (Fig. 2.13) and liquid (Fig. 2.14) states, respectively. Atoms of elements with small volumes, which are covalently (strongly) bonded, melt at higher temperatures than atoms with large volumes, which are ionically bonded. In periods, melting and boiling temperatures increase at the ends of the periodic table, towards group 14, and in groups 3-12 they increase with Z. Notable examples are Hg which melts at -38.84 °C and boils at 357 °C being the easiest to reach the vapor state of all metals and W which melts at 3410 °C (being the most refractory) and boils at 5930 °C (being the hardest to reach the vapor state) but it is also worth noting the melting temperature of carbon (3823 °C, an estimated value at standard pressure for the allotropic form of diamond since it sublimes under these conditions) and the boiling point (4827 °C, one of the highest values in the periodic table, being surpassed only by W, Re, Ta, Hf, Os, Nb, and Tc - in this order, and surpassing Th, Mo and Ir - in that order). The noble gases (monatomic) have the lowest melting and boiling points.

• Electronegativity (Fig. 2.15) is the tendency to attract electrons to form a bond. It increases in periods from left to right and in groups from bottom to top. The most electronegative element

Fig. 2.13: Melting temperature of the elements (allotropic forms that are most difficult to fuse)

Γ	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Н 14		Μ	elti	ng	po	ints	s of	c h	em	ica	l el	em	ent	s []	K]		He 1
2	Li	Be											В	С	Ν	0	F	Ne
	453	1551											2573	3820	63	55	54	24
2	Na	Mg											Al	Si	Р	S	Cl	Ar
2	371	922											933	1683	317	386	172	84
4	Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ľ	336	1112	1814	1933	2160	2130	1517	1808	1768	1726	1357	693	303	1211	1090	490	266	117
4	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
-	312	1042	1795	2125	2741	2890	2445	2583	2239	1825	1235	594	429	505	904	723	387	161
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ро	At	Rn
	302	1002	1963	2503	3269	3680	3453	3327	2683	2045	1338	234	577	600	545	527	575	202
-	Fr	Ra	Lr	Rf														
ĺ	300	973	1900	2400														
L																		
			T	G	D	37.1	D	a	F	<u></u>	771	D		F	-	3 71		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Тb	Dy	Но	Er	Tm	Yb		
L			1194	1072	1204	1294	1441	1350	1095	1586	1629	1685	1747	1802	1818	1097		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		
1			1338	2023	2113	1405	913	914	1267	1610	1259	1173	1133	1800	1100	1100]

Fig. 2.14: Boiling temperature of elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Н 20	Boiling points [K]												He 4				
2	Li	Be											B 4200	-C 4300	N 77	0	F 85	Ne 27
3	Na 1156	Mg 1363											Al	Si 3538	P	S 718	Cl 239	Ar 87
4	K 1032	Ca 1757	Sc 3109	Ti 3560	V 3680	Cr 2944	Mn 2334	Fe 3134	Co 3200	Ni 3186	Cu 2835	Zn 1180	Ga 2673	Ge 3106	As 887	Se 958	Br 332	Kr 120
5	Rb 961	Sr 1655	Y 3609	Zr 4682	Nb 5017	Mo 4912	Tc 4538	Ru 4423	Rh 3968	Pd 3236	Ag 2435	Cd 1040	In 2345	Sn 2875	Sb 1860	Te 1261	I 457	Xe 165
6	Cs 944	Ba 2170	Lu 3675	Hf 4876	Та 5731	W 5828	Re 5869	Os 5285	Ir 4701	Pt 4098	Au 3129	Hg 630	Tl 1746	Pb 2022	Bi 1837	Po 1235	At 610	Rn 211
7	Fr 890	Ra 2010	Lr	Rf 5800	Db 2477	Sg 3273	Bh	Hs	Mt	Ds	Rg	Cn 340	Nh 1400	Fl 420	Mc 1400	Lv 1100	Ts 883	Og 450
F			La 3737	Ce 3716	Pr 3793	Nd 3347	Pm 3273	Sm 2067	Eu	Gd 3546	Tb 3503	Dy 2840	Ho 2993	Er 3141	Tm 2223	Yb 1469		
F			Ac 3471	Th 5061	Pa 4300	U 4404	Np 4273	Pu 3501	Am 2880	Cm 3383	Bk 2900	Cf 1743	Es 1269	Fm 1615	Md	No		

is fluorine and the least electronegative is francium. Nonmetals, located in the upper left corner of the periodic table, have high electronegativity values and easily pass into negative ions, in the elemental state they are gaseous or slightly volatile, and are poor conductors of heat and electricity.

Several electronegativity scales have been proposed: Pauling [22], Revised Pauling [23], Mulliken [24], Allred-Rochow [25], Sanderson [26], Allen [27]. There is no single electronegativity scale in use because each of these explains an important series of other properties (for details see how each was defined). An example is ionic character (Fig. 2.16).

• Ionic character (Fig. 2.16) can be defined as the extent to which atoms share electrons in bonds, the alternative being that electrons are transferred from one atom to another. In addition to the monotonous, almost linear association between ionic character and electronegativity, another important element illustrated in Fig. 2.16 is the linear approximation - the real dependence

-	1		r	1		ı —	1				1				ı —	1	1	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Н		\mathbf{F}^{1}	act	roi	ne	rat	1371	1.7	[re	1772	CO	4 E	0011	lir	ر م		He
1	2.20		LI		101	ΠCž	gai	1 V 1	ιy	LIV		30	uI	au		īg]		
	Li	Be											В	С	Ν	0	F	Ne
2	0.98	1.57											2.04	2.55	3.04	3.44	3.98	шшш
	Na	Mg											Al	Si	Р	S	Cl	Ar
3	0.93	1.31											1.61	1.90	2.19	2.58	3.16	
F	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4	0.82	1 00	1 36	1 54	1.63	1 66	1 55	1 83	1 88	1 91	1 90	1.65	1 81	2 01	2 18	2 55	2 96	3 00
F	Rb	Sr	Y	Zr	Nb	1.00 Mo	Tc	R11	Rh	Pd	1.90 Ασ	Cd	In	Sn	Sh	<u>2.55</u> Те	2.90 I	3.00 Xe
5	0.82	0.05	1 22	1 2 2	1.60	2 16	1 00	2 20	2.28	2 20	1 02	1.60	1 78	1.06	2.05	2 10	2 66	2 60
┝	0.62	0.95	1.22 T	1.55	1.00 T	2.10	1.90 D	2.20	2.20 T	2.20 D/	1.95	1.09	1./0 T1	1.90 Dl	2.05 D'	2.10 D	2.00	2.00 D
6	CS	ва	Lu	HI	1a	w	ке	Os	Ir	Pt	Au	нg		Pb	B1	PO	At	ĸn
ſ	0.79	0.89	1.27	1.30	1.50	2.36	1.90	2.20	2.20	2.28	2.54	2.00	2.04	2.33	2.02	2.00	2.20	2.20
	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Fl	Mc	Lv	Ts	Og	Fl
/	0.70	0.90	1.31															
ľ																		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb		
			1.10	1.12	1.13	1.14	1.13	1.17	1.20	1.20	1.20	1.22	1.23	1.24	1.25	1.10		
ľ			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		
			1.10	1.30	1.50	1.38	1.36	1.28	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30		
L_	1		-					-									J	

Fig. 2.15: Revised Pauling electronegativity scale





between the 2 quantities is almost sigmoidal, but it is much more convenient for us to operate with the linear function, having a much simpler model. The approximation errors (as can be seen in Fig. 2.16) are larger at very small and very large differences in electronegativity, respectively. Electropositivity can be defined by symmetry with respect to electronegativity as the opposite trend to it. Thus fluorine is the least electropositive and francium the most electropositive. The ease with which an element ionizes (forming a positive ion) gives its electropositive character.

• The ionization energies of atoms (Fig. 2.17), in periods, with exceptions, increase from left to right (due to the increase in the charge of the nucleus and the weak mutual screening of electrons from the same outer shell) and in groups decrease from top to bottom (due to the screening by an increasing number of electrons from the inner shells).

To tear an electron from the shell of an atom, energy is consumed (Fig. 2.18).

Ionization is achieved either by electron bombardment or by light absorption. The ionization energy (or potential) is the quantity I_E , measured in eV (electron-volts), $e \cdot V$, where e is the

Π	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Н 13.6		First ionization potential [eV]											He 24.6				
\sim	Li	Be											В	С	Ν	0	F	Ne
2	5.4	9.3											8.3	11.3	14.5	13.6	17.4	21.6
3	Na	Mg											Al	Si	Р	S	Cl	Ar
5	5.1	7.6											6.0	8.2	10.5	10.4	13.0	15.8
4	Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
-	4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	7.9	9.8	9.8	11.8	14.0
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
	4.2	5.7	6.2	6.6	6.8	7.1	7.3	7.4	7.5	8.3	7.6	9.0	5.8	7.3	8.6	9.0	10.5	12.1
6	Cs	Ba	Lu	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	T1	Pb	Bi	Ро	At	Rn
	3.9	5.2	5.4	6.8	7.9	8.0	7.9	8.7	9.1	9.0	9.2	10.4	6.1	7.4	7.3	8.4	9.5	10.7
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Fl	Mc	Lv	Ts	Og	F1
'	3.9	5.3	4.6	6.0	6.9	7.9	7.7	7.6	8.3	9.9	10.6	12.0						
			т	C	D	NT 1	D	C	Г	<u>C</u> 1	T 1	D	TT	Г	т	3.71		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gđ	1b	Dy	Ho	Er	Im	Yb		
L			5.6	5.5	5.5	5.5	5.6	5.6	5.7	6.2	5.9	5.9	6.0 E	6.1 E	6.2	6.3		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		
			5.2	6.1	5.9	6.2	6.3	6.1	6.0	6.0	6.2	6.3	6.4	6.5	6.6	6.7		

Fig. 2.17: First ionization potential $(M \rightarrow M^{1+} + 1e^{-})$

Fig. 2.18: Ionization



elementary electric charge, and V the electron acceleration potential used to cause ionization. Ionization energy is the energy required to remove electrons from an atom of an element, to transform it into a positive ion.

Metallic character refers to the level of reactivity of a metal (metals share electrons in a network with many atoms which then ensure electrical and thermal conduction at 0 K). Nonmetals readily dissociate into negative ions, are gaseous or slightly volatile in their elemental state, are poor conductors of heat and electricity, and are located in the upper right corner of the periodic table. The elements B, Si, As, Te, At, Al, Ge, Sb, Po are called semimetals and have intermediate properties. Metals tend to lose electrons in chemical reactions, as indicated by their low ionization energies. Electropositive elements, which

are mainly metals, have all the characteristics of nonmetals, only in the opposite direction. The electronegativity of transition metals decreases from top to bottom in the group. If we arrange the most common metals in order of ease with which they give up the first electron to form ions with a positive charge, we obtain the decreasing series (\rightarrow) of chemical activities⁴ of metals in which hydrogen is the reference (Fig. 2.19).

Fig. 2.19: Series of chemical activities, with hydrogen as a reference (in the presence of water)

Li, Ca, K, Ba, Na, Mg, Al, Zn, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Ag, Hg, Au, Pt

- Chemical stability. Electronegativity and electropositivity are qualitative properties of elements, which can be seen partly as complementary and can also be defined quantitatively ([28], expressing the tendency to attract or give up electrons, transforming atoms into negative ions and positive ions respectively). The elements in group 18 have their outer electron shell completely occupied, which ensures their great chemical stability and they do not tend to form ions or combinations. Elements in the other groups tend to transform into ions with an inert gas electronic configuration, via the shortest path: elements with few electrons in the outer layer easily give up these electrons, becoming positive ions, and those with many electrons, accept electrons, becoming negative ions.
- Thermal conductivity (Fig. 2.20 in W cm⁻¹ K⁻¹, the property of metals to be crossed by a heat flux under the action of a temperature difference) and electrical conductivity of metals (Fig. 2.21 in nm⁻¹ Ω^{-1} , the property of metals to be crossed by an electric current under the action of a potential difference) are also periodic properties.



Fig. 2.20: Thermal Conductivities of Solid State Elements

The best thermal conductivity is for silver, followed by copper, gold, aluminum, calcium, beryllium, etc. The best electrical conductivity is for silver, followed by copper, gold, aluminum, beryllium, calcium, etc. The two properties are strongly correlated ($r_{adj}^2 = 92\%$). It is also important to note that aluminum is the most efficient conductor when relating conduction to density - it is approximately 2 times more efficient than copper - making it very useful for transporting electricity over long distances through suspended wires.

• The valency of an atom measures its combination with other atoms. Valency is defined as the number of bonds it forms (or the number of univalent atoms - hydrogen, chlorine, etc. - that can combine with the atom in question). Valency is expressed as a natural number. Tab. 2.1 contains examples of typical valencies for elements.

⁴see also http://en.wikipedia.org/wiki/Reactivity_series





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Table 2.1 :	valencies (or chemical	elements	and compounds	– examples
				1	1

Valency	Elements	Examples of compounds
0	He, Ne, Ar	He, Ne, Ar
1	H,	H_2 , LiH, HF, H_2O , CH ₄ ,
	Li, Na, K, Rb, Cs, Fr,	LiOH, Li ₃ N, Li ₂ CO ₃ ,
	F, Cl, Br, I, At	NaF, KF, NaCl, KCl
2	O, FeO, Fe ₂ O ₃ ,	O ₂ ,
	Be, Mg, Ca, Sr, Ba, Ra	BeO, MgF ₂ , CaO, Sr(OH) ₂ , BaO
	S, Se, Te, Po	H_2S , CS_2 , H_2Se ,
	Zn, Cd, Hg	ZnO, CdO, HgCl ₂
3	N, P, As, Sb, Bi	NH ₃ , PH ₃ , NF ₃ , BiF ₃ ,
	B, Al, Ga, In, Tl,	BH ₃ , AlCl ₃ , GaCl · GaCl ₃ , GaOOH,
	Sc, Y, Lu, Lr, Cr	ScF_3 , $ScPO_4 \cdot 2H_2O$, Cr_2O_3
4	C, Si, Ge, Sn, Pb,	CO_2 , $Si(OH)_4$, PbO_2 ,
	Ti, Zr, Hf, Rf	TiO_2 , ZrO_2 , HfO_2 , RfF_4
5	P, As, Sb, Bi	P_2O_5 , H_3AsO_4 , Sb_2O_5 , $NaBiO_3$,
	V, Nb, Ta, Db	V_2O_5 , NH_4VO_3
6	S, Se, Te, Po,	H_2SO_4 ,
	Cr, Mo, W	$K_2Cr_2O_7$
7	Cl, Br, I, At,	HClO ₄ ,
	Mn, Tc, Re, Bh	KMnO ₄
8	Ru, Os, Hs, Xe	RuO_4 , OsO_4 , $Os(NCH_3)_4$, XeO_3F_2
9	Ir	IrO_4^+ ([29], also reporting IrO_6^+ in [30])

In Tab. 2.1 it can be seen that an element can have (and for most elements does have) more than one valence. Very low valences (0, 1) and very high valences (7, 8) are reached in few combinations. Transition metals are almost all polyvalent; in the higher valence state they behave like nonmetals and in the lower, like metals [31].

A concept associated with valence is the coordination number. The coordination number of an atom can be greater than its valence to the extent that it manages to transfer electrons from other atoms (the atoms most exposed to losing electrons by transfer are hydrogen atoms). The coordination number is limited on the one hand by the number of free electronic levels (up to the complete electronic configuration of a rare gas) located in the vicinity of the occupied ones on the one hand and by steric hindrances (up to 4 other atoms can be arranged around small atoms, up to 6 around slightly larger atoms, and up to 12 or 14 around very large ones,

and according to some authors [32] even 24) on the other hand.

- The oxidation state represented numerically by the oxidation number is a number with a sign $(Ox(\cdot)$ below), defined as the formal electric charge (established based on electronegativity) that the respective element has in a chemical combination. A series of precedence rules are used to determine $Ox(\cdot)$, based on electronegativity (see Fig. 2.15):
 - 1. For molecules formed from the same element (homomolecules), E_n ($n \ge 1$), Ox(E) = 0 (solid-state elements, F_2 , O_2 , N_2);
 - 2. Ox(F) = -1; exception: F₂, and similarly for the rules below;
 - 3. Alkali M^I (Li, Na, K, Rb, Cs, Fr) have $Ox(M^I) = +1$; exception: NaK (Ox(Na) = -1, Ox(K) = +1), NaRb (Ox(Na) = -1, Ox(Rb) = +1), etc.;
 - 4. Ox(H) = +1 for more electronegative elements (and Ox(H) = -1 with the less electronegative alkali);
 - 5. Ox(O) = -2; exceptions: OF₂, peroxides (eg: HO–OH, NaO–ONa, , KO–OK) and superoxides (eg: KO₂);
 - 6. Halogens X (Cl, Br, I, At) have Ox(X) = -1 and precedence (among them) is based on electronegativity;
 - 7. alkaline earth metals M^{II} (Be, Mg, Ca, Sr, Ba, Ra) have $Ox(M^{II}) = +2$;
 - 8. For elements in the main groups, the valence is considered to be the smallest number between the group number and 8 the group number, and the oxidation state is the number associated with the sign (one of the values: group number, 8 group number, group number 8).

Fractional oxidation states are also in use (see Tab. 2.2).

Table 2.2: Fractional oxidation states: examples and counterexamples

Compound	$Ox(\cdot)$	Remarks
Fe ₃ O ₄	$Ox(Fe) = +\frac{8}{3}$	Wrong: Fe_3O_4 is $Fe_2O_3 \cdot FeO$ and $Ox(Fe) \in \{+2, +3\}$
C ₃ H ₈	$Ox(C) = -\frac{8}{3}$	Wrong: C ₃ H ₈ is CH ₃ -CH ₂ -CH ₃ and $Ox(C) \in \{-3, -2\}$
NO ₂	$Ox(O) = -\frac{3}{2}$	Correct: $O=N=O$ and $Ox(N) = +3$
C ₆ H ₆	$Ox(C) = +\frac{3}{2}$	Correct:CH and from $\frac{n_{leg.}}{n_{at.}} Ox(C) = \frac{3 \cdot 1 + 3 \cdot 2}{6} = +\frac{9}{6}$

Acidity (acid character) i.e. the strength (or degree of dissociation of) hydracids ($H_nA \implies H^+ + H_{n-1}A^-$) varies increasing with the electronegativity of the element (A) and the basicity (basic character) i.e. the strength (or degree of dissociation of) the bases ($B(OH)_n \implies HO^- + B(OH)_{n-1}^+$). The trends are shown in Tab. 2.3.

Table 2.3: Trends for Acidic and Basic Character in Groups and Periods

Dissociation	In Group	In Period
Basic Character	LiOH < NaOH < KOH	$Al(OH)_3 < Mg(OH)_2 < NaOH$
Acidic Character	HF < HCl < HBr < HI	$CH_4 < NH_3 < H_2O < HF$

It is also notable that $Al(OH)_3$ has an amphoteric character (or ambivalent as an acid and as a base): $H^+ + H_2AlO_3 \implies H_3AlO_3 \implies Al(OH)_3 \implies HO^- + Al(OH)_2^+$.

Acidity and basicity can be defined quantitatively by means of the acidity constants (pK_a) and basicity constants (pK_b). More details and a range of values for pK_a are given in [33].


3.1 Atomic and molecular models

3.1.1 The atom

The atom consists of a nucleus (where almost the entire mass of the atom is concentrated) and an electron shell. The nucleus has extremely small dimensions compared to the distances from the nucleus to the outermost electron shell, in which the neutrons and protons are compacted.

Using experimental data from [34], the nuclear radius r_{n+p} can be approximated by Eq. 3.1:

$$r_{n+p} = \frac{(n_n + n_p)^{0.75_{\pm 0.05}}}{(n_n)^{0.42_{\pm 0.06}}} \text{ fm}$$
(3.1)

where n_n is the number of neutrons ($n_n = A - Z$), n_p is the number of protons (or atomic number, $n_p = Z$), and 1 fm = 10^{-15} m = 1000 pm. The order of magnitude of the nuclear radius is from about 2 fm to about 12 fm.

Using the experimental data in [35], the atomic radius r_a in crystals can be approximated by Eq. 3.2:

$$r_{a,c} = a_0 + a_1 \cdot n + a_2 \cdot sp + a_3 \cdot d + a_4 \cdot n \cdot sp + a_5 \cdot n \cdot f + a_6 \cdot sp \cdot f + a_7 \cdot n \cdot sp \cdot d + a_8 \cdot n^2 + a_9 \cdot sp^2 + a_{10} \cdot d^2 a_{11} \cdot f^2 + a_{12} \cdot n^3 \text{ pm}$$
(3.2)

where $a_0 = -79.4_{\pm 38.9}$, $a_1 = 160.4_{\pm 30.6}$, $a_2 = -21.3_{\pm 10.6}$, $a_3 = -22.7_{\pm 2.7}$, $a_4 = -4.5_{\pm 2.4}$, $a_5 = -1.4_{\pm 0.4}$, $a_6 = 1.2_{\pm 0.3}$, $a_7 = 0.3_{\pm 0.1}$, $a_8 = -24.7_{\pm 7.4}$, $a_9 = 2.4_{\pm 1.0}$, $a_{10} = 1.6_{\pm 0.3}$, $a_{11} = 0.3_{\pm 0.2}$, $a_{12} = 1.4_{\pm 0.6}$, *n* the period number, *sp* the number of electrons in the s and p orbitals (total), *d* the number of electrons in the d orbitals, and *f* the number of electrons in the f orbitals. There is a good agreement ($r_{adj.}^2 > 95\%$; Fig. 3.1) between the experimental observations and those predicted by the model 3.2.

On the same drawing in Fig. 3.1 the nuclear radii are also represented with a corresponding scaling factor (25965) which shows the proportion between the size of the nucleus and the size of the atom with the electron shell.

Electrons are elementary particles charged with a quantized negative electric charge (1 e⁻ = $-1.6 \cdot 10^{-19}$ C) and a very small mass (the rest mass of the electron m_e has been calculated to be approximately 1/1836 of the mass of a proton). In atoms, electrons are located in orbitals characterized by a certain energy and follow the Pauli exclusion principle (the possibility of 2 particles with the same quantum state occupying the same orbital is excluded [36]).



Fig. 3.1: Atomic radii in the crystalline state observed vs. estimated by Eq. 3.1

Electrons are fermions, particles that follow the Fermi-Dirac distribution [37]. The nucleus of the atom is composed of elementary particles with relative atomic mass 1: protons (charged with positive electrical energy $1.6 \cdot 10^{-19}$ C) and neutrons (electrically neutral), both of these particles being bosons, particles that follow the Bose-Einstein distribution [37]. Conventionally, the relative atomic mass is defined as 1/12 of the atomic mass of the isotope ₁₂C, a standard chosen due to the stability of this nucleus (₁₂C, along with ₄₀Ca is one of the most stable nuclei), the high abundance of this isotope in nature and its low chemical reactivity [38].

The electronic shell has a layered structure, the location of electrons in orbits being a problem of its own [39]. Solving this problem involves obtaining the eigenvalues of the orbital energies [40]. Formally, orbitals can be characterized by the so-called quantum numbers [41]: the principal quantum number (n), the secondary quantum number (l), the magnetic quantum number (m), and the spin quantum number (s). Some liken the arrangement of electrons in orbitals to the construction of a multi-story house (Fig. 3.2).

3.1.2 Chemical bonds

Chemical bonds are the result of electrical forces that are established between atoms as a result of the pairing of their electrons, the transfer of electrons, or simply as a result of local irregularities in the distribution of electrical charge. A special case is the Hydrogen atom, which by releasing its only electron can become involved in bonds with its nucleus. This is why the bonds that Hydrogen forms are a special case – hydrogen bonds.

The strength of the bond - sometimes expressed in terms of the energy required to break the bond - determines the stability of chemical compounds.

The following list classifies chemical bonds according to the way they are formed:

- Nonpolar covalent sharing of electrons between elements of similar electronegativity; preferably between atoms of the same element: $2A \rightarrow A-A$
 - examples: $H + H \longrightarrow H-H$; $O + O \longrightarrow O=O$; $N + N \longrightarrow N \equiv N$
 - general case: $nA \longrightarrow A_n$; examples: P₄; S₆; S₇; S₈
 - − limiting case $n \rightarrow \infty$: metallic bond; example: Fe_∞
- Polar covalent sharing of electrons between elements of different electronegativity: A + B → A-B
 - examples: $H + F \longrightarrow H-F$; $H + Li \longrightarrow H-Li$
 - general case: $mA + nB \longrightarrow A_mB_n$; examples: $2H + O \longrightarrow H_2O$; $2O + C \longrightarrow CO_2$



Fig. 3.2: Atomic neighborhood (source: chem.libretexts.org)

- limiting case electron transfer: ionic bond; example: Fe + O \longrightarrow Fe²⁺O²⁻
- Covalent coordination transfer of electron pairs from abundant elements to electron-deficient elements: A □ + :B → A:B symbolized A ← B (or B→A)
 - example transfer of an electron pair from NH₃ to BF₃ and formation of a coordinate bond: H₃N→BF₃
 - example ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$, 'EDTA'), complexes metal ions (anticoagulant in blood preservation because it complexes the calcium ion, essential for blood clotting): $Ca^{2+} + EDTA^4 \longrightarrow (CaEDTA)^{2-}$
- Intermolecular define interactions between molecules, which are weaker than intramolecular ones (listed above)
 - Hydrogen bonds: H-A + H-A \longrightarrow H-A-H-A; examples: H-F + H-F \longrightarrow H-F-H-F; H-Li + H-Li \longrightarrow H-Li-H-Li; OH₂ + OH₂ \longrightarrow HO-H-OH₂
 - Dipole-dipole bonds: similar to hydrogen bonds but with the participation of (heavier) 'heavy' atoms; example: I−Cl + I−Cl → I−Cl −I−Cl
 - Ion-dipole bonds: similar to coordination bonds; example: $O_2 + K^+ \rightarrow O_2K^+$.
 - caused by dispersion forces between electron shells or Van der Waals forces (named after Johannes Diderik van der Waals, 1837-1923, known for the equation of state that describes the behavior of gases near the liquid phase, and their condensation to the liquid phase), today subclassified into:
 - Keesom forces and bonds (1876-1956, who developed the first mathematical description of dipole-dipole interactions)
 - Debye forces and bonds (named after Peter Joseph William Debye, 1884-1966, known for applying the concept of dipole moment to the distribution of charge in asymmetric molecules)
 - London forces and bonds (named after Fritz Wolfgang London, 1900-1954, with fundamental contributions to chemical bonding theories)

The type of chemical bond is dictated by a number of factors, including the need to obtain a lower energy system, electronegativity, ionization energy, electron affinity, valence and oxidation numbers of atoms, and the size of atoms and ions, and the tendency of atoms to reach more stable

doublet or octet electronic structures. There are other factors that can give indications of the type of chemical bond. Due to the complex nature of chemical bonding, there is no single model that covers the entire spectrum of chemical bonding.

3.1.3 Hybridization

The hybridization model¹ is able to explain the energy differences (at the level of electronic orbitals) when they come together in chemical bonds (see Representation of the hybridization process). Hybridization conserves the total number of energy levels (orbital levels). Thus, from m + n atomic orbitals m + n molecular orbitals (hybrids) result.

Chemical bonds are explained by the modification of electronic orbits by their displacement in space, the space between the two nuclei being preferred, and thus electrical forces are established that favor the approach of the nuclei to a distance at which the repulsive nuclear forces equal the attractive electrical forces. The process of chemical bond formation is thus accompanied by a process of modification of electronic orbits, called hybridization (see Fig. 3.3).



Fig. 3.3: Representation of the hybridization process

Based on the formation of bonding orbitals (located between the nuclei) and antibonding orbitals (located outside the space between the nuclei), the bond order is calculated (as the number

¹see also http://en.wikipedia.org/wiki/Orbital_hybridisation

of occupied bonding orbitals minus the number of antibonding orbitals) and the molecular stability is explained (see Fig. 3.3). In the case of delocalized bonds, the bond order also admits fractional values, a special case being for NO₂.

3.2 Graphical Representations

Fig. 3.4 represents the distribution of negative electric charge within the water molecule, model obtained using the B3LYP 6-31G* level of theory within the Spartan program (v. 10).

Fig. 3.4: Electron density in water



Fig. 3.5 represents in 3D using the filled sphere model the molecules of the 6 known chlorophylls (thus illustrating the importance of 3D representations) and respectively represents in 2D (using lines to represent chemical bonds) the porphin molecule, the common effector (similar part) of all 6 chlorophylls (thus illustrating the importance of 2D representations especially in highlighting similarity).

Fig. 3.6 represents different arrangements (called phases) of ice (Wikipedia lists 25). The hydrogen bonds (intermolecular, 285 pm) are 66% longer than the usual ones in the molecule (intramolecular, 172 pm).

Fig. 3.7 represents 2 coordination complexes, representative for bond formation by electron pair transfer. Typically M is an alkali, alkaline earth or transition metal with sufficient electronic sublevels in the outermost level to accommodate a large number of electron pairs.

Fig. 3.8 represents the allotropes of sulfur. It is the element with more than 30 allotropes (more than any other).

Fig. 3.9 represents the allotropes (different arrangements) of phosphorus. The simplest arrangement in the solid state is P_4 .

Fig. 3.10 represents two situations of coordinate bonds without oxidation state and the first of these is a special case: the chemical bonds that the metal establishes are located only at one end - on it - while the second end is in the center (empty) of a pentagon formed by carbon atoms.

Fig. 3.11 represents 2 hemes. A heme consists of an iron ion contained in the center of a large organic heterocyclic ring called porphyrin (relative to the porphin in chlorophylls). Heme is a component of hemoglobin but is also a component of other hemoproteins (such as myoglobin).

Polarity is the separation of electric charges and results in an electric dipole or multipole in the molecule.

Polarizability is the measurement of changes in the distribution of electrons in response to an



Fig. 3.5: Chlorophylls (carbon atoms in red, oxygen in blue, nitrogen in yellow, magnesium in black)

Fig. 3.6: Ice phases (H_2O in the solid state)



applied electric field.

Permanent dipole is independent of the environment. Induced dipole is when a molecule with a permanent dipole induces a dipole in another molecule.

Dipole moment: the product of the magnitude of the charge and the distance between two charges of equal magnitude and opposite sign.

Electronic polarizability is the ratio of the dipole moment induced on an atom to the electric field that produces this dipole moment (DM/E).

Fig. 3.12 shows the calculated values for two series of compounds for two related quantities: polarity and polarization.

Even molecules without a dipole and without an external polarization field still interact because of the asymmetric charge distribution around the nucleus. The forces that hold atoms together are

Fig. 3.7: Dibenzo-18-crown-6 (left) EDTA (right)



Fig. 3.8: Most abundant allotropes of sulfur (S₆, S₇, S₈, S₁₂, S₁₈)



Fig. 3.9: Allotropes of phosphorus



London dispersion forces. For Helium $(1s^2 2s^2)$ these forces are so small that liquid helium 'wets' all surfaces of the container in which it is stored (Fig. 3.13).

Fig. 3.10: Special cases of coordinate bonds



Fig. 3.11: Hemes A and B and their common component (porphyrin)



Fig. 3.12: Polarization-related concepts face to face



Fig. 3.13: Liquid helium wets the walls of the container in which it is stored





4.1 Coordination number

An important concept is the coordination number¹ (used in chemistry and crystallography).

For an atom in a molecule, the coordination number counts the number of its bonds. For a crystal, the atoms are represented by spheres and the bulk coordination number counts the atoms (spheres) that touch each other; at the surface of a crystal, the same procedure counts for the surface coordination number.

The coordination number always has a non-negative value. For example, $[Cr(NH_3)_2Cl_2Br_2]^{1-}$ has as its central cation Cr^{3+} (and +3 is the hypothetical charge), but a coordination number of 6. To obtain these values, it is usually necessary to represent the structural formula (Fig. 4.1).

Fig. 4.1: Structural formula and geometry [Cr(NH₃)₂Cl₂Br₂]¹⁻



4.2 Chemical formulas

The chemical composition of substances is given by formulas (Fig. 4.2).

-		Structure	Peculiarity
	Che	mical formula	Refers to a chemical compound with 'a defined and unique molecular structure'
	- Ra	w formula	Give the number of atoms of each element relative to one of the elements
	- N	Aolecular formula	Additionally give the number of atoms of each element contained in a molecule
	-	Rational formula	It also expresses the structural groups in the molecule
		+ Geometry formula	It also expresses the geometry of the molecule

¹see also https://en.wikipedia.org/wiki/Coordination_number

4.2.1 Raw formula

The crude formula expresses the composition by the number of atoms of each element in relation to one of the elements. Knowing the atomic masses of the elements, the number of atoms of each element, in relation to one of the elements, can be calculated. The percentage content of each element is divided by the atomic mass of the element; the ratios obtained are divided by the smallest of them.

Example. Calculate the molecular formula of calcium chloride (anhydrous) knowing that the substance contains 36.1% Ca and 63.9% Cl (M(Ca) = 40.08; M(Cl) = 35.453). *Solution:*

Ca: 36.1% Cl: 63.9%Ca: 36.1/40.08 = 0.90 Cl: 63.9/35.453 = 1.80Min $(0.9, 1.80) = 0.9; 0.9/0.9 = 1; 1.8/0.9 = 2 \Rightarrow$ Ca:Cl = 1:2

From the above calculations it follows that the molecular formula of calcium chloride is Ca_1Cl_2 or in common writing $CaCl_2$. This formula has the following meaning: in calcium chloride the ratio between the number of calcium atoms and the number of chlorine atoms is 1:2.

Examples of molecular formulas: P_2O_5 (P:O = 2:5), CH (C:H = 1:1), CH₂ (C:H = 1:2), Cl₂PN (Cl:P:N = 2:1:1)

4.2.2 Molecular formula

The molecular formula gives, in addition to the molecular formula, the number of atoms of each element contained in the molecule, when the molecular mass of the substance is known. The molecular formula can therefore be established experimentally by obtaining the molecular formula and the molecular mass. The molecular formula may coincide with the molecular formula or may be an integer multiple of it.

Example. For the above calcium chloride (Ca:Cl = 1:2) a molecular mass of 111 was experimentally obtained. Express the molecular formula. *Solution:*

 $M((CaCl_2)_n) = n \cdot (40.08 + 2 \cdot 35.453) = n \cdot 110.986 = 111 \Rightarrow n = 0.99987 \approx 1$ and the molecular formula is: CaCl2. Examples of molecular formulas:

 $P_4O_{10} ((P_2O_5)_2), C_2H_2 ((CH)_2), C_6H_6 ((CH)_6), Cl_6P_3N_3 ((Cl_2PN)_3)$

4.2.3 Rational formula

The rational formula additionally expresses the structural groups in the molecule. It is mainly used for organic compounds.

Example. Rational formulas of the molecular formula C₃H₈O. Solution:

```
1-propanol: CH_3-CH_2-CH_2-OH
OH
2-propanol: CH_3-CH-CH_3
methyl ethyl ether: CH_3-O-CH_2-CH_3
```

4.2.4 Structural formula

The structural formula shows the structure of molecules (all the atoms that make up the molecule together with all the bonds that are established between them).

Example. Structural formulas for the molecular formula C:H = 1:1. *Solution:*



4.2.5 Isomerism

Two or more compounds are structural isomers when they have the same molecular formula and different structural formulas (1-propanol, 2-propanol, and methyl ethyl ether are structural isomers (see the example above).

Structural isomerism is the easiest type of isomerism to distinguish. However, it is not as easy to list. Nonane (C_9H_{20}) has 35 structural isomers ([42], Fig. 4.3).



Fig. 4.3: Structural isomers of nonane (C_9H_{20})

Structural isomers can be further classified into skeletal isomers, positional isomers (or regioi-

somers), functional isomers, tautomers, and structural isotopomers (see §3 in [43]).

However, it is possible for the atoms and bonding pattern to be the same, and the relative spatial arrangement of the atoms to be different, in which case the isomerism is geometric (or stereoisomerism).

4.2.6 Geometric representation

Molecular geometry can be represented by expressing the distances between atoms and the angles between bonds, defining the geometric formula (in internal coordinates of the molecule). A simple example is CHFClBr (Fig. 4.4).

Fig. 4.4: Geometry of CHFClBr



Even the last level of refinement (geometric formula) is not always sufficient to faithfully represent the molecular structure. A simple example is butane (C_4H_8). The "Gauche g-" and "Gauche g+" conformers are not distinguished by internal coordinates (bond angles and distances between atoms) and an external observer (a reference system fixed outside the molecule) is needed to distinguish between them (Fig. 4.5).

	Fig. 4.5:	Conformers	of <i>n</i> -butane	("n"	in normal)
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4.2.7 Conformational isomers

Two or more compounds are conformational isomers when they have the same structural formula and have different geometries. Types of structural isomers are:

- Enantiomers v. enantiomers CHClBrF in Fig. 4.6
- Diastereoisomers:
 - Cis-trans isomers see cis-butene and trans-butene in Fig. 4.6
 - Conformers see butane "gauche g-" & "gauche g+" in Fig. 4.5
- Rotamers see "anti" butane in Fig. 4.5

Fig. 4.6: Conformers of CHClBrF (bromochlorofluoromethane) and butene (C₄H₈)



4.3 Chemical Reactions

A chemical reaction is generally expressed in the form "Reactants \rightarrow Products". Example:

$$\sum_{i=1}^{m} R_i \longrightarrow \sum_{j=1}^{n} P_j$$

where the symbol \rightarrow expresses the formation of reaction products ("Products") from reactants ("Reactants").

The state of aggregation can be specified for each participant in the reaction using the following abbreviations:

- g gas
- 1 liquid
- s solid
- aq solution

Examples: $C(s) + S(s) \longrightarrow CS_2(l), H_2(g) + O_2(g) \longrightarrow H_2O(l), H_2(g) + O_2(g) \longrightarrow H_2O(g),$ HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H₂O(l)

The sign separating products from reactants (" \rightarrow ") can differ:

• \longrightarrow has a general purpose, shows the action, when it expresses a chemical transformation (in general) or highlights the (total) transformation of reactants into products (under certain conditions); $\xrightarrow{\#}$ shows the lack of action (does not react); similar meanings have $\xleftarrow{}$ and $\xleftarrow{\#}$. Examples:

$$C + O_2 \longrightarrow CO_2, C(s) + O_2(g) \longrightarrow CO_2(g)$$

• designates an equilibrium, when it highlights the existence of an equilibrium between products and reactants (all of which are represented at the final moment of the reaction). Example:

$$H_2O(l) \Longrightarrow HO^-(aq) + H^+(aq)$$

• \iff denotes a reaction in both directions. Example:

$$N_2O_4(g, 25^\circ) \xrightarrow{\text{heating}} NO_2(g, 75^\circ)$$

• \leftrightarrow a resonance between different forms. Example:

$$\bigcirc \longleftrightarrow \bigcirc$$

• → (and ←) designates a half-reaction when it highlights a reaction conditioned by the existence of another and is frequently used in reactions involving electric current. Example:

$$Fe^{2+} + 2e^{-} \rightarrow Fe^{-}$$

other symbols [44]: ⇒ and ⇐ for retrosynthesis (reverse route of production), --→ for hypothesization (a desired transformation),
 ,
 ,
 ,
 and
 for shifted equilibria (towards reactants or towards products)

Vertical arrows are used to indicate transformations:

- ↑ defines a phase change with transition to the gaseous state (vaporization or sublimation) and expresses the formation of a gas; example: H₂CO₃ → H₂O + CO₂↑
- \downarrow defines a phase change with the transition to the solid state (condensation or deposition) and expresses the formation of a precipitate; example: AgNO₃ + KCl \longrightarrow KNO₃ + AgCl \downarrow
- ↑↓ defines a reflux, a technique used in chemistry to apply energy to reactions over a long period of time that involves boiling a liquid in a vessel attached to a condenser so that the vapors continuously condense for reboiling [45]

Chemical reactions can be classified according to the nature of the changes that occur in:

- rearrangement, $A \longrightarrow B$, when A and B are isomers (of structure)
- combination, $\sum_{i=1}^{m} R_i \longrightarrow B$; example: Ca + S \longrightarrow CaS
- decomposition, $A \longrightarrow \sum_{j=1}^{n} P_j$; example: $H_2CO_3 \longrightarrow CO_2 + H_2O_3$
- substitution, A + BC \longrightarrow AC + B; example: Br₂ + KI \longrightarrow KBr + I₂
- exchange, AB + CD \longrightarrow AD + BC; example: H₃CC₆H₅ + HH \longrightarrow C₆H₆ + CH₄

An equally important issue is the specification of the conditions of the process, which include:

• the presence of substances that favor (catalysts) the transformation of reactants into products and/or substances that disfavor (inhibitors) alternative transformations; example: Fig. 4.7

Fig. 4.7: Beckmann rearrangement of cyclohexanone oxime to ε -caprolactam)



• the presence of other special conditions for the transformation to occur (in the presence of light, electric field, magnetic field, microwaves, etc.); example: the formation of carbohydrates in plants in the presence of light (through photosynthesis)

• temperature and pressure conditions; example: Haber process in ammonia formation
$$450^{\circ}C$$

$$N_2 + 3 H_2 \xrightarrow{450 \circ C} 2 NH_3$$

4.3.1 Stoichiometry

An important problem is the determination of the proportions of the participants, which result naturally from the application of the conservation principles that operate during the course of the reactions, and which, once established, are expressed as coefficients in the reaction equations². The convention for expressing the coefficients of a chemical reaction is that the coefficients are the smallest whole numbers that express the proportion of participation. In certain cases, such as those in which the value of a physicochemical property associated with a chemical reaction is expressed, the values of these coefficients are adjusted (divided by an integer) so as to reflect the property expressed (see Tab. 4.1).

Table 4.1: Conventions for expressing chemical reactions: example of water formation

Equation	Convention
$H_2 + O_2 \longrightarrow H_2O$	Expresses the formation of water from elements
$H_2:O_2:H_2O = 2:1:2$	Expresses the ratio of combination and formation
$2 H_2 + 1 O_2 \longrightarrow 2 H_2 O$	Expresses the coefficients with the smallest integers
$2 H_2 + O_2 \longrightarrow 2 H_2O$	Unitary coefficients are no longer specified
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	Expresses the formation of water in the liquid state
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	Expresses the formation of water in the gaseous state

The determination of the coefficients of chemical reactions (or stoichiometry) is done in accordance with the application of one or more conservation principles. These are:

• The principle of conservation of mass (at rest) states that the total mass before the reaction

²see also http://en.wikipedia.org/wiki/Stoichiometry

occurs is equal to the total mass after the chemical reaction occurs (Eq. 4.1).

$$\sum_{i=1}^{m} mass(R_i) = \sum_{j=1}^{n} mass(P_j)$$
(4.1)

For a reaction equation expressed in the form Eq. 4.2:

$$\sum_{i=1}^{m} a_i R_i \longrightarrow \sum_{j=1}^{n} b_j P_j \tag{4.2}$$

where $(a_i)_{1 \le i \le m}$ are the coefficients of the reactants $(R_i)_{1 \le i \le m}$ and $(b_j)_{1 \le j \le n}$ are the coefficients of the reaction products $(P_j)_{1 \le j \le n}$, the principle conservation of mass can be expressed using molar masses (M(U) denotes the 'molar mass' of the chemical compound U) with Eq. 4.3:

$$\sum_{i=1}^{m} a_i M(R_i) = \sum_{j=1}^{n} b_j M(P_j)$$
(4.3)

The authors of the paper [46] report an exception to this principle for reactions between heavy particles of matter and antimatter, having as support an experiment for which the hypothesis of the development of a reaction of this type with energy formation was formulated: $p^+ + p^- \longrightarrow \pi^+ + \pi^- + K^+ + K^- \longrightarrow energy$

• The principle of conservation of the number of atoms (for each element) states that for each element (let 'E' an element) the number of atoms (let N('E', U) the number of elements 'E' in the chemical compound U) before is equal to the number of atoms for each element after the chemical reaction has taken place. For the reaction equation expressed above, the principle of conservation of the number of atoms generates an equality relation for each element (see Eq. 4.4):

$$\sum_{i=1}^{m} a_i N(E', R_i) = \sum_{j=1}^{n} b_j N(E', P_j)$$
(4.4)

Exceptions to this principle are known to be fission and fusion reactions, such as the reaction: ${}_{1}^{2}H + {}_{1}^{3}H \longrightarrow {}_{2}^{4}He + {}_{0}^{1}n$

• The principle of conservation of the number of electrons states that the number of electrons participating as reactants is equal to the number of electrons participating as reaction products (Eq. 4.5).

$$\sum_{i=1}^{m} a_i n_e(R_i) = \sum_{j=1}^{n} b_j n_e(P_j)$$
(4.5)

It is obvious that this principle does not apply to 'half-reactions' involving electric current (such as the reaction: $2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$) but only to global reactions (such as the second half-reaction: $2 OH^-(aq) - 2 e^- \longrightarrow H_2O(1) + \frac{1}{2} O_2(g)$), when this principle is respected (summing and reducing such terms results in: $2 H^+(aq) + 2 OH^-(aq) \longrightarrow H_2O(1) + H_2(g) + O_2(g)$)

The coefficients of chemical equations are used to determine the amount of reactants needed. For example, starting from the equation of the chemical reaction between sulfur and carbon, determining the coefficients allows the calculation of the amount of sulfur needed for a given mass of carbon (see Tab. 4.2).

Equation	Convention		
Equation of the reaction	$C(s) + S(s) \longrightarrow CS_2$	(1)	
Balancing the equation	$C(s) + 2S(s) \longrightarrow CS$	$S_2(1)$	
Mass balance	1 'molecule' of C(s)	reacts with	2 'molecules' of S(s)
	$1 \mod C(s)$	reacts with	2 mol S(s)
	$M(\mathbf{C}) = 12 \text{ g } \mathbf{C}(\mathbf{s})$	reacts with	M(S) = 32 g S(s)
	<i>x</i> g C(s)	reacts with	y g S(s)
	$\implies y = x \cdot 32 \text{ g}/12 \text{ g}$	g = 8x/3	

Table 4.2: Example of a chemical reaction mass balance calculation

It is obvious, however, that the coefficients of the equation of a chemical reaction can only be determined if all the active participants (those undergoing transformations) in the reaction are known. Once this framework is defined, there are several ways to obtain the values of the coefficients of the chemical reaction equation, and for 3 of these, the algorithms are described below using a concrete example, namely for the reaction of copper with nitric acid:

 $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

4.3.2 Oxidation number method

The oxidation number method is perhaps the most complex method, involving a thorough knowledge of the chemical properties (specifically, knowledge of the possible oxidation states and electronegativities) for elements and chemical combinations. To exemplify, in the series HCl, Cl_2 , HClO, HClO₂, HClO₃, HClO₄, all stable chemical compounds, the oxidation state of chlorine is determined by the oxidation state of the other two constituents of the chemical formula (when they appear, namely H for HCl and H and O for HClO, HClO₂, HClO₃ and HClO₄) because the electronegativity of chlorine is intermediate (on any electronegativity scale, see Fig. 2.15) between the electronegativity of hydrogen and that of oxygen (for example on the revised Pauling scale H: 2.20, Cl: 3.16, O: 3.44) which makes the oxidation numbers associated with the elements in the listed compounds to be those in Fig. 4.8

Compound	HCl	Cl ₂	HClO	HClO ₂	HClO ₃	HClO ₄
Structure	H-Cl	Cl-Cl	H-O-Cl	H-O-Cl=O	$H-O-Cl(=O)_2$	H-O-Cl(=O) ₃
Order	(1, minimum	electronega	tivity): H→H	; (2, maximum e	electronegativity): O	$\rightarrow O^{2-}; (3): Cl \rightarrow Cl^{x}$
Oxidation numbers	H: +1	Cl-Cl	H: +1	H: +1	H: +1	H: +1
(steps)	\rightarrow Cl: -1	\rightarrow Cl: 0	O: -2	O: -2	O: -2	O: -2
			\rightarrow Cl: +1	\rightarrow Cl: +3	\rightarrow Cl: +5	\rightarrow Cl: +7

Fig. 4.8: Example of determining oxidation numbers

Of course, determining oxidation numbers also requires knowledge of the chemical structure, because based on electronegativity and the bonds that are established between atoms, the convention of moving electrons (towards more electronegative elements) and implicitly of the electric charge is applied (see Fig. 4.8). Once the procedure for determining oxidation numbers has been defined, the oxidation number method involves applying the following sequence of steps (see Fig. 4.9).

As can be seen (see Fig. 4.9) the oxidation number method offers the advantage of containing a step (ON9) that allows the verification of the calculations performed.

The ion-electron method starts from the hypothesis that the reaction takes place in an aqueous medium, so that it benefits from the dissociation of water and solving the chemical reaction equation involves writing a series of half-reactions in which each dissociated species between the reactants and products is transformed with the help of the protons and electrons present in the water. It involves applying the following sequence of steps (see Fig. 4.10).

$112. \pm$: Steps in the oxidation number met	.n(о
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Step	Action
ON0	Identify oxidation numbers: $Cu=Cu^{0}$; $HNO_{3}=H^{+}(NO_{3})^{-}=H^{+}N^{5+}(O^{2-})_{3}$; $NO=N^{2+}O^{2-}$; $Cu(NO_{3})_{2}=Cu^{2+}((NO_{3})^{-})_{2}$
ON1	Identify changes in states (reactants \rightarrow products): Cu: Cu ⁰ \rightarrow Cu ²⁺ ; N(în NO produs): N ⁵⁺ \rightarrow N ²⁺
ON2	Applying conservation of e-number (obtaining coefficients): $3Cu^0 - 32e^1 + 2N^{5+} \rightarrow 3Cu^{2+} + 2N^{2+} - 23e^{-1}$
ON3	Writing the equation using the identified coefficients: $(3)Cu + (2+?)HNO_3 \rightarrow (3)Cu(NO_3)_2 + (2)NO + (?)H_2O$
ON4	Labeling the unknowns (here x and y): (3)Cu + (2+x)HNO ₃ \rightarrow (3)Cu(NO ₃) ₂ + (2)NO + (y)H ₂ O
ON5	Applying the principle of conservation of atomic number for N: $2+x = 3 \cdot 2 + 2 \rightarrow x = 6$
ON6	Writing the equation using the identified coefficients: $(\beta)Cu + (2+6)HNO_3 \rightarrow (\beta)Cu(NO_3)_2 + (2)NO + (y)H_2O_3 \rightarrow (\beta)Cu(NO_3)_2 + (2)NO + (2)NO_3 \rightarrow (\beta)Cu(NO_3)_2 + (2)NO + (2)NO_3 \rightarrow (\beta)Cu(NO_3)_2 + (2)NO_3 \rightarrow$
ON7	Applying the principle of conservation of atomic number for O: $8 \cdot 3 = 3 \cdot 6 + 2 + y \rightarrow y = 4$
ON8	Writing the equation using the identified coefficients: $(\beta)Cu + (2+6)HNO_3 \rightarrow (\beta)Cu(NO_3)_2 + (2)NO + (4)H_2O$
ON9	Verification using the principle of conservation of number of atoms for H: $8 = 4.2$;

Fig. 4.10: Steps in the ion-electron method

Step	Action
IE0	Dissociation of electrolytes: $HNO_{3(aq)} \Longrightarrow H^{+}_{(aq)} + NO_{3(aq)}; Cu(NO_{3})_{2(aq)} \Longrightarrow Cu^{2+}_{(aq)} + 2NO_{3(aq)}$
IE1	Writing all half-reactions (in aqueous medium, involving H^+ , e ⁻ and H_2O):
	IE1.1: $HNO_3 + (3H^+ + 3e^-) \rightarrow NO + 2H_2O$
	IE1.2: $Cu^0 + H_2O \rightarrow Cu^{2+} + (2e^- + 2H^+)$
IE2	Applying conservation of number of e ⁻ (obtaining coefficients): $3Cu^0 + 2HNO_3 (+6e^-) \rightarrow 3Cu^{2+} + 2NO (+6e^-)$
IE3	Summation of half-reactions: $(3)Cu + (2+x)HNO_3 \rightarrow (3)Cu(NO_3)_2 + (2)NO + (y)H_2O$
IE4	Continue cu ON5 (from Steps in the oxidation number method)

As can be seen (see Fig. 4.10) the ion-electron method offers the advantage that it only requires knowledge of the electrical charges of the ions resulting from electrolytic dissociation (which does not require knowledge of electronegativity and/or structure) and from this point of view it is a more advantageous method (requires less time to solve) but at the same time it has the disadvantage that it is applicable only to reactions that take place in an aqueous environment.

The algebraic method is, from a certain point of view (that of the number of calculations), the most elaborate method and from another point of view (of the necessary initial knowledge) the least elaborate: it only involves applying the principle of conservation of the number of atoms for each chemical element found among the participants in the reaction (see Fig. 4.11).

Step	Action
Alg0	Labeling all coefficients with unknowns: (a)Cu + (b)HNO ₃ \rightarrow (c)Cu(NO ₃) ₂ + (d)NO + (e)H ₂ O
Alg1	Conservation of the number of atoms for each element: (Cu): a=c; (N): b=2c+d; (H): b=2e; (O): 3b=6c+d+e
Alg2	Solving the system of equations by successive substitutions:
	Alg2.1: c =a
	Alg2.2: b=2a+d; b=2e; 3b=6a+d+e; b=2e
	Alg2.3: 2e=2a+d; 6e=6a+d+e; d=2e-2a
	Alg2.4: 6e=6a+2e-2a+e; 3e=4a
Alg3	Solving in the set of non-zero integers (as the smallest numbers): $\rightarrow e=4, a=3; d=2, b=8, c=3$
Alg4	Writing the reaction equation: $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \square$

As can be seen (see Fig. 4.11) solving algebraically involves solving a system of equations, this time with fewer equations than unknowns (in the other two methods - see Fig. 4.9 and Fig. 4.11 - we always had an equation at the final step that allowed us to verify the calculations and thus had associated over-determined systems of equations). It is very important, however, that in the algebraic method the application of the convention regarding the values of the coefficients becomes very visible: the smallest non-zero (positive) integers that verify the system of equations (which verify the principle of conservation of the number of atoms for each element represented in the reaction participants), which is actually the implicit convention regarding the writing of the

coefficients of the equation of a chemical reaction.

The advantage of the algebraic method is of course the fact that the associated calculation algorithm does not contain 'heuristics' regarding oxidation states or number of electrons exchanged, which makes it very attractive in terms of implementing a program for automatic calculation of the coefficients of the chemical reaction equation. At the same time, the disadvantage of this method is the same: if the application of heuristics regarding oxidation states or number of electrons can play an important role in detecting errors in writing chemical formulas, in the case of the algebraic method this possibility no longer exists.



A state of matter is a distinct form in which matter can exist. Three states of matter are observable in everyday life: solid, liquid, and gas (Fig. 5.1). There are intermediate states (e.g., liquid crystals), and others exist only under extreme conditions, such as extreme cold, extreme density, or extremely high energy.

Fig. 5.1: Representations of the gaseous, liquid, and solid states



The liquid and solid states have in common a density that varies insignificantly with temperature compared to the gaseous state. In Fig. 5.2 it can be seen that the influence of the increase in temperature (which is the effect of heating) is similar in the liquid state to that in the solid state. For this reason they are called condensed (states).





Some authors note [47] that from an energetic point of view, the liquid state is closer to the solid state than to the gaseous state, an argument supported by the ratio between the heats required to pass from one state to another (Tab. 6.1)

Substance	He	O ₂	H ₂ O	Cl ₂	NaCl	В
Heat of fusion	0.0138	0.444	6.02	6.4	28.16	50.2
Heat of vaporization	0.0829	6.82	40.7	20.41	130.05	480

Table 5.1: Examples of heats of fusion and vaporization (values in kJ/mol)

The liquid and gaseous states have in common the mobility of the constituents (atoms or molecules) compared to the solid state. For this reason they are called (states of) fluids.



Fig. 5.3: Fluid flow: narrowing of the section

For fluid flow (Fig. 5.3) Bernoulli's law [48] applies.

• If the fluid is compressible (such as gases, e.g. applied to the transport of CH₄), then Eq. 5.1 applies:

$$\rho \frac{v^2}{2} + \rho gh + \frac{\gamma}{1 - \gamma} p = \text{constant}$$
(5.1)

where v is the flow velocity, g is the acceleration due to gravity, h is the altitude, γ is the specific heat ratio, p is the pressure, and ρ is the density.

• If the fluid is incompressible (such as liquids, e.g. applied to the transport of H_2O), then Eq. 5.2 applies:

$$\rho \frac{v^2}{2} + \rho g h + p = \text{constant}$$
(5.2)

In the laboratory, the gas sampling is studied qualitatively (p. 15-18 in [49]). The associated quantitative analysis can be performed using Eq. 5.1.

For incompressible liquids, with Eq. 5.3 knowing the difference z the flow rate can be calculated:

$$v_1 = \sqrt{\frac{2gz}{(S_1/S_2)^2 - 1}} \tag{5.3}$$

5.1 Liquid State

Liquids and liquid solutions are vital to our lives. Water is the most important liquid (essential for life, medium for food preparation, for transportation, cooling in machines and industrial processes, etc.)

Liquids have many characteristics that help us understand their nature. They have low compressibility, no rigidity, and high density compared to gases.

The properties of liquids give us direct information about the forces that exist between particles. When a liquid is poured onto a solid surface, it tends to form droplets, a phenomenon that depends on intermolecular forces. Although the molecules inside the liquid are completely surrounded by other molecules, those at the surface of the liquid are subject to attractions only from the sides and from below (Fig. 5.1). The effect of this uneven pull on the surface molecules tends to pull them into the body of the liquid and causes a liquid drop to take the shape that has the minimum surface area - a sphere (Fig. 5.4).

Fig. 5.4: Shape of liquids (in a vessel, in free fall, and in the absence of gravitational attraction forces)



In the absence of other forces (Fig. 5.4), ensuring a minimum surface area/volume ratio can be formulated mathematically (Eq. 5.4).

$$\int_{V} \nabla \cdot \vec{r} dV = \oint_{S} \vec{r} \cdot \vec{n} dS = \min. \implies \vec{r} \cdot \vec{n} = 0 \implies \vec{r} \perp \vec{n} \text{ everywhere}$$
(5.4)

The divergence theorem ¹ (Gauss-Ostrogradsky, [50, 51]) relates the first integral expression over the volume V of a body to the second one expressing the same quantity in terms of its surface area S (Eq. 5.1). The minimum condition requires that $\vec{r} \perp \vec{n}$ at any point. This is the sphere.

To increase the surface area of a liquid, molecules must move from the interior of the liquid to the surface. This requires energy, because some intermolecular forces must be overcome. The resistance of a liquid to increasing its surface area is called the surface tension of the liquid.

As we would expect, liquids with relatively high intermolecular forces, such as those with polar molecules, tend to have high surface tensions.

Polar liquids typically exhibit capillary action, the spontaneous rise of a liquid in a narrow tube. Two different types of forces are responsible for this property: cohesive forces, the intermolecular forces between the molecules of the liquid, and adhesive forces, the forces between the molecules of the liquid and their container.

¹http://en.wikipedia.org/wiki/Divergence_theorem

Adhesive forces occur when a container is made of a substance that has polar bonds. For example, a glass surface contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water. This ability of water to "wet" the glass causes it to slide down the walls of the tube where the water surface touches the glass. This, however, tends to increase the surface area of the water, which is opposed by cohesive forces that try to minimize the surface area.

Thus, because water has both strong cohesive (intermolecular) forces and strong adhesive forces on the glass, it "self-pulls" a glass capillary tube (a tube with a small diameter) to a height where the weight of the water column just balances the tendency of the water to be attracted to the glass surface.

The concave shape of the meniscus (Fig. 5.5) shows that the adhesive forces of water to the glass are stronger than its cohesive forces. A nonpolar liquid, such as mercury (see Fig. 5.5), exhibits a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces towards the glass.



Fig. 5.5: Interaction between liquids and contacting surfaces

Another property of liquids that is strongly dependent on intermolecular forces is viscosity, a measure of the liquid's resistance to flow. As expected, liquids with high intermolecular forces tend to be very viscous. For example, glycerol, has an unusually high viscosity due mainly to its high ability to form hydrogen bonds using its OH groups.

$$\begin{array}{cccc} H & H & H \\ I & I & I \\ H - C - C - C - C - H \\ I & I \\ OH & OH & OH \end{array}$$

Molecular complexity also leads to higher viscosity, because very large molecules can tangle with each other. For example, gasoline, a non-viscous liquid, contains hydrocarbon molecules of the type $CH_3O(CH_2)_nOCH_3$, where *n* ranges from about 3 to 8. Grease, which is more viscous, contains larger hydrocarbon molecules, where *n* ranges from 20 to 25.

A model for liquids presents greater challenges than for the other two states of matter. In the gaseous state, the particles are so far apart and move so fast that intermolecular forces are negligible under most circumstances. This means that we can use a relatively simple model for gases. In the solid state, although intermolecular forces are large, molecular motions are minimal, and fairly simple models are again possible.

The liquid state has both strong intermolecular forces and significant molecular motions. Such a situation precludes the use of truly simple models for liquids. Recent advances in spectroscopy, the study of how substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids. As a result, our models of liquids are becoming increasingly accurate. As a starting point, a typical liquid might best be viewed as containing a large number of regions in which the arrangements of components are similar to those found in the solid, but with more disorder and a smaller number of regions where holes are present. The situation is very dynamic, with rapid fluctuations occurring in both types of regions.

The best-known polar solvent is water. The water molecule has an asymmetric electronic structure. Oxygen is the most electronegative element, so the electrons of the hydrogen atoms of the water molecule move towards the oxygen and water is a polar molecule with the negative pole close to the oxygen atom and the positive pole near the hydrogen atoms (Fig. 5.6).

Fig. 5.6: Charge separation in water molecules, stratification of water molecules in the liquid phase and dissociation of water molecules in aqueous solutions



5.1.1 Ions dissolved in water

Fig. 5.7: NH₄⁺ in water (d(O–H) = 95 pm, d(O–H) = 208 pm, d(N–H) = 101 pm, \angle (H–O–H) = 105°, \angle (H–N–H) = 109°, \angle (H–O–H) = 113°)



Fig. 5.8: Li^+ in water surrounded by $4 \text{ H}_2\text{O}$ ($d(\text{O}-\text{Li}) \in \{193, 194, 196, 200\}$ pm, $\angle(\text{O}-\text{Li}-\text{O}) \in \{99, 104, 110, 111, 116, 117\}^\circ$)



Fig. 5.9: F⁻ in water surrounded by $6 H_2O(d(F-H) \in \{179, 182, 183, 184, 187\} \text{ pm}, \& (H-F-H) \in \{77, 85, 85, 86, 87, 88, 89, 89, 90, 93, 98, 109, 162, 165, 177\}^{\circ})$



Fig. 5.10: Na⁺ in water surrounded by $5 H_2O$



Fig. 5.11: Cl⁻ in water surrounded by $5 H_2O$



Fig. 5.12: K^+ in water surrounded by $6 H_2O$







Fig. 5.16: Topaz: Al₂SiO₄(F,OH)₂



Vari

eties						
paz	Colorless	Yellow	Pink	Blue	Green	Purple
urities	-	Fe	Mn	Cr, Ti	Cr, Fe	Ti, Mn

5.2 Solid State

From a geological point of view, minerals are divided into classes (see. Tab. 5.2).

Table 5.2: Minerals

Mineral Class	Examples
Native	Diamond, coal, S, Au, Ag, Cu, Pt, Pd
Halogens	NaCl (known as table salt), KCl, CaF ₂ , KCl \cdot MgCl ₂ \cdot 6 H ₂ O
Oxides and hydroxides	Al ₂ O ₃ , AlO(OH), Al(OH) ₃ , Fe ₂ O ₃ , FeO, Fe ₃ O ₄ , MnO ₂ , TiO ₂ , SnO ₂ , SiO ₂ , UO ₂ ,
	U_3O_8
Sulfides, Arsenides	FeS ₂ , PbS, ZnS, HgS, CuS, Sb ₂ S ₃ , Bi ₂ S ₃ , MoS ₂ , CuFeS ₂ , NiAs, CoAsS
Carbonates	CaCO ₃ , MgCO ₃ , CaCO ₃ ·MgCO ₃ , FeCO ₃ , MnCO ₃ , Cu ₂ (CO ₃)(OH) ₂ ,
	$Cu_3(CO_3)_2(OH)_2$
Nitrate	NaNO ₃ , KNO ₃

Solids can be classified into:

- amorphous example: glass (SiO₂)
- crystalline example: quartz (SiO₂)

but in fact there can also be intermediate forms (see Fig. 5.17).

The term "amorphous" comes from the Greek word for form "morph" and means disordered or formless. Amorphous solids do not exhibit a repeating three-dimensional arrangement. The most common amorphous solid is glass.

Fig. 5.17: Crystalline (e.g. diamond), microcrystalline (e.g. graphite) and amorphous (e.g. coal) arrangements



The following table (Tab. 5.3) classifies the glasses (Fig. 5.18):

Table 5.3: Glass

Soda-lime-silica glass	1675 °C ←	$SiO_2 + NaOH + Ca(OH)_2 + CaMg(CO_3)_2 + Al_2O_3$
Borosilicate glass	1650 °C ←	$B_2O_3 + SiO_2 + Na_2CO_3 + Al_2O_3$
Crystal glass (with Pb)	1400 °C ≺───	$SiO_2 + PbO + K_2O$
Aluminosilicate glass	1613 °C ←	$SiO_2 + Al_2O_3 + Li_2O + Na_2O + ZrO_2 + K_2O + MgO + B_2O_3$
Quartz glass	2000 °C	SiO ₂
Flint	1800 °C	$SiO_2 + B_2O_3 + ZnO + BaO + La_2O_3$





5.2.1 Crystals

In a crystal, the particles are arranged in rows, the planar and 3D networks ordered, symmetrical and considered infinite. The distance between atoms is 3-5 Å. In 1 mm³ there are $\approx 10^{21}$ particles (which gives the assumption of practically infinity).

Crystal systems are classified into:

- Triclinic ($a \neq b \neq c$ and $90^{\circ} \neq \alpha \neq \beta \neq \gamma$, see Fig. 5.19). Ex.: Ta₂O₅, CaSiO₃
- Monoclinic $(a \neq b \neq c \text{ and } 90^\circ = \alpha = \gamma \neq \beta$, see Fig. 5.19). Ex.: FeAl₂(SO₄)₄·22 H₂O, Ca₂B₅O₉Cl·H₂O, CaSO₄·2 H₂O
- Orthorhombic $(a \neq b \neq c \text{ and } 90^\circ = \alpha = \beta = \gamma$, v. Fig. 5.19). Ex.: MgSO₄ · 7 H₂O, Zn₄Si₂O₇(OH)₂ · H₂O, (Mg,Fe)₂SiO₄
- Tetragonal ($a = b \neq c$ and 90° = $\alpha = \beta = \gamma$, v. Fig. 5.19). Ex.: MgB₂O₄ · 3 H₂O, Na₄(AlBeSi₄O₁₂)Cl, CaWO₄, NaAl₃(PO₄)₂(OH)₄ · ₂(H₂O), Pb₂CuCl₂(OH)₄, CuFeS₂, TiO₂
- Hexagonal ($a = b \neq c$ and $90^{\circ} = \alpha = \beta$, $120^{\circ} = \gamma$, v. Fig. 5.19). Ex.: KFe₃(SO₄)₂(OH)₆, CaMg(CO₃)₂, Sn₂₁O₆(OH)₁₄Cl₁₆, LiTaO₃, Fe₂O₃, (Na,K)AlSiO₄, Ca₂Na₃[(OH)(SO₄)₃], Ca₅(PO₄)₃(F,Cl,OH), KAlSiO₄, (Zn,Fe)S, BaTiSi₃O₉, Be₃Al₂Si₆O₁₈

Fig. 5.19: Structure of salt (NaCl: model and scheme) and the general case of elementary unit



• Cubic $(a = b = c \text{ and } 90^\circ = \alpha = \beta = \gamma$, v. Fig. 5.19). Ex.: NaClO₃, FeS₂, Ag₃AuTe₂, (Zn,Fe)S, NaCl

The ratio of atoms within the unit cell can be misleading with respect to the chemical formula (see Fig. 5.20).





The reason we work with crystallographic systems is the huge number of polyhedra formed by chemical compounds (Tab. 5.4, Tab. 5.5 and Tab. 5.6).

A series of common polyhedra in chemistry are shown in Fig. 5.21.

Table 5.4: The number of polyhedra for a given number of vertices (or faces; see also [52])

п	polyhedra	n	polyhedra	n	polyhedra
4	1	9	2606	14	1496225352
5	2	10	32300	15	23833988129
6	7	11	440564	16	387591510244
7	34	12	6384634	17	6415851530241
8	257	13	96262938	18	107854282197058

Table 5.5: The number of polyhedra for a given number of edges (see also [53])

n	polyhedra	n	polyhedra	n	polyhedra	n	polyhedra	n	polyhedra
6	1	12	12	18	4199	24	5623571	30	10204782956
7	0	13	22	19	13384	25	19358410	31	36249143676
8	1	14	58	20	43708	26	67078828	32	129267865144
9	2	15	158	21	144810	27	233800162	33	462669746182
10	2	16	448	22	485704	28	819267086	34	1661652306539
11	4	17	1342	23	1645576	29	2884908430	35	5986979643542

Table 5.6: Number of polyhedra as a function of the number of vertices and faces (edges = vertices + faces - 2; (see also [54]))

11
38
58
34
26

Fig. 5.21: Common polyhedra in chemistry



5.3 Concentration of solutions

A series of ways to express concentration² is given in Tab. 5.7.

Table 5.7: Ways to express concentrat	ion and associated standard notations [55]
---------------------------------------	--

Size	Formula	Units of measurement					
m_j, V_j, n_j, N_j : mass, volume, amount (in moles), number of constituent entities j							
e_j : number of constituent reactive s	species j upon dissolu	ution (H ⁺ + HO ⁻ , $n_j e^-$ + M ^{n_j+})					
m, V, n: mass, volume, and amount	<i>m</i> , <i>V</i> , <i>n</i> : mass, volume, and amount (in moles) of mixture $(n = \sum_{j} n_j)$						
Mass concentration	$\rho_j = m_j/V$	$kg m^{-3} = g l^{-1}$					
Molar concentration (molarity)	$c_j = n_j/V$	$M = mol \ l^{-1} = 10^3 \ mol \ m^{-3}$					
Normal concentration (normality)	$\mathbf{v}_j = c_j / e_j$	$N = Eq \ l^{-1}$					
Molal concentration (molality)	$b_j = n_j/m$	$mol kg^{-1} = 10^{-3} mol g^{-1}$					
Number concentration	$C_j = N_j/V$	$m^{-3} = 10^{-3} l^{-1}$					
Titre	$T_j = m_j/V$	$kg l^{-1} = 10^{-3} g m l^{-1}$					
Mass fraction	$w_j = m_j/m$	-					
Mole fraction	$x_j = n_j/n$	-					
Volume fraction	$\phi_j = V_j/V$	-					
Mass ratio	$\zeta_j = m_j / (m - m_j)$	kg : kg					
Molar ratio	$r_j = n_j / (n - n_j)$	mol : mol					
Volume ratio	$z_j = V_j / (V - V_j)$	1:1					
Mass percent concentration	$W_j = 100 w_j$	%					
Molar percent concentration	$X_j = 100 x_j$	%					
Volume percent concentration	$\Phi_j = 100 \phi_j$	%					

One observation can be kept in mind: molar concentration varies with temperature, because volume varies with temperature while molality is a temperature-independent quantity. A dilute solution is a solution containing at most 10^{-2} mol·l⁻¹ of solute. Note: in dilute solutions, the solvate ions are separated by at least 10 solvent molecules.

The properties of the fraction (mass, molar and volume) are to be remembered: $\sum_j x_j = 1$ (for a binary mixture, $x_1 + x_2 = 1$) and $0 < x_j < 1$ ($x_j = 0 \implies$ component *j* does not exist in the mixture; $x_j = 1 \implies$ component *j* is in a pure state).

5.3.1 Molar fraction is an intensive quantity

Problem: prove that molar fraction is an intensive quantity.

Solution: let a mixture have the composition expressed by the ratio of the number of molecules of each component in the mixture by $\alpha_1 : \alpha_2 : ... : \alpha_J$ (such as for $C_2O_4H_2$, $\alpha_1 : \alpha_2 : \alpha_3 = 2:4:2 = 1:2:1 = ...$) and *n* the number of moles. Of the $N = n \cdot N_A$ molecules of the mixture, to respect the proportion, the number of molecules in component *j* is $N_j = N \cdot \alpha_j / \sum_j \alpha_j$. The mole fraction of the mixture with the given composition by proportion is:

$$x_j = \frac{n_j}{\sum_j n_j} = \frac{N_j / N_A}{\sum_j N_j / N_A} = \frac{N_j}{\sum_j N_j} = \frac{N \cdot \alpha_j}{\sum_j N \cdot \alpha_j} = \frac{\alpha_j}{\sum_j \alpha_j}$$

The resulting expression depends only on the given composition by proportion and does not depend on the number of moles or molecules involved, so it has been shown to be an intensive quantity.

²see also http://en.wikipedia.org/wiki/Concentration

5.4 Gas state

In the gaseous state, atoms and molecules are located at relatively large distances. Since a very large number of particles are found in a small volume (in 1 cm³ of air there are approximately $3 \cdot 10^{19}$ molecules under normal pressure and temperature conditions), the quantities that relate the gaseous state at the macroscopic level are statistical. An example of such a quantity is temperature (see Fig. 1.3). Two other examples are pressure and mean free path (see Tab. 5.8).

Table 5.8: Orders of magnitude for pressure and mean free path

Ref.	Pressure	Mean free path	Molecule	Length
Ambient air	10^{5} N/m^{2}	66 nm	H_2	0.1 nm
Low vacuum	10^2 N/m^2	0.1 mm	O ₂	0.3 nm
At 170 km altitude	10^{-4} N/m^2	1 m	CO_2	0.5 nm

For comparison, in the same table 5.8 the lengths of several molecules are given, compared to which the distances are large. Considering a man with a height of 2 m by comparison his nearest neighbor is on average at 400 m. The speeds of the molecules are even higher - the average speed of N₂ molecules in air at 25 °C is 475 m/s [56], the average distance being covered in less than half a second.

Pressure is defined as the force exerted by molecules per unit area and is as an effect of their momentum transfer (Fig. 5.22).





The simplest model to approximate the gaseous state is the ideal gas model (Eq. 5.5).

$$pV = nRT \tag{5.5}$$

where p - pressure (p = F/S), V - volume, n - amount of substance ($n = N/N_A = m/M$), R - Regnault's constant ($R = k_B N_A = 8.31446261815324 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T - temperature (T = 273.15 + t). This model assumes that the particles are tiny spheres (atoms and molecules) and that collisions are perfectly elastic (momentum and energy are conserved). The ideal gas law gives a very simple expression that relates their state parameters (pressure, volume, temperature), as in Fig. 5.23.

Even though they occupy the same space inside a container, the molecules have different speeds and energies [57] and temperature and pressure are statistical quantities that express their manifestation through average values.

Problem. Airbags are activated when severe deceleration (such as in a crash, Fig. 5.24) causes a steel ball to compress a spring and electrically ignite a detonator cap, which in turn causes





Fig. 5.24: Airbag inflation takes less than 45 ms



sodium azide (NaN₃) to decompose explosively, forming sodium and nitrogen gas: $2 \text{ NaN}_3(s) \longrightarrow 2 \text{ Na} + 3 \text{ N}_2$.

Knowing that the volume of the inflated airbag is 601 (p. 72-81 in [58]), calculate how much sodium azide is needed. *Solution:* Approximating N₂ with an ideal gas,

$$m = \frac{2}{3} \frac{MpV}{RT} = \frac{2}{3} \cdot \frac{65 \text{ g/mol} \cdot 101325 \text{ N/m}^2 \cdot 601}{8.314 \text{ J/molK} \cdot (273 + 22) \text{ K}} = 107.4 \text{ g}$$

To reduce the errors in the approximation of the gaseous state, various models have been formulated that take into account the deviations in the behavior of real gases from the ideal gas model. The Abel-Noble [59], Van der Waals [60], Redlich-Kwong [61], Clausius [62], Wohl [63] and virial [64] models are briefly presented on pp. 36-43 in [65].

The kinetic theory of gases, a bridge between the microscopic realm of particles and the macroscopic realm of statistics, has preoccupied researchers since ancient times. In 1867 Maxwell noted the first evidence in this regard as dating back to 50 BC [66]. The first kinetic model for gases (and at the same time the first statistical law in physics) was formulated by Maxwell [67, 68] and generalized by Boltzmann [69]. A summary of these results is given in [57]. Two important limiting cases of the distribution of molecules by energy are Bose-Einstein and Fermi-Dirac [37]. A brief presentation is given on p. 28-25 in [65].

There are also situations in which gas atoms can diffuse into the volume of a solid. Examples are the diffusion of helium through the glass tube of lasers [70] and the adsorption of hydrogen in

platinum 5.25.





Processes at the phase interface, such as the transition from the liquid to the gaseous state (formation and release of a gas into the atmosphere, e.g.: Fig. 5.24 and the corrosion of Zn in H_2SO_4) and the transition from the liquid to the solid state (e.g.: the precipitation of AgCl following the reaction between AgNO₃ and KCl) are very important theoretically and practically in chemistry, allowing the easy obtaining of different reaction products and the separation of some from others in mixtures 5.25.

Fig. 5.26: Scheme of separation by precipitation with H₂S





A first problem might arise regarding the type or nature of an observation regarding the progress of a chemical transformation. In this sense, the transformation can be represented as a continuous process. Is it really a continuous process? - the general opinion is that it is, given that a very large number of molecules participate and the observability of any such process in a finite time interval far exceeds our possibilities of observing discontinuities. To exemplify, the transformation of one mole of reactant (there are approximately $N_A = 6.022 \cdot 10^{23}$ molecules in a mole) in one year (there are approximately $3.15 \cdot 10^7$ seconds in a year) will proceed at an average speed (of $1.9 \cdot 10^{16}$ molecules per second) that makes it impossible to highlight individual transformations. Operating in analytical precision (with 4 significant figures) we have in each precision figure on average $1.9 \cdot 10^{11}$ molecules, which makes any chemical transformation a continuous process. As listed, a series of factors compete (favoring or disfavoring) the development of a chemical reaction. This phenomenon is illustrated (see Fig. 6.1) with the help of the total energy of the reaction participants, when the evolution over time of the system is represented as a continuous path between the initial moment (when only the 'reactants' are in the system) and the final one (when only the 'reaction products' are in the system).

Fig. 6.1: The role of reaction conditions



The role of reaction conditions is on the one hand to ensure that the energy threshold necessary for the transformation of reactants into products is exceeded (if the path with a maximum illustrated in the Role of Reaction Conditions is followed), for example by heating (when energy is transferred to the system by increasing the temperature) and on the other hand to alter the path aiming at reducing the altitude of the energy maximum point (when another path is followed, see Fig. 6.1), for example by using catalysts which in this case become participants in the reaction without being subjected to chemical transformations.

From another perspective, in a closed system (with which its surrounding system does not transfer substance) total chemical reactions (in which the entire amount of reactants is transformed into reaction products) cannot be evidenced. In these cases, the ('reacting') system evolves towards an equilibrium that implies the existence (at the moment of establishing equilibrium) of both reactants and reaction products (see Fig. 6.2).

Fig. 6.2: The reactants meet (are simultaneously) in the same region of space to form the reaction products



For chemical reactions in equilibrium, equilibrium is characterized by the value of an equilibrium constant (see Eq. 6.1) that is the same under the same given experimental conditions (pressure, temperature, light, magnetic field, electric field).

$$K = \frac{\prod_{j=1}^{n} [P_j]^{\beta_j}}{\prod_{i=1}^{m} [R_i]^{\alpha_i}}$$
(6.1)

for $\sum_{i=1}^{m} a_i R_i \longrightarrow \sum_{j=1}^{n} b_j P_j$ where [U] is the concentration (molar, in moles per unit volume, in liters), $(\alpha_i)_{1 \le i \le m}$ and $(\beta_j)_{1 \le j \le n}$ 'activity coefficients' with $\alpha_i \to a_i$ and $\beta_i \to b_i$ when $[R_i] \to 0$ and $[P_j] \to 0$.

In a system, it is possible to shift the chemical equilibrium (towards the formation of a greater or lesser amount of the reaction products) if the transformation is accompanied by a transfer of substance to another phase (or from another phase) than the one in which the chemical reaction takes place. Typical examples of this kind are the formation of gases or precipitates in reactions that take place in an aqueous medium. Thus, the reaction $Zn(s) + 2 HCl(aq) \implies ZnCl_2(aq) + H_2(g)$ that takes place at the contact surface between Zn (solid) and the solution of HCl (liquid) is a total reaction if the released hydrogen leaves the system (for example, the surface of the liquid is in contact with the atmosphere, where H₂ reaches, thus being removed from the reaction medium). In these cases, the chemical reactions can be considered to be total (the entire amount of Zn or the entire amount of HCl is consumed - whichever comes first).

6.1 Chemical Transformations

6.1.1 Kinetics of Simple Chemical Reactions

Chemical reactions proceed according to a mechanism that is itself a subject of research. From this point of view, a series of models constitute a knowledge base to which research into the mechanism of a reaction under study is related.
6.1.2 Rate laws

As previously highlighted at equilibrium (see Eq. 6.1) for at least a large category of chemical reactions that take place in solution, the coefficients of chemical reactions approximate well the parameters of the mathematical models of the development of chemical reactions. Indeed, let there be a chemical reaction in the general form (see Eq. 4.2). In order to obtain the reaction products $(P_i)_{1 \le i \le n}$ there must be in the reaction medium the reactant molecules $(R_i)_{1 \le i \le m}$ in the necessary proportions $(a_i)_{1 \le i \le m}$. With each transformation, a_i molecules of the reactant R_i are consumed. If at a certain point in time one of the reactants is exhausted, the reaction ceases to proceed. Narrowing the 'space' even further, for a_i reactants of type R_i to transform into reaction products in a certain region of space of volume dV all of them $(a_i R_i)_{1 \le i \le m}$ must meet in that region of space. Under given experimental conditions the probability of observing a transformation is proportional to the probability of encounters (in the absence of encounters the transformation is not possible). In the hypothesis of homogeneity the reactant molecules are uniformly distributed in space and the probability of being in the region of space (of volume dV) is given by the number of molecules (N) in the unit volume (V). The probability that for a given i (from 1 to n), a_i molecules of the reactant R_i are in the same region of space (dV) is obtained as the probability of coincidence of a_i simultaneous events as the product of probabilities. We can express the number of molecules (N) in terms of the number of moles (n) and regroup the terms. There is a proportionality between the probability of encounter and the number of transformations, in which the constant of proportionality depends on the experimental conditions (see Fig. 6.3).

nical reaction equation	$\sum_{i=1}^m a_i R_i \to \sum_{j=1}^n b_j P_j$
ability that 1 molecule of R_i is in the volume element dV	$P(R_i \mid dV) = \frac{N(R_i)}{V}$
ability that ai molecules of Ri are in the volume element dV	$P(a_i R_i \mid dV) = P^{a_i}(R_i \mid dV)$
ability (Pa) that $\sum_{1 \le i \le m} a_i R_i$ is in the volume element dV	$P\left(\sum_{i=1}^{m} a_i R_i \middle dV\right) = \prod_{i=1}^{m} P^{a_i}(R_i \mid I)$
ber of molecules (N) as a function of the number of moles (n)	$N(R_i) = N_A \cdot n(R_i)$
ortionality between presence (Pa) and encounter (Pr) in the volume element dV	$P_r \sim P_a = \prod_{i=1}^m \left(\frac{N_A \cdot n(R_i)}{V}\right)^{a_i}$
ability (Pr) that $\Sigma_{1 \le i \le m} a_i R_i$ is encountered in the volume element dV	$P_r \sim \prod_{i=1}^m N_A^{a_i} \cdot \prod_{i=1}^m \left(\frac{n(R_i)}{V}\right)^{a_i}$
ortionality between the frequency of encounters and the frequency of transformations	$v_r \sim P_r \sim \left(N_A\right)^{\sum_{i=1}^m a_i} \cdot \prod_{i=1}^m \left[R_i\right]^{a_i}$
(v_r) of the transformation $\Sigma_{1 \leq i \leq n} a_i R_i \longrightarrow \Sigma_{1 \leq j \leq n} b_j P_j$	$v_r = k \cdot \prod_{i=1}^m [R_i]^{a_i}$

Fig. 6.3: Derivation of the rate law

It is worth noting that the presence of (a_iR_i) in the same volume element dV can be disadvantaged by electrostatic repulsion (or attraction) forces such that each of the probabilities $P(R_i|dV) = N(R_i)/V$ and the concentrations $[R_i]$ are diminished (or amplified) with effect in terms of the frequency of transformations such that the terms $[R_i]$ are replaced by the terms $a(R_i) = f(R_i) \cdot [R_i]$ where $f(R_i)$ is called the force ionic (or molecular) of the reagent R_i .

Following a similar reasoning, the more molecules must be in the same region in space, the less likely they will be in the positions most favorable to the transformation, so that each of the coefficients a_i has a contribution diminished by a certain amount in the chance of the transformation occurring, and therefore in the expression of the rate law.

These last two considerations cause the kinetics of reactions to deviate from the general law derived previously (see. Derivation of the rate law) and the deviation to be all the greater the greater the number of participants and the greater their concentration.

Another remark is very important here: the kinetics of the reaction (see Fig. 6.3) was derived

from the principle of collisions (meetings) that take place between molecules and it was assumed that there is a proportional relationship between these and the transformation of reactants into reaction products. This assumption is true only if the transformation process takes place exactly according to the model, namely in a single 'phase' (stage). Most often, however, chemical reactions proceed in several stages, in which several 'elementary' transformations are involved (simpler processes in which not all reactants necessarily participate in each of them). As an example, the mechanism of the gas-phase reaction between H_2 and Br_2 is given (see [71], [72] and Fig. 6.4).

Stage	Туре	Elementary reaction equation	Rates constants (400K)	Energetic relation
"E1"	Equilibrium (1)	$Br_2 \rightarrow 2Br$	$\log_{10}(k_1) = -19.709$	"E1"="C"+"C"
"E5"	Equilibrium (1)	$2Br \rightarrow Br_2$	$\log_{10}(k_5) = 19.709$	"E5"=-"C"-"C"
"E3"	Propagation	$H + Br_2 \rightarrow HBr + Br$	$\log_{10}(k_3) = 23.327$	"E3"="A"-"B"+"C"
"E2"	Equilibrium (2)	$Br + H_2 \rightarrow HBr + H$	$\log_{10}(k_2) = -8.717$	"E2"="A"+"B"-"C"
"E4"	Equilibrium (2)	$HBr + H \rightarrow Br + H_2$	$\log_{10}(k_4) = 8.717$	"E4"="C"-"A"-"B"
Equation	Туре	Elementary reaction equation	$K_{\rm f}(\Delta G_{\rm f} = -{\rm R} \cdot T \cdot \ln(K_{\rm f}))$	$\Delta G_{\rm f}(400{\rm K},1{\rm bar})$
"A"	Tabulated (CRC)	$\frac{1}{2}H_2 + \frac{1}{2}Br_2 \rightarrow 1HBr$	$\log_{10}(K_{\rm f}) = 7.305$	-55.940 kJ/mol
"B"	Tabulated (CRC)	$1/_2H_2 \rightarrow 1H$	$\log_{10}(K_{\rm f}) = -25.875$	198.149 kJ/mol
"C"	Tabulated (CRC)	$\frac{1}{2}Br_2 \rightarrow 1Br$	$\log_{10}(K_{\rm f}) = -9.854$	75.460 kJ/mol

Fig. 6.4: Mechanism of the reaction $H_2 + Br_2 \longrightarrow 2 HBr$

As can be seen in Fig. 6.4, the evaluation of the rate constants of the process steps requires the use of physicochemical property catalogs (such as [73]). For an approach involving graph theory in solving the kinetics of chemical reactions, see [74].

6.1.3 The order of the rate of a reaction

In general, chemical reactions have complex mechanisms (see Fig. 6.4), few of which even have an elucidated mechanism. What is important to note, however, is that the mechanism of reactions depends on the experimental conditions. Thus, experimental conditions can be constructed in which the influence of a single factor on the rate of the chemical reaction can be followed.

For example, let's take the reaction: $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$

Under given experimental conditions (for example at 1 bar and 18 °C) the rate of the reaction is influenced only by the molar concentrations of the reactants (see Fig. 6.3). It is possible to isolate only the influence of a single factor if the reaction mixture is adjusted accordingly. For example, if 200 moles of O_2 and 2 moles of H_2 are introduced into the reaction vessel (the initial moment, before the reaction) and the reaction is followed by recording the amount of water formed, the final moment of the reaction will find 199 moles of O_2 , 0 moles of H_2 and 2 moles of water, which expressed in molar concentrations brings a change of 1/200 = 0.005 = 0.5% of the molar concentration of O_2 , which makes the effect of the variation of the concentration of O_2 on the rate of the reaction negligible, and thus the effect of the variation of the concentration of H_2 on the rate of the reaction can be followed 'almost' exclusively. A reaction carried out under such conditions will reveal a rate law that depends only on $[H_2]$. In this case, the power (*a*) of the rate law v = $k \cdot [H_2]^a$ is the rate order of the reaction with respect to one of the reactants (H₂) and for the given conditions of development it represents at the same time the observed rate order of the reaction.

In general, the rate order of a reaction whose mechanism is known may differ from the reaction order observed for that reaction under certain experimental conditions of the type exemplified previously (see Fig. 6.5).

In fact, the possibility of adjusting the experimental conditions constitutes an extraordinary advantage in the study of chemical reactions and the identification of reaction orders with respect to each reactant (called partial reaction orders) is possible by adjusting the reactant concentrations.

From the point of view illustrated by Fig. 6.5 for consistency one can refer to the 'order of a reaction' actually referring to the global order of the reaction as well as the pseudo-order of

Fig. 6.5: Order of reaction

$\Sigma_{1 \leq j \leq m} a_i R_i \longrightarrow \Sigma_{1 \leq j \leq m} b_j P_j$	Chemical reaction equation
$\ln(v_r) = \ln(k) + \sum_{1 \le i \le m} a_i \cdot \ln([R_i])$	Chemical reaction rate equation
$\ln(v_1) = \ln(k_1) + a_1 \cdot \ln([R_1])$	Rate equation for reactive excess excepting R_1
Reactions orders:	
\div $(a_i)_{1 \le i \le m}$: reaction partial orders	
\div $\Sigma_{1 \le i \le m} a_i$: global (total) order of reaction	
\div a_1 în v_1 ; reaction pseudo-order (and $\ln(l)$	$k_1 = \ln(k) + \sum_{k \in w} q_k \ln([R_i])$ embedding the effect of other factors)

the reaction, which is the case for the following sections that discuss particular cases of 'order of reaction'.

6.2 **Chemical equilibrium**

6.2.1 Dynamics of complex chemical reactions

The dynamics of simple chemical reactions is when the reaction is of a defined order:

- Order 0: $\Box \longrightarrow \sum_{1 \le j \le n} b_j P_j$, with the equations for the rate v = k; $d[R_i] = -a_i v dt$; $d[P_j] = -a_i v dt$ $b_j v dt$. Example: NO₂-C₆H₄-OH + 3 SO₃²⁻ + hv_{UV} + H₂O \longrightarrow NH₂-C₆H₄-OH + 3 SO₄²⁻
- Order 1: $R_1 \longrightarrow \sum_{1 \le j \le n} b_j P_j$, with the equations for velocity $v = k[R_1]$; $d[R_i] = -a_i v dt$; $d[P_i] = -a_i v dt$ $b_i v dt$. Examples: SO₂Cl₂(g) \rightarrow SO₂(g) + Cl₂(g); C₄H₉Cl + H₂O \rightarrow C₄H₉OH + HCl [75]; Sucrose + $H_2O \longrightarrow$ Glucose + Fructose (in acidic medium)
- Order 2: $R_1 + R_2 \longrightarrow \dots$ or $2R_1 \longrightarrow \dots$, with the equations for the rate of the reaction. Examples:
 - $\begin{array}{c} 10^{\circ}\text{C} \\ -2 \text{ NOBr(g)} \xrightarrow{10^{\circ}\text{C}} 2 \text{ NO(g)} + \text{Br}_2(1) \\ -2 \text{ NO}_2(g) \xrightarrow{300^{\circ}\text{C}} 2 \text{ NO(g)} + \text{O}_2(g) \\ \text{H}_2(g) + \text{I}_2(g) \xrightarrow{400^{\circ}\text{C}} 2 \text{ HI(g)} \\ \text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I} \longrightarrow \text{C}_2\text{H}_5\text{OCH}_3 + \text{NaI (in CH}_3\text{CH}_2\text{OH)} \end{array}$

 - $N_2O + O_2 \xrightarrow{100 \, ^{\circ}C} N_2 + NO_2$
- Order k
- Opposites $(v \longrightarrow = k \longrightarrow \prod_{1 \le i \le m} R_i^{a_i}, v \longleftarrow = k \longrightarrow \prod_{1 \le j \le n} P_j^{b_j})$. Examples: $- CO(g) + NO_2(g) \implies CO_2(g) + NO(g)$
 - $BaCl_2(aq) + H_2SO_4(aq) \implies BaSO_4(s) + 2 HCl(aq)$
 - $3 \text{HNO}_2(\text{aq}) \implies \text{HNO}_3(\text{aq}) + 2 \text{NO}(\text{aq}) + \text{H}_2\text{O}(1)$
 - $\text{NH}_4\text{OCN}(\text{aq}) \implies (\text{NH}_2)_2\text{CO}(\text{aq})$
 - HCOOH(aq) + C₂H₅OH(aq) \implies HCOOC₂H₅(aq) + H₂O(l)
 - $H_2O(1) \implies H^+(aq) + HO^-(aq)$
- Consecutive $(\sum_{1 \le i \le m} a_i R_i \longrightarrow \sum_{1 \le j \le n} b_j P_j, \sum_{1 \le j \le n} b_j P_j \longrightarrow \sum_{1 \le k \le o} c_j Q_j)$
- Parallels $(\sum_{1 \le i \le m} a_i R_i \longrightarrow \sum_{1 \le j \le n} b_j P_j, \sum_{1 \le i \le m} a_i R_i \longrightarrow \sum_{1 \le k \le o} c_j Q_j)$

By 'complex' reaction is meant any reaction whose dynamics is not described by one of the dynamics models described above.

In order to be able to develop a dynamics model, it is necessary to obtain the reaction mechanism. For those reactions for which the mechanism is unknown, the procedure for developing the mechanism and reaction dynamics is chained in a life cycle: a mechanism model is developed, the associated dynamics model is developed, and then the agreement between the observation and the model is measured. The life cycle of developing the mechanism and dynamics continues with the refinement (modification) of the mechanism and the reconstruction of the dynamics until the agreement between the observation and the model can be accepted from a statistical point of view (being less than or equal to the maximum risk of being in error of 5

Since the process of developing the reaction mechanism and dynamics involves a large number of parameters - the rate constants of the elementary steps, it is not always sufficient to provide a statistical assurance of the dynamics model, and sometimes a phenomenological validation is also necessary, which should follow recipes for isolating the influence of the variation of the reagent concentrations one by one, as illustrated in the Reaction Order. In the dynamic solution of complex reaction mechanisms, the rate laws are applied for each process involved and with their help the total differentials for each participant in the reaction are expressed. This type of analysis is exemplified below for a series of concrete situations.

6.2.2 Tetracyclines in chemical equilibrium

The following sequence of chemical reactions characteristic of the chemical equilibrium for tetracyclines is considered [76], v. Fig. 6.6:



Fig. 6.6: Tetracyclines in chemical equilibrium

For the mechanism proposed above (see Fig. 6.6), the dynamics equations can be obtained. In this transformation, no less than 4 chemical equilibria are established, in which 8 rate constants are involved (see Fig. 6.7).

A general remark regarding the calculation formulas that can be entered into Excel calculation cells: in order to represent a real concentration variation, it must be imposed that the values are always non-negative numbers, which modifies the simple expressions entered into the cells from "=A2+..." to "=IF(A2+...>0,A2+...,0)".

Fig. 6.7: Dynamics of tetracycline equilibrium

```
1. Writing elementary reactions; writing rate equations (A, B, C, D, E: tetracycline)

(AB): A \rightarrow B, v_{AB} = k_{AB} \cdot [A]; (BA): B \rightarrow A, v_{BA} = k_{BA} \cdot [B]

(BC): B + H^+ \rightarrow C, v_{BC} = k_{BC} \cdot [B][H^+]; (CB): C \rightarrow B + H^+, v_{CB} = k_{CB} \cdot [C]

(CD): C \rightarrow D + H^+, v_{CD} = k_{CD} \cdot [C]; (DC): D + H^+ \rightarrow C, v_{DC} = k_{DC} \cdot [D][H^+]

(CE): C \rightarrow E + H^+, v_{CE} = k_{CE} \cdot [C]; (EC): E + H^+ \rightarrow C, v_{EC} = k_{EC} \cdot [E][H^+]
```

6.3 Thermodynamics

Chemical thermodynamics has as its object the study of physico-chemical phenomena accompanied by energy transformations in which heat directly or indirectly intervenes.

Thermodynamics establishes quantitative relationships between macroscopic variables (volume, pressure, temperature, concentration) that define a physical-chemical system of large proportions, compared to the dimensions of the constituent corpuscles (atoms, molecules, etc.).

6.3.1 Thermodynamic systems

The universe of observation can be viewed as consisting of 2 parts, system and environment:

- system part of the universe that interests us in a particular way (e.g. reaction vessel, engine, electrochemical cell, biological cell)
- environment the place where we make our observations

The two parts are separated by a surface and to specify the system and its environment we must specify the separation surface between them.

The type of system is determined by the characteristics of the separation surface:

- open / closed system matter can / cannot be transferred through the separation surface; closed and open systems can exchange energy with the environment;
- isolated system a closed system that is not in mechanical and thermal contact with the environment;

A process is a transformation of state (expansion, cooling) or transformation in the physical state (melting, solidification) or complex chemical transformation (new substances are formed).

Work is done by the system if a process results in energy with which a weight can be lifted in the environment.

Work is done on the system if the environment transfers energy with which a weight would have been lifted in the environment. When work is done on an isolated system, its capacity to do work increases, its energy increases. When an isolated system performs work, its capacity to do work decreases, its energy decreases.

The energy of a system can also vary as a result of heat transfer:

- adiabatic separation surfaces do not allow heat transfer
- exothermic process process in which energy is released in the form of heat
- endothermic process process that absorbs energy in the form of heat
- adiabatic process process that takes place in an adiabatic isolated system

It is easy to see that an adiabatic endothermic process is done with a decrease in the temperature of the system and an exothermic process is done with an increase in the temperature of the system.

6.3.2 First Principle of Thermodynamics

The internal energy U is the total energy of a system. It is a state function:

$$\Delta U = U_f - U_i = \text{variation of internal energy}$$
(6.2)

U is a function of the properties that determine the state of the system at a given time and independent of the path by which that state was reached: U = U(n, p, ...) Heat and work are

(6.5)

equivalent paths for the variation of the internal energy of a system. If a system is isolated from its surroundings then no variation of internal energy occurs, or, there is no machine that performs mechanical work without energy consumption (perpetuum mobile of the first kind):

Principle I: the internal energy of an isolated system is constant. (6.3)

A consequence derived from this experimental principle and the previous logical reasoning is in fact another formulation of the first principle: "the work required to pass an adiabatic system from a certain state to another is the same, regardless of the way the work is performed".

The formulation of the first principle does not mention heat, but implies it and allows a definition of heat based on work.

If infinitesimal variations are considered, we have:

 $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \tag{6.4}$

6.3.3 Enthalpy

Usually the pair of independent state variables: temperature and pressure represent the natural conditions for the development of chemical reactions and physico-chemical processes. Many processes take place under atmospheric pressure and ambient temperature. Thus, adapting the first principle of thermodynamics to the conditions mentioned above, a new state function called enthalpy was born, which is denoted by H and which sums the internal energy with the mechanical work necessary for the system to occupy its own volume V at the working pressure p (see Fig. 6.8).

Fig. 6.8: Conversion of heat into work



H = U + pV

The study of heat produced or required in chemical reactions is called thermochemistry. Thermochemistry is a branch of thermodynamics. A reaction vessel together with its contents forms a system. Chemical reactions produce a change in energy between the system and the surroundings. Calorimetry can be used to measure the heat produced or absorbed by a chemical reaction. If the chemical reaction occurs at constant volume, then the heat measured by the calorimeter corresponds to the change in internal energy. If the chemical reaction occurs at constant pressure then the heat measured by the calorimeter corresponds to the change in enthalpy. Conversely, if ΔH or ΔU for a reaction is known, the heat of reaction that could occur can be predicted. Heat release represents a decrease in the enthalpy of a system. Thus, an exothermic process is a process for which $\Delta H < 0$ and conversely, an endothermic process is a process for which $\Delta H > 0$. The standard enthalpy change ΔH_0 is defined as the change in enthalpy recorded at a standard pressure of 1 bar. The standard state of a substance at a given temperature is its pure form at a pressure of 1 bar.



6.3.5 The meaning of spontaneous processes

Some processes occur naturally, by themselves, others do not. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, and a chemical reaction proceeds preferentially in a certain direction. The meaning of spontaneous transformations is the meaning that does not require the performance of work to carry out the process. A gas can be reduced in volume, cooled, and some reactions can be made to proceed in the opposite direction (electrolysis of water), but none of these processes occur spontaneously; each can only occur by performing work. The distinction between the two types of processes, spontaneous and nonspontaneous, is the subject of the second law of thermodynamics. The second law -a process whose sole result is the absorption of heat from a reservoir and its complete transformation into work is not possible. The possibility of the process illustrated in Figure 6.1, in which heat is completely converted into work, with no other transformation, is denied by the II principle and is not denied by the I principle, since energy is conserved. In an isolated system, the direction of a process cannot be determined by its total energy. The I principle states that energy is conserved and it cannot be stated that in any process the system tends towards a state with minimum energy, because in an isolated system the total energy is constant. When a process takes place, the total energy of an isolated system remains constant, but it is distributed in different ways. Thus, the direction of the processes can be correlated with the way in which the energy is distributed. Thus, spontaneous processes are always accompanied by a dissipation of energy in a more disordered form. A ball hit by the floor does not rise to the same level (Fig. ??); there are inelastic losses in the ball and in the floor; the kinetic energy of the ball is partially converted into thermal motion.

Fig. 6.9: The direction of the spontaneous transformation is towards increasing the share associated with disordered motion



The direction of the process is towards the transformation of ordered kinetic energy into disordered thermal motion:

6.3.6 Entropy

The first principle led to the introduction of internal energy U. Internal energy as a state function allows us to determine whether a process is possible; in an isolated system, only those processes (represented in the energy diagram U = U(T, V), for example) can take place in which the internal energy remains constant (the internal energy surface U is constant). The second principle, which allows us to appreciate the meaning of spontaneous processes, can be formulated through another state function, the entropy S. Entropy shows whether one state of a system is spontaneously accessible from another. Principle I used the internal energy U to identify the possible processes of a system:

$$\Delta U = q + w \tag{6.6}$$

Principle II uses the entropy *S* to identify spontaneous processes among the possible processes of a system:

$$\Delta S > 0 \tag{6.7}$$

so that, reformulated based on the notion of entropy, principle II is: in an isolated system, entropy increases in spontaneous processes $|\Delta S_{tot} > 0$, where ΔS_{tot} is the total entropy of the isolated system that contains the system under analysis. The rigorous definition of entropy can be made based on statistical thermodynamics. Starting from various experimental observations, Ludwig Boltzmann proposed as a formula for calculating entropy as a degree of disorder:

$$S = k \cdot \ln W \tag{6.8}$$

where k the Boltzmann constant and W the number of ways in which the energy of the system can be rearranged by rearranging atoms and molecules into different accessible states. The definition of entropy based on the relation also results in its unit of measurement: $\langle S \rangle_{SI} = JK^{-1}$. Let N molecules of HCl. At T = 0 there is a single state, characterized by a minimum energy ordering, in which the molecules are arranged so that the H and Cl atoms follow each other (W = 1, S = 0). Let N molecules of CO. Due to the small dipole moment, the energy is the same regardless of the orientation of the dipole formed by the two atoms, so that at T = 0 there are two possible states of arrangement. The disorder is greater than in HCl, so it is expected that the entropy will also be greater. The number of possible states depends on the number of molecules considered W = W(N). If N = 1 then W(1) = 2 (two possible states). If N = 2 then W(2) = 4 (each in one of the two possible states). Thus, W is generally W(N) = 2N. The entropy is $S = k \cdot \ln 2N = N \cdot k \cdot \ln 2$.

6.3.7 Boltzmann's distribution of states by energy and Arrhenius' law

In a system with *n* indistinguishable particles that can have *m* energy states, each characterized by an energy $\varepsilon_1 < ... < \varepsilon_m$ and having an associated probability $\{p_1, ..., p_m\}$, the probability of observing a certain configuration of the system $\{n_1, ..., n_m\}$ is given by the multinomial distribution (see [57]):

$$\frac{n!}{n_1!\dots n_m!} p_1^{n_1}\dots p_m^{n_m} \tag{6.9}$$

The maximum observation chance (see [77]) applied to the system subject to two constraints $(n = n_1 + ... + n_m, \varepsilon = n_1\varepsilon_1 + ... + n_m\varepsilon_m)$ is obtained from the Lagrange multiplier method (see [78]) and is found in the form of the Boltzmann distribution of particles by energy (see [79]):

$$p_i = \left(\sum_{j=1}^m e^{-\frac{\varepsilon_j}{\kappa T}}\right)^{-1} e^{-\frac{\varepsilon_i}{\kappa T}}$$
(6.10)

where T is the temperature and κ is Boltzmann's constant identified from ideal gas experiments (see [80]).

Arrhenius's law (see [81]) which gives the dependence of the rate constant (k) of a chemical reaction on temperature can be seen as a consequence of the energy distribution:

 $k = A \mathrm{e}^{-\frac{E_a}{\mathrm{R}T}} \tag{6.11}$

where k is the rate constant of a reaction, E_a is the molar activation energy (in the previous equation $\varepsilon_a = E_a/N_A$, with N_A Avogadro's number) and R the gas constant ($E_a/R = \varepsilon_a/\kappa$ in the previous equation). It can be seen that the coefficient A in the Arrhenius equation corresponds to the canonical partition function in the Boltzmann equation:

$$A \propto \left(\sum_{j=1}^{m} e^{-\frac{\varepsilon_j}{\kappa T}}\right)^{-1} \tag{6.12}$$

6.3.8 Heat of dissolution

The heat of dissolution is the change in enthalpy H associated with the dissolution of a substance in a solvent at constant pressure, with infinite dilution (Fig. 6.10).

Fig. 6.10: Dissolving NaOH in H₂O



 $NaOH(s) \implies NaOH(aq), NaOH(aq) \implies Na^{+}(aq) + HO^{-}(aq), H_2O(l) \implies H^{+}(aq) + HO^{-}(aq)$

The enthalpy of solution is most often expressed in kJ/mol at constant temperature.

Essentially it involves breaking bonds in the solute and within the solvent and forming bonds between the solute and solvent. An ideal solution has zero enthalpy of mixing. Examples:

- The dissolution of ammonium nitrate in water is endothermic. The energy released by solvating the ammonium ions and nitrate ions is less than the energy absorbed in breaking the ionic lattice of ammonium nitrate and the attractions between water molecules.
- The dissolution of potassium hydroxide is exothermic because more energy is released during solvation than is used to decompose the solute and solvent.

A series of values for the heat of dissolution are given in Tab. 6.1.

Table 6.1: Values of the heat of dissolution $(\Delta H^{\Theta}_{H_2O,25^{\circ}C})$

HCl	NH ₄ NO ₃	NH ₃	KOH	CsOH	NaCl	KClO ₃	CH ₃ COOH	NaOH
-74.84	25.69	-30.50	-57.61	-71.55	3.87	41.38	-1.51	-44.5

6.3.9 Heat of reaction

The standard enthalpy of reaction for a chemical reaction is the difference between the total molar enthalpies of the products and reactants, calculated in their standard states (Fig. 6.11).

Standard states can be defined at any temperature and pressure, so both temperature and standard pressure must always be specified.

For reactions that are completed quickly, it is often possible to measure the heat of reaction directly using a calorimeter. An example is the combustion of organic compounds by reacting with molecular oxygen (O_2) to form carbon dioxide (CO_2) and water (H_2O) .

It is also possible to evaluate the enthalpy of a reaction from the enthalpies of a number of other reactions whose sum is the reaction of interest, and these do not have to be formation reactions. This method is based on Hess's law [82], which states that the enthalpy change is the same for a chemical reaction that occurs as a single reaction or in multiple steps (Fig. 6.12).

Fig. 6.11: Reaction in H₂O



 $\begin{array}{l} MgO(s) + 2 \, HCl(aq) & \mathchoice {\longrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} MgCl_2(aq) + H_2O(l), \\ MgCl_2(aq) & \mathchoice {\longrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} Mg^{2+}(aq) + 2 \, Cl^-(aq), H_2O(l) & \Huge {\longrightarrow}{\leftarrow}{\leftarrow} H^+(aq) + HO^-(aq) \end{array}$

Fig. 6.12: Enthalpy (of reaction) is a state function





Electrochemistry deals with the production of electric current through chemical reactions and vice versa. A chemical reaction usually involves the transfer of an electrical charge from one chemical species (atom, molecule, ion) to another, see Tab. 7.1.

Table 7.1: From chemistry to electrochemistry

Reaction Remarks

Reaction	itematiks
$AgNO_3(aq) + NaCl(aq) \longrightarrow$	The phase change (liquid \longrightarrow solid) causes the equi-
\rightarrow NaNO ₃ (aq) + AgCl(s)	librium to shift to the right
$Na(g) + F(g) \longrightarrow NaF(g)$	Thermal energy allows the electron transfer: $(Na^+ + e^-) + F \longrightarrow Na^+ + (e^- + F) \longrightarrow Na^+ + F^$
$Fe \longrightarrow Fe^{2+} + 2e^- \longrightarrow Fe^{3+} + 3e^-$	Rusting is a complex and spontaneous process that occurs
$O_2 + 2 H_2 O + 4 e^- \longrightarrow 4 HO^-$	on the surface of iron in the presence of oxygen and water
$Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+$	
$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$	
$Fe(OH)_2 \longrightarrow FeO + H_2O$	
$Fe(OH)_3 \longrightarrow FeO(OH) + H_2O$	
$2 \operatorname{FeO}(OH) \longrightarrow \operatorname{Fe}_2O_3 + H_2O$	
$(+)Zn(s) Zn^{2+}(aq) H^{+}(aq) H_{2}(g)(-)$	The voltaic cell in Fig. 7.1 adapted from [2]
$(+)Zn(s) Zn^{2+}(aq) Cu^{2+}(aq) With(s)(-$	Daniell's pile in Fig. 7.2 adapted from [3]
)	

Although it also deals with the study of electrochemical processes that occur spontaneously (such as rusting), electrochemistry involves the construction and/or use of a circuit of electrical charges outside the environment in which the reaction takes place.

If water is produced from oxygen and hydrogen then the battery is non-polluting, the first being proposed in 1839 [83]. The solution is of particular interest, being included in the space program for the supply of electricity and drinking water, hydrogen and oxygen being readily available from the tanks of spacecraft [84]. A future solution is the use of proton exchange membranes (see Fig. 7.3), when water management is successful: if the water evaporates too slowly then the flow of oxygen is prevented, but if the water evaporates too quickly, the membrane will dry out and its resistance will increase (both affecting stability and efficiency).

From the point of view of the operating principle, electrochemical systems are classified as in Tab. 7.2.

Fig. 7.1: Voltaic pile: the first battery that supplied continuous electric current [2]



Fig. 7.2: Daniel's pile: battery without the release of H_2 , the first definition of the volt [3]



Fig. 7.3: The hydrogen engine



Table 7.2: Galvanic and electrolytic cells

Cell Characteristic

Galvanic Electricity is produced as a result of a spontaneous chemical reaction Electrolytic Chemical reactions occur by applying an external source of current

7.1 Electrochemical potential

The potential of a galvanic cell can be obtained using the tabulated values of the standard reduction potential (see Tab. 7.3, see §9.13 "Electrochemical Series" in [73]).

Exercise: Calculate the electrochemical potential created by the formation of NaF. *Solution*: The reaction $F + 1e^- \longrightarrow F^-$ produces a potential of 1.433 V and the reaction Na \longrightarrow Na⁺ + 1e⁻ produces a potential of 2.710 V (see Tab. 7.3). Cumulatively, $E^{\oplus}(F + Na \longrightarrow NaF) = 4.143$ V.

Half-reaction	Potential	Half-reaction	Potential
$Na^+ + 1e^- \longrightarrow Na$	-2.710 V	$Cu^{2+} + 2e^- \longrightarrow Cu$	0.342 V
$Zn^{2+} + 2e^{-} \longrightarrow Zn$	-0.762 V	$O_2 + 2H_2O + 4e^- \longrightarrow 4HO^-$	0.401 V
$Fe \longrightarrow Fe^{2+} + 2e^{-}$	-0.447 V	$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$	0.771 V
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^2$	− −0.359 V	$O_2 + 4 H^+ + 4 e^- \longrightarrow 2 H_2O$	1.229 V
$Fe \longrightarrow Fe^{3+} + 3e^{-}$	-0.037 V	$F + 1 e^- \longrightarrow F^-$	1.433 V
$2 \text{ H}^+ + 2 \text{ e}^- \longrightarrow \text{H}_2$	0.000 V	$PbO_2 + SO_4^{2-} + 4 H^+ + 2 e^- \rightarrow PbSO_4 + 2 H_2O$	1.691 V
At:			

Table 7.3: Values of the standard reduction potential (E^{Θ})

• 298.15 K & absolute partial pressure of 101325 Pa for each gaseous reactant

• effective concentration (activity) of 1 mol/L for each aqueous (aq) or amalgamated (alloyed with Hg) species & unit activity for each solvent and pure solid or liquid species

Exercise: Calculate the electrochemical potential of the Daniell cell. Solution: The reaction $Zn \longrightarrow Zn^{2+} + 2e^{-}$ produces a potential of 0.762 V and the reaction $Cu^{2+} + 2e^{-} \longrightarrow Cu$ produces a potential of 0.342 V (see Tab. 7.3). Cumulatively, $E^{\Theta}(Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu) = 1.104$ V.

Exercise: Calculate the electrochemical potential of a cell in a car battery. Solution: The battery in heat engine cars is of the Pb/acid type (see Tab. 7.4). The reaction $PbO_2 + SO_4^{2-} + 4H^+ +$ $2e^- \rightarrow PbSO_4 + 2H_2O$ produces a potential of 1.691 V and the reaction $PbSO_4 + 2e^- \leftarrow Pb + PbSO_4 + 2e^- \leftarrow PbSO_4 + 2e^- \leftarrow$ SO_4^{2-} produces a potential of 0.359 V (see Tab. 7.3). Cumulatively, $E^{\Theta}(Pb + PbO_2 + 2H_2SO_4 \longrightarrow$ $2 \text{ PbSO}_4 + 2 \text{ H}_2\text{O} = 2.050 \text{ V}.$

A rechargeable battery, such as a phone, laptop, or car battery, will operate using both principles stated in Tab. 7.2. Examples of batteries are in Tab. 7.4.

Table 7.4: Various batteries

Battery	Semi-reactions	Potential (nonstandard)	Reference
	$LiCoO_2 + C_6 \implies CoO_2 + LiC_6$	3.92 V	Fig. 2 in [85]
Li ion	$\text{LiNiO}_2 + \text{C}_6 \implies \text{NiO}_2 + \text{LiC}_6$	3.85 V	Fig. 4 in [86]
	$LiMn_2O_4 + C_6 \implies Mn_2O_4 + LiC_6$	4.04 V	Fig. 2 in [87]
Pb/acid	$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \Longrightarrow$		
	\implies 2 PbSO ₄ (s) + 2 H ₂ O(l)	2.05 V	p. 42 in [88]
Ni <i>M</i> H	$Ni(OH)_2 + M \implies NiOOH + MH$		
	M = LaCePrNdNiCoMnAl + Mg	1.27 V	Fig. 1 in [89]
Alkaline	$Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$	1.43 V	Tab. 3 in [90]

7.2 Nernst equation. Sensors

The Nernst equation (Eq. 7.1) expresses the electrochemical potential as a function of the standard potential, temperature, number of electrons involved, and activities (often approximated by concentrations) of the chemical species.

$$E = E^{\Theta} - \frac{\mathbf{R}T}{n\mathbf{F}} \ln \frac{a_{Red}}{a_{Ox}}$$
(7.1)

where E^{Θ} is the standard potential of a reaction or half-reaction (see Tab. 7.3), T is the temperature (in K), a_{Red} and a_{Ox} are the activities of the species that are reduced and oxidized respectively (the activity is 1 in the solid phase and is the fraction of the total pressure in the gas phase), R is the gas constant (Regnault [91], R = 8.31446261815324 J/molK) and F is the Faraday constant ([92], F =96485.3321233100184 C/mol) and n the number of electrons involved.

pH sensors exploit the dependence of the electrochemical potential on the concentration of hydrogen ions (Nernst's law [93], Eq. 7.1). The pH is measured using a two-electrode arrangement: an indicator electrode and a reference electrode, or a combined electrode that can perform both functions¹ (see Fig. 7.4).

Fig. 7.4: Measuring pH with a millivoltmeter



pH, or hydrogen potential, is a logarithmic scale that expresses the acidity/basicity of solutions:

$$pH = -\log_{10}a_{\rm H^+} \tag{7.2}$$

pH can be measured using the Nernst equation (Eq. 7.1), in which case a reference electrode is used (see Fig. 7.4), or, an indicator (see Fig. 7.5) if only its approximate value is necessary or just the point at which it suddenly changes its value.

	Indicator	Color low	Range	Color high
	Picric acid		0.6-1.3	
Th	ymol 'blue'		0.6-1.3	
2,4-di	nitrophenol		0.6-1.3	
Met	hyl 'yellow'		2.9-4.0	
Bromopl	nenol 'blue'		3.0-4.6	
1	Congo 'red'		3.0-5.0	
Met	hyl 'orange'		3.1-4.4	
Bromocr	esol 'green'		3.8-5.4	
Ν	Methyl 'red'		4.3-6.2	
	Azolitmin		4.5-8.3	
Bromocre	sol 'purple'		5.2-6.8	
Bromoth	ymol 'blue'		6.2-7.6	
]	Phenol 'red'		6.4-8.0	
Tol	uylene 'red'		6.8-8.0	
	Cresol 'red'		7.2-8.8	
Naphtholphth	alein 'blue'		7.3-8.7	
Th	ymol 'blue'		8.0-9.6	
Phen	olphthalein		8.3-10.0	
Thym	olphthalein		8.3-10.0	
Alizari	ine 'yellow'		10.1-12.0	
Picrylnitrom	ethylamine		10.8-13.0	
	Cvanidin	<3.0	7.0-8.0	>11

Fig. 7.5: pH Indicators

For the effect of pH use Fig. 7.6 as a guide.

¹see http://en.wikipedia.org/wiki/Glass_electrode



Hydrogen atoms are very small, and H^+ ions are even smaller, so in some situations even solid-state pH can be meaningful (see Fig. 7.7).

Fig. 7.7: Water pH as a function of temperature



A temperature sensor (Fig. 7.8) will exploit the dependence of the electrochemical potential on temperature (Nernst's law [93], Eq. 7.1).

Fig. 7.8: Electrochemical temperature sensor (v. [4])

Usually in analytical chemistry the concentration and associated chemical activity are expressed in logarithmic units, but this time the logarithm is in base 10 (see a_{H^+} in Eq. 7.2) so the transformation is useful:

$$\frac{R}{F}\ln(x) = \frac{R}{F}\ln(10)\log_{10}(x)$$
(7.3)

where R, F and ln(10) are all constants ($\frac{R}{F}$ ln(10) $\approx 1.9842143110777 \cdot 10^{-4} \text{ V/K}$).

When equilibrium is established, the electrochemical potential is zero. Referring again to Eq. 7.1, at equilibrium E = 0 and if T = 298.15 K ($t = 25^{\circ}$ C, standard temperature conditions):

$$E^{\Theta} = \frac{\mathbf{R}T}{n\mathbf{F}} \ln \frac{a_{Red}}{a_{Ox}} \implies \frac{a_{Red}}{a_{Ox}} = \mathrm{e}^{n\frac{F}{\mathbf{R}T}E^{\Theta}} = 10^{n\frac{F}{\mathbf{R}T}\ln(10)E^{\Theta}} \approx 10^{\frac{nE^{\Theta}}{0.05916\ \nabla}}$$
(7.4)

Example: Calculate the equilibrium constant for the reaction $\text{Co} + \text{Ni}^{2+} \longrightarrow \text{Co}^{2+} + \text{Ni}$ under standard temperature conditions $(E^{\Theta}(\text{Co}^{2+} + 2e^{-} \rightarrow \text{Co}) = -0.280 \text{ V}, E^{\Theta}(\text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni}) =$ -0.257 V). Solution:

 $E^{\Theta}(\text{Co} + \text{Ni}^{2+} \Longrightarrow \text{Co}^{2+} + \text{Ni}) = E^{\Theta}(\text{Ni}^{2+} + 2e^{-} \longrightarrow \text{Ni}) - E^{\Theta}(\text{Co}^{2+} + 2e^{-} \longrightarrow \text{Co}) = 0.023 \text{ V}$ Using Eq. 7.4, $\frac{a_{\text{Co}^{2+}}}{a_{\text{Ni}^{2+}}} \approx 10^{\frac{2.0023 \text{ V}}{0.05916 \text{ V}}} = 5.9916$. Using the definition of the equilibrium constant Eq. 6.1, $K(\text{Co} + \text{Ni}^{2+} \Longrightarrow \text{Co}^{2+} + \text{Ni}) = \frac{a_{\text{Co}^{2+}}}{a_{\text{Ni}^{2+}}} = 5.9916$. Application. The chemical laser uses electrical energy to produce a very energetic chemical

reaction that emits radiation in the form of light (see Fig. 7.9).



Fig. 7.9: HF chemical laser

7.3 Electrolysis. Faraday's Law

Electrolysis is the main process for separating and purifying elements from ores and mixtures. Examples: electrolysis of NaCl (Fig. 7.10 and Fig. 7.11), CaCl₂ (Fig. 7.12) and Al₂O₃ (Fig. 7.13).



Fig. 7.10: Electrolysis of NaCl from melt





Fig. 7.12: Obtaining Ca by electrolysis from the melt



Fig. 7.13: Obtaining Al from alumina (Al₂O₃)



The phenomenon of electrolysis occurs when the applied potential difference exceeds the value of the electrochemical potential of the created cell. Tab. 7.5 contains the equations of the chemical reactions and the potential required for electrolysis.

The carriers of electric charge in solutions are ions, which makes the intensity of the electric current and the amount of substance deposited two correlated quantities (Faraday's law [98], Eq. 7.5).

Table 7.5: Examples of electrolysis

Fig.	Half-reactions	E [⊕] in V	Reference
7.10	$2 \operatorname{Na}^{+}(l) + 2 \operatorname{Cl}^{-}(l) \longrightarrow 2 \operatorname{Na}(l) + \operatorname{Cl}_{2}(g)$	-4.06827	Downs [94]
7.11	$2 \operatorname{Na}^+(aq) + 2 \operatorname{Cl}^-(aq) + 2 \operatorname{H}_2O(l) \longrightarrow \operatorname{Cl}_2(g) + \operatorname{H}_2(g) + 2 \operatorname{Na}OH(l)$	-2.18597	Castner [95]
7.12	$Ca^{2+}(l) + 2 Cl^{-}(l) \longrightarrow Ca(l) + Cl_2(g)$	-4.22627	Yamaguchi [96]
7.13	$4 \operatorname{Al}^{3+}(l) + 6 \operatorname{O}^{2-}(l) + 3 \operatorname{C}(s) \longrightarrow 4 \operatorname{Al}(l) + 3 \operatorname{CO}_2(g)$	-1.72707	Haupin [97]

For a process in which ions are discharged and then precipitated at the cathode:

$$(-): A^{z+} \longrightarrow A + ze^{-} \text{ with } It = Q = \eta z N e^{-} \text{ and } \frac{N}{N_A} = \frac{m}{M} \implies m = \eta \frac{M}{N_A} \frac{It}{ze^{-}} = \eta \frac{MIt}{zF}$$
(7.5)

where Q the total amount of electricity transported through the solution establishing a current intensity I in time t of a number of N ions having charge z (A^{z+}), mass m, and molar mass M, and where N_A Avogadro's number (N_A = 6.02214076 $\cdot 10^{23} \text{ mol}^{-1}$), e^- the electric charge of an electron ($e^- = 1.602176634 \cdot 10^{-19} \text{ C}$) and F (F = e^-N_A) is Faraday's constant (F $\approx 9.648533212 \cdot 10^4 \text{ C/mol}$), and η the efficiency (yield) of energy conversion ($0 < \eta < 1$).

When $\eta = 1$, the relation 7.5 allows the quantitative determination of the mass deposited at the cathode (*m*) as a function of the current intensity (*I*) and time (*t*), but this is an idealization, since part of the electrical energy is dissipated in heat by heating ($\eta < 1$).

Exercise: A square Fe sheet with side l of 1 m is introduced into a 10 l electrolytic bath containing 5.5 kg ZnSO₄ · 5 H₂O, 0.25 kg Al₂(SO₄)₃ · 18 H₂O, 0.75 kg Na₂SO₄ · 10 H₂O and 25 g dextrin. Calculate the galvanizing current intensity and the mass of zinc theoretically deposited at the cathode (on the sheet). The source voltage is known as $U = 1.8 \div 2$ V, the nickel plating time, t = 10 min. and the optimal current density $j = 3.5 \div 5$ A/dm². Solution: Zinc plating takes place at the cathode, Zn²⁺ + 2 e⁻ \longrightarrow Zn. In Eq. 7.5 z = 2, M(Zn) = 65.38 g/mol, $\eta = 1$, I = jS. Substituting numerically, $I = 700 \div 1000$ A, $m = 142.3 \div 203.3$ g.

In mass spectrometry (Fig. 7.14) the position (d_x) at which the cation is detected is a function of the mass/charge ratio $(m/q \text{ v. equations of motion 7.6}, [m,q,\tilde{v},B,U,d_y] \rightarrow v_x \rightarrow v_y \rightarrow t_1 \rightarrow [d_x])$.

Fig. 7.14: Separation of cations by mass/charge ratio in mass spectrometry



$$v_0 \leftarrow \sqrt{\frac{2hc\tilde{v}}{m}}, v_x \leftarrow v_0 + \frac{qU}{md_x}t_1, v_y \leftarrow qB\int_0^{t_1}v_x dt, d_x = \int_0^{t_1}v_x dt, d_y \leftarrow \int_0^{t_1}v_y dt$$
(7.6)



8.1 Alkali metals (Li, Na, K, Rb, Cs, Fr)

8.1.1 Chemical properties

They are placed in the first group of the periodic table. In air and oxygen they are reactive: Na and K lose their luster quickly when exposed to air, Rb and Cs burn in air. Li, Na, K are kept covered with paraffin, Rb, Cs, Fr are kept in evacuated glass vials. They release hydrogen upon contact with water, and the reaction becomes more energetic from Li to Fr: $M(s) + HOH(1) \rightarrow M^+(aq) + HO^-(aq) + \frac{1}{2}H_2(g)$. With other metals under hot conditions they lead to alloys or intermetallic compounds. In cold conditions, Hg + Na $\rightarrow Na(Hg)$ - sodium amalgam - with a solid state at room temperature. Combinations with O₂:

•
$$\text{Li} + \text{O}_2 \longrightarrow \text{Li}_2\text{O}$$

• Na + O₂
$$\longrightarrow$$
 Na₂O $\xrightarrow{t^{0}C}$ Na₂O₂

•
$$K + O_2 \longrightarrow KO_2$$

In air, side reactions occur: $Na_2O + H_2O \longrightarrow NaOH$, $NaOH + CO_2 \longrightarrow Na_2CO_3$.

8.1.2 Uses

Important uses include:

- NaCN & KCN in electrolytic processes (see Monatana Red);
- Na₂O₂ & Li₂O₂ air freshening in closed spaces (Na submarines, Li spacecraft, ρ (Li) = 0.55 ρ (Na)): Na₂O₂(s) + CO₂(g) \longrightarrow Na₂CO₃(s) + $\frac{1}{2}$ O₂(g)
- TiCl₄ + Na is a thermal agent in nuclear reactors high thermal conductivity, low melting point
- monochromatic lamps based on Na, K, ... vapors
- alloys as alloying elements in small quantities
- Na-K in liquid thermometers for high temperatures
- Rb, Cs: cathodes in solar cells
- Li in rechargeable batteries
- Na in detergents

Fig. 8.1: Detergents: trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium tetraphosphate



Fig. 8.2: Dibenzo-18-crown-6 - alkali complexes



8.2 Alkaline-slag metals (Be, Mg, Ca, Sr, Ba, Ra)

8.2.1 Perovskites

It is one of the most abundant structural families, with a huge number of compounds with a very wide range of applications [99]. With the discovery of perovskite solar cells, perovskites have experienced great interest [100].

Fig. 8.3: CaTiO₃ - the representative of perovskites



 $M^{II}M^{IV}O_3, M^{IV}$: Ti, Zr, Hf; M^{II} : Ca, Sr, Ba, Zn $M^{I}M^{V}O_3, M^{V}$: Nb, Ta; M^{I} : Li, Na, K $M^{II}M^{V}O_6, M^{V}$: Nb, Ta; M^{II} : Ca, Sr, Ba

8.2.2 Spinels

Spinel looks like glass but has significantly higher compressive strength and has military and commercial applications. [101].

8.2.3 Applications

Magnesium plays an essential role for plants, being the central ion of chlorophylls.

Fig. 8.4: MgAl₂O₄ - representative of spinels



M^{II}*M*^{III}²O₄, *M*^{III}: Al, Fe^{III}, Co^{III}, Cr^{III}, Mn^{III}, Ga; *M*^{II}: Mg, Fe, Co, Ni, Zn, Cd, Cu

Fig. 8.5: Chlorophylls



Magnesium alloys have many uses as replacements for heavier iron components in automobiles (see Fig. 8.6 and Fig. 8.7).

Magnesium oil massage provides a powerful medical treatment against muscle contractures.

X-rays are electromagnetic radiation with higher energy than visible light and can pass through most objects, including the body. In medicine, medical X-rays are used to generate images of tissues and structures inside the body. Due to its low density and atomic mass, beryllium is relatively transparent to X-rays, making it useful in windows for X-ray equipment and components of particle detectors (see Fig. 8.9).

James Webb's primary mirror (see Fig. 8.10) is of 18 hexagonal mirror segments made of gold-plated beryllium giving a light-collecting area of about 25 m² being designed to observe from long-wavelength visible light (red) through mid-infrared (0.6–28.5 μ m).

When added as an alloying element to Al, Cu, Fe, and Ni, Be improves many physical properties (see Fig. 8.11).

The uses of Ca are diverse, including paints, dust suppression on unpaved roads, gypsum (with gypsum), fertilizers, welding in metal structures, food additives, medicines, lime and mortar for construction (see Fig. 8.12).

A healthy diet is rich in vitamins, calcium and magnesium. The recommended daily intake is approximately 0.25 g Mg and 1 g Ca with slight increases with age (see Fig. 8.13).



Fig. 8.6: Mg alloys for vehicle parts

1 12. 0.7. Composition and characteristics of Mig anoys

						Data	N	Am. D	ie Cas	t. Ass.	A-3-1	0-06 standard
Mechanical	proper	ties	Manuf	actural	oility _I	RE	Rare earths (50% Ce, 25% La, 15% Nd)					
Density Vohiala (Sefet				I	S	Imp	pact str	ength	(J)			
Density venicle		ural -	salety		HD	Hardness, Brinell hardness number						
Homogonoity - Cost			Cost	ΥS	Yie	ld stre	ngth (1	MPa)				
Homogeneity component Cost				I	El	Elo	ngation	n (%)				
Chemical resistance Working regime				eime 🛛	ГΕ	The	ermal e	xpans	ion (µn	n/m·K))	
		-]	ГС	The	ermal c	onduc	tivity (W/m·ł	K)
	Alloy	of Mg	AZ81	AZ91	AM60	AM	[50	AM20	AS41	AE42	AE44	
	()	Al	8	9	6	5		2	4	4	4	
	2	Zn	0.7	0.7	6							
	ves	Mn	0.2	0.2	0.3	0.	4	0.6	0.4	0.3	0.4	
	litiv	Si							1			
	Ado	RE								2.5	4	
	ł	ΣOth	< 0.07	< 0.15	< 0.35	<0.	35	< 0.25	< 0.20	< 0.30	< 0.03	
		IS	N/A	2.2	6.1	9.	5	N/A	4.1	5.8	5.5	
	ies	HD	72	75	62	57	7	47	75	57	56	
	erti	YS	150	160	130	12	0	105	140	140	140	
	top	El	3	3	7	8		10	6	9	9	
	P	TE	25	25	25.6	20	5	26	26.1	26.1	26.2	
		TC	51	72	62	62	2	60	68	68	68	

Fig. 8.8: Benefit of Mg Oil for the Body



Fig. 8.9: Be X-ray Window (FMB Oxford, 2009)



Fig. 8.10: James Webb Space Telescope (Launch Date: 25.12.2021)



Fig. 8.11: F-35B (electrical and mechanical components with beryllium alloys)



8.3 The d-block

The d-block metals are characterized by a multitude of oxidation states (see Fig. 8.14).

The human eye detects wavelengths from about 380 to about 750 nm. Opsins are responsible for detecting light by absorbing it (see Fig. 8.15).

When sunlight falls on the surface of objects, some of this light is absorbed. When absorption is almost total, we see objects in black color. When reflection is almost total, we see objects in white. When red color is absorbed, we see the complementary color - green (see Fig. 8.16).

Due to the very frequent electronic levels in the ground state but especially in the excited state - in chemical combinations - the transitions between these levels are frequently in the visible range - which makes the compounds of these metals colored or even intensely colored (see Fig. 8.17).

The presence of electronic orbitals "d" (5) together with those of type "p" (3) and "s" (1) gives a

Fig. 8.12: Ca Uses



Fig. 8.13: Foods rich in Ca and Mg



Fig. 8.14: Oxidation states in the d-block

P-4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
e	d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	d ¹⁰ s ¹	$d^{10}s^2$
O.N.				Ι					Ι	
	II	II								
	III									
		IV								
			V	V	V	V	V			
				VI	VI	VI				
					VII					
P-5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
P-6	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
P-7	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn



Fig. 8.15: Transitional elements - color source





Fig. 8.17: The color of transition ions $(M^{n+}, M \in \text{Block "d"})$

Compound/Ion	Color	Name	#R−G−B
(MnO ₄) ³⁻ (aq)		DarkBlue	#00008B
Cu2+ _(aq)		MediumBlue	#0000CD
(VO) 2+ (aq)		Blue	#0000FF
(MnO ₄) ²⁻ (aq)		DarkGreen	#006400
Cr ³⁺ (aq)		Teal	#008080
$CuCl_2 \cdot 2H_2O$		DarkTurquoise	#00CED1
Fe ²⁺ (aq)		DodgerBlue	#1E90FF
$(Cu(NH_3)_4)^{2+}_{(aq)}$		RoyalBlue	#4169E1
(Ni(NH ₃) ₆) ²⁺ (aq)		MediumSlateBlue	#7B68EE
V ³⁺ (aq)		DarkSeaGreen	#8FBC8F
Ni ²⁺ (aq)		LightGreen	#90EE90
(MnO ₄) ⁻ (aq)		DarkViolet	#9400D3
NiCl ₂ ·6H ₂ O		PaleGreen	#98FB98
(CuCl ₄) ²⁻ (aq)		YellowGreen	#9ACD32
Fe ³⁺ (aq)		Chocolate	#D2691E
V ²⁺ (aq)		Lavender	#E6E6FA
Ti ³⁺ (aq)		Violet	#EE82EE
Zn ²⁺ (aq)		AliceBlue	#F0F8FF
CoCl ₂ · 6H ₂ O		Magenta	#FF00FF
(Cr ₂ O ₇) ²⁻ (aq)		Orange	#FFA500
$MnCl_2 \cdot 4H_2O$		LightPink	#FFB6C1
Co ²⁺ (aq)		Pink	#FFC0CB
$(Co(NH_3)_6)^{3+}_{(aq)}$		Gold	#FFD700
(VO ₂) ⁺ (aq)		Yellow	#FFFF00

surplus of degeneracy and the possibilities of electronic transitions on close energy levels multiply significantly. Visible light corresponds energetically to these transitions. This is the reason why transition metal ions are colored, and their colors are among the most diverse, and change easily (see Fig. 8.18).

Ligands	Co ³⁺ complex	Absorbed	Seen
6(I ⁻)	$[Co(I)_6]^{3-}$	800 nm	pale yellow
6(Br)	[Co(Br) ₆] ³⁻	770 nm	yellow
6(Cl ⁻)	[Co(Cl) ₆] ³⁻	740 nm	lime
6(F)	$[Co(F)_6]^{3-}$	700 nm	green
6(HO ⁻)	[Co(OH) ₆] ³⁻	650 nm	sky blue
4(OH ₂); 2(HO ⁻)	$[Co(OH_2)_4(OH)_2]^{1+}$	620 nm	
6(H ₂ O)	$[Co(OH_2)_6]^{3+}$	600 nm	violet
5(NH ₃); 1(Br)	$[Co(NH_3)_5(Br)]^{2+}$	540 nm	brown
5(NH ₃); 1(Cl)	$[Co(NH_3)_5(Cl)]^{2+}$	522 nm	red
5(NH ₃); 1(OH)	$[Co(NH_3)_5(OH)]^{2+}$	502 nm	carmine
5(NH ₃); 1(OH ₂)	[Co(NH ₃) ₅ (OH ₂)] ³⁺	487 nm	orange
6(NH ₃)	$[Co(NH_3)_6]^{3+}$	472 nm	gold
5(NH ₃); 1(NO ₂ ⁻)	$[Co(NH_3)_5(NO_2)]^{2+}$	456 nm	yellow
6(NO ₂ ⁻)	[Co(NO ₂) ₆] ³⁻	365 nm	light yellow
6(NC ⁻)	[Co(CN)6]3-	310 nm	pale yellow

Fig.	8.18	: Co	ions
<u></u>			

The alloy 90%Ti, 6%Al, 4%V (4.43 g/cm³) has good mechanical properties and is used for gas tanks (H₂, O₂, F₂) and missiles (see Fig. 8.19)



Fig. 8.19: F2 fighter jet - Ti and alloy uses

Pigments (in the form of powders or powders) are almost insoluble and chemically unreactive in water or other media. Their coloring ability is given by the efficiency (measured in number of atoms out of their total) and the intensity (measured in number of lines per atom) with which radiation of a certain wavelength is emitted in the presence of light. Chromium pigments are known for their strength (see Fig. 8.20).

High-speed steels are designed for cutting tools and maintain their cutting properties at high cutting speeds, up to temperatures generated in the cutting zone of 550-600 $^{\circ}$ C (see Fig. 8.21).

Technetium: Technetium-99m (Z = 43, A = 99, metastable) is used in 20 million diagnostic nuclear medicine procedures each year. 85% of diagnostic nuclear medicine imaging uses it as a radioactive tracer (see Fig. 8.22).

The platinum group metals have similar physical and chemical properties and tend to occur together in the same mineral deposits. Their distribution follows a Poisson distribution (see Fig. 8.23).

Hemes are a molecular component of hemoglobin that contains iron bound to a porphyrin ring that binds O_2 and CO_2 in the bloodstream. The most abundant are hemes B and A (see Fig. 8.24).

Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the concentration of the chemical in the environment. Examples of toxic

Fig. 8.20: Chromium Pigments



Fig. 8.21: Cr-W-Co-C 'super hard high-speed tool steel'

С	Cr	W	Mo	V	Co	Si	Mn	Fe
1.7-4.1%	3-10%	1-20%	1-15%	1-15%	≤15%	≤2%	≤1%	remaining
Carbon	0.1≤C-	Ceq≤0.	6; Ceq=	=0.06C	r+0.03	3W+(0.063	Mo+0.2V
Molybdenum 18% W+2Mo 40%								
Steel	(88%-9	98%) at	ove mi	xture a	nd (2-1	2%)	G1, C	G2, or G3
G1	nitrides	s of M,	M= Ti,	V, Zr,	Nb, Hi	f, Ta		
G2	carbide	es of M	, M= Ti	i, V, Zr	, Nb, H	lf, Ta		
G3	3 carbonitrides of M, M= Ti, V, Zr, Nb, Hf, Ta							
Hardness	\geq HRC	71 (AS	TM E1	8 & EN	I ISO (6508)		
USPTO	US488	0461 (1	Norima	sa UCH	IIDA, I	Nove	mber	14, 1989)

Fig. 8.22: CT (Computer Tomograph)



bioaccumulants are: Hg, Cd (behaving similarly to Zn), CO (behaving similarly to O_2), and polychlorinated biphenyls (see Fig. 8.25).









8.4 F-block

Because they have an almost perfect similarity of chemical and electrochemical properties, separating the elements of the actinide and lanthanide groups, one by one, in pure form, is very difficult to achieve. The first attempts were based on separation by fractional crystallization of double salts of nitrates, hydroxides or fractional decomposition of oxalates - these processes were long and approximately 20,000 operations were required to obtain pure samples of a single element. Today, separation is easier thanks to the advent of ion exchangers (see Fig. 8.26).

There is a pronounced tendency for lanthanide ions to have unpaired f electrons, which leads to a magnetic moment. The maximum number of unpaired electrons is 7, in Gd^{3+} , but the largest magnetic moments occur in Dy^{3+} and Ho^{3+} (see Fig. 8.27).

The biochemical function of 1FCK is cell membrane destabilizing activity and the biological process involved is the negative regulation of the development of cells involved in the destruction of bone tissue (see Fig. 8.28).

U enrichment is achieved technologically, through isotopic separation processes. Increasing the content in fissile isotope is necessary in order to use the enriched fuel for nuclear fission in nuclear power reactors or nuclear bombs (see Fig. 8.29).

In a constant magnetic field, a particle with electric charge and mass is acted upon by a force perpendicular to the plane defined by the velocity and field vectors. If the initial velocity and the magnetic field are in perpendicular directions, the particle thus moves in a circular path. The perpendicular magnetic field passing vertically through the electrodes of a cyclotron forces the





Fig. 8.26: The f-block: difficult separation



ions to move in a circular path, so that they repeatedly pass through the narrow gap between two electrodes. A high-frequency alternating potential difference applied between the two metal electrodes generates a uniform electric field in this space. The oscillation frequency of the applied



Fig. 8.27: Lantanides - strong magnets

Fig. 8.28: Diceric lactoferrin - 1FCK



Fig. 8.29: Uranium enrichment - nuclear energy



voltage is applied so that the ions are accelerated (see Fig. 8.30).

In fission, larger atoms are split into smaller atoms. Fusion combines two lighter atoms to form a heavier atom (see Fig. 8.31).



Fig. 8.30: Cyclotron - synthesis of new chemical elements

Fig. 8.31: Fission and fusion





9.1 General

Ceramics are classified by use into (see Fig. 9.1):

- Structural (for construction) bricks, pipes, flooring and tiles
- Refractory furnace linings, gas-fired radiants, crucibles for steel and glassmaking
- Earthenware cutlery, cookware, earthenware, other household ceramic products and sanitary ware
- Technical (engineering, advanced, special) used in space shuttles, rocket nose cones, gas burner nozzles, ballistic protection, UO₃ vanes as nuclear fuel, biomedical implants, jet turbine blade coatings on engines, ceramic brake discs

Fig. 9.1: Types of ceramics



Ceramics are classified by composition into:

- Oxides; e.g. alumina, beryl, ceria, zirconia
- Non-oxides: carbides, borides, nitrides, silicons
- Composite materials: Particle-reinforced, fiber-reinforced, combinations of oxides and non-oxides

The formation of BeO from Be and O_2 releases more energy per mass of reactants for a chemical reaction, close to 24 MJ/kg (see Fig. 9.2).

As a result, it has a special stability under very energetic conditions (see Fig. 9.3).

9.2 High voltage insulators

Transporting electrical energy over long distances requires its conversion to high voltage. High-voltage insulators must have very good electrical and mechanical properties (see Fig. 9.4).

The composition of low-voltage porcelains does not differ much from that for high voltage (Tab. 9.1). They are used as fuses, lamp sockets, and handles. The advantage of ceramic insulators,

Fig. 9.2: BeO structure



Fig. 9.3: Nuclear reactor



Fig. 9.4: Anchoring device for high-voltage wires (220 kV)



which frequently indicates their use, is their superior electrical properties, the absence of cracking or deformation under stress at room temperature, and greater resistance to environmental changes. One of the great advantages of ceramics as insulators is that they are not sensitive to minor changes in composition, manufacturing technique, and firing temperature.

Ore	Feldspar	Quartz	Clay
Composition	KAlSi ₃ O ₈ + NaAlSi ₃ O ₈ + CaAl ₂ Si ₂ O ₈	SiO ₂	Al ₂ Si ₂ O ₅ (OH) ₄
SiO ₂	43÷69 %	$\geq 98~\%$	50÷70 %
Al_2O_3	18÷37 %	$\leq 1 \%$	20÷35 %
Na ₂ O	0÷20 %	$\leq 1 \%$	$\leq 1 \%$
K ₂ O	0÷17 %	$\leq 1 \%$	$\leq 1 \%$
CaO	0÷12 %	$\leq 1 \%$	$\leq 1 \%$

Table 9.1: The composition of porcelain for high voltage

Fig. 9.5: SiO₂



9.3 Feroelectrics

These materials combine good dielectric constants with low electrical loss factors. If a ferroelectric is placed between the plates of a capacitor, and the intensity of the electric charge field is increased, the resulting charge exhibits hysteresis cycles (see Fig. 9.6⁻¹). The diagram represents the applied

Fig. 9.6: Hysteresis cycle



field (*H*) on the abscissa and the induced magnetization (*B*) on the ordinate. From the point without magnetic conditions (0) the relationship between H and B evolves as an S-shaped curve (with an inflection point). At the point of maximum applied magnetic intensity H_S , the induced magnetization is $+B_S$. If the field now applied decreases, the magnetization evolves on curves 2, 3 and 4, intersecting the ordinate at B_R (remanent magnetization), the abscissa at $-H_C$ (cancellation of the residual magnetization field intensity) and if the magnetization continues $-H_S$ will then be $-B_S$. Re-applying now the increasing magnetic field will determine the magnetization that evolves on curves 5, 6 and 7, with the same meaning for the points $-B_R$, $+H_C$ and $+B_S$. Even if no

¹Hysteresis (or lagging behind) is the phenomenon by which the state of a system induced by a certain cause depends not only on the magnitude of the cause but also on the previous states through which the system has passed. The term is used to describe the behavior of some magnetic materials, in which the magnetization at a given time depends both on the applied magnetic field and on the previous magnetization states.

magnetic field is applied for a long time, the curve from 0 to $+B_S$ will never be followed by the ceramic material unless it is demagnetized. This can be achieved, for example, by heating above the Curie temperature ². The second quadrant, or demagnetization curve, is very important for materials used in the manufacture of permanent magnets.

Many ferroelectric materials have a perovskite structure (see Fig. 9.7).





9.4 Ferromagnets and Ferrites

Ferromagnetic materials possess an irreversible relationship between the applied field H and the induced magnetization B and this causes hysteresis.

When not magnetized, the magnetic field produced is random. When partially magnetized, there is some alignment, but not total. Only when magnetically saturated are all fields aligned (see Fig. 9.8).





Ferrites are light magnetic materials with a spinel structure: MFe_2O_4 where *M* can be Mg, Ni, Co, Cd, Zn or Mn (see Fig. 9.9). Ferrites are used for antenna wires, magnetostrictive materials, memory cores, discharge components in cathode ray tubes, and transformers. They must have

²The Curie temperature is the temperature at which a material loses its magnetic properties
Fig. 9.9: Computer memories: $Mn_{0.25}Zn_{0.75}Fe_2O_4 \xrightarrow{(optim.)} Mn_xZn_{1-x}Fe_{2+\delta}O_4$



both good physical and electrical properties, and these properties must be uniform both throughout the mass and from one component to another. Special ferrites with a square hysteresis shape (see Fig. 9.10) are used as memory elements in high-speed computers.





9.5 Permanent Magnets

 $Pb(Fe,Mn)_{12}O_{19}$ has long been known to have magnetic properties (see Fig. 9.11). This mineral is still the basis of many permanent ceramic magnets today.

9.6 Radioceramics, piezoelectrics, pyroelectrics & ferroelectrics

Several types of ceramics have been manufactured capable of delivering high-frequency radio wave fluxes with minimal distortion. The materials used are alumina, corundite and sintered silicon oxide (see Fig. 9.13).

It is essential that the porosity, if any, is distributed uniformly and, therefore, have a very low tolerance surface. (see Fig. 9.14).

 $NaNbO_3$ is an antiferroelectric while $KNbO_3$ is a ferroelectric. The typical composition of an actuator includes in addition to the two LiNbO₃, SrTiO₃ and BiFeO₃.





Fig. 9.12: Strong Magnets

NdFeB strong permanent magnets								
Nd ₂ Fe ₁₄ B	Remanence	Coercivity	Intrinsic H	$B_H max$	t max	Comparison		
(std)	(B_r, T)	H _{cB} (kA/m)	H_{cJ} (kA/m)	kJ/m ³	°C	Magnet	kA/m	Т
N35	1.17-1.21	868	955	263-287	80	BaFe ₁₂ O ₁₉	360	0.4
N38	1.21-1.25	899	955	287-310	80	Co10Fe7Ni4Ti2CuAl	50-150	0.6
N40	1.25-1.28	923	955	302-326	80	Fe ₅₀ Ni ₁₀ Al ₂ Nb	50	1.2
N42	1.28-1.32	923	955	318-342	80	MnBi	370	0.5
N45	1.32-1.38	876	955	332-366	80	Ce(CuCo) ₅	450	0.7
N48	1.38-1.42	835	876	366-396	80	SmCo ₅	1000	0.8
N50	1.38-1.45	835	876	374-406	80	Sm ₂ Co ₁₇	600	1.1
N52	1.44-1.48	836	876	390-422	80	Nd ₂ Fe ₁₄ B	1100	1.2
N35M	1.17-1.21	868	1114	263-287	100			
N38M	1.21-1.25	899	1114	287-310	100			
N40M	1.25-1.28	923	1114	302-326	100			
N42M	1.28-1.32	963	1114	318-342	100			
N45M	1.32-1.38	995	1114	332-366	100			
N48M	1.37-1.42	1018	1114	358-390	100			
N50M	1.40-1.45	1042	1114	374-406	100			
N28AH	1.04-1.10	772	2786	207-231	220			
N30AH	1.08-1.17	812	2786	223-255	220			
N33AH	1.14-1.22	851	2786	247-279	220			
N35AH	1.17-1.25	876	2786	263-295	220			

Fig. 9.13: Typical composition for a radioceramic





9.7 Conductive Ceramics

One of the best-kept secrets of Corning Glass Co was the tinning material for the oxide electrodes used in kinescope tubes (1952, 1963, 1966). Today, conductive ceramics have a wide variety of applications (see Fig. 9.15, Fig. 9.16, Fig. 9.17).





Resistors with large positive temperature coefficients find many applications in thermostats and thermal switches. Barium titanate doped with a rare metal is used in the manufacture of fine grains, which are then sintered into ceramics. For this, lanthanum is used in amounts of 0.001-0.005 mole percent. Barium titanate can be precipitated, then mixed with rare metals and heated in a controlled atmosphere to 1400 $^{\circ}$ C.

Metalloid electric heating elements consist of silicon carbide and molybdenum oxides. In the form of a rod or spiral tube, CSi elements are widely used for high-temperature electric heating. They can be used at temperatures of 1600 °C for short periods and at 1500 °C, below which they work continuously. $MoSi_2O_6$ heating elements can be used at temperatures of 100-200 °C above the limit of SiC elements and are used for parts exposed to high temperatures, in furnaces. Heating elements such as zirconium oxide and thorium oxide become conductive when heated to red heat. Furnaces constructed with these elements are capable of temperatures of 2000°C in air.





9.8 Refractory ceramics

A refractory material retains its strength at high temperatures. High-temperature ceramics are good choices for several extreme applications: thermal protection materials on hypersonic aerospace vehicles or reusable atmospheric re-entry vehicles, specific propulsion components, furnace elements, refractory crucibles, etc. This family of ceramic compounds is made of borides, carbides, nitrides such as ZrB₂, HfB₂, ZrC, HfC, TaC, HfN which are characterized by high melting points.

Compound	Density (g/cm ³)	Melting (°C)		
HfC	12.8	3900		
TaC	14.5	3800		
ZrC	6.6	3400		
HfN	13.9	3385		
HfB_2	11.2	3380		
ZrB_2	6.1	3245		
TiB ₂	4.5	3225		
TiC	4.9	3100		
TaB ₂	12.5	3040		
ZrN	7.3	2950		
TiN	5.4	2950		
TaN	14.3	2700		
SiC	3.2	2545*		
* dissociates				

Fig. 9.10. Heale	Fig.	9.18:	Heater
------------------	------	-------	--------



By definition, a polymer is a large molecule (or macromolecule) made up of repeating units called monomers. The formal definition is therefore

 $Polymer = (Monomer)_n$

(10.1)

Regarding the repeating unit, if it is repeated:

- One structural unit \rightarrow homopolymers
- Two structural units \longrightarrow copolymers
- Three structural units \longrightarrow terpolymers

According to the number of repetitions, *n*, polymers are:

- Short: n ≤ 50 (terminology for amino acid sequences: peptides for n ≤ 50; proteins for n > 50);
- Usual: $10^3 \le n \le 10^4$;
- Long: $10^5 < n$

Polymers most often exist as mixtures:

- Both natural and synthetic polymerization lead to mixtures of polymers of different sizes
- Polymers of different lengths but made up of the same monomers are called homologs, and their "molecular mass" is an average value for the mixture of polymers

Referring to arrangements of two repeating units (copolymers):

- By *alternation* of monomer units: A-B-A-B-A-B-etc; general formula: [AB]_m;
- *periodic* groups of monomer units: AAABBAAABBetc; general formula: $[A_m B_n]_p$;
- *random* or statistically determined arrangement of monomer units; no general formula, only proportions and arrangement rules (AABAAABABBAetc);
- *block* groups of monomer units: AAAAAABBBBetc; general formula: A_mB_netc;
- Grafted: (grafted polymers): following one of the above rules but with a tree structure with/without cycles (Fig. 10.1);

Fig. 10.1: Graft copolymers



Polymers only in rare cases possess a regular alternation of two monomers and even more rarely a deterministic length. Therefore, polymers in the solid state are, generally, amorphous substances. Certain properties have a clear rule of variation with increasing number of units *n*:

- impact resistance and viscosity increase;
- chemical stability decreases;
- other properties are strongly dependent on the type of monomers; for example, the boiling point of alkanes, silanes and silicones increases with the length of the chain;

1

Examples of polymers:

- Alkanes: C_nH_{2n+2} ; derivatives of alkanes: C_nR_{2n+2} , R = H, Cl, CH₃, C_6H_5 , ...;
- Siloxanes: $(SiO)_n R_{2n+2}$, R = H, Cl, CH₃, C₆H₅, ...;
- Silanes: Si_nR_{2n+2} , R = H, Cl, CH₃, C₆H₅, ...;

Polymer formation:

•
$$R-Si-OH + HO-Si-R \longrightarrow H_2O + R-Si-O-Si-R$$

• $R-Si-OH + HO-Si-OH \longrightarrow H_2O + R-Si-O-Si-OH$
• $HO-Si-OH + HO-Si-OH \longrightarrow H_2O + HO-Si-O-Si-OH$

Natural polymers:

• Latex is the natural polymer of isoprene (Fig. 10.2). Usually, a small amount (up to 5%) of other substances (proteins, fatty acids, resins, salts) are found in natural rubber. It was discovered in 1736. Rubber - vulcanization of latex - heat treatment of latex with sulfur - was discovered in 1839;



• Guncotton (wick) is obtained by nitration (+ HNO₃) of cellulose (the addition of NO₂ groups to it) was discovered in 1832 (Fig. 10.3). It is the precursor of celluloid (which is the 'plasticization of it with camphor);

Fig. 10.3: Nitrocellulose



• Galalith (the material for shirt buttons) is obtained by condensing casein (80% of cow's milk protein) with formaldehyde was discovered in 1897 (Fig. 10.4);

Fig. 10.4: Protein aldehydes



• Bakelite is obtained by the polymerization of phenol with formaldehyde (Fig. 10.5); it was discovered in 1907;





• Polylactide is obtained by the polymerization of corn starch, tapioca roots or sugar cane (Fig. 10.6); was discovered in 1932;





• Cellulose is the most common biopolymer (Fig. 10.7). Approximately 33% of the dry matter in plants is cellulose. Cotton contains 90% cellulose while wood approximately 50%.



• Peptides are short strings of amino acids. Peptides (20AA):



Fig. 10.8: Wood



Ala-Arg-Asn-Asp-Cys-Glu-Gln-Gly-His-Ile-Leu-Lys-Met-Phe-Pro-Ser-Thr-Trp-Tyr-Val. The long strings are proteins;

AA	Formula	AA	Formula	AA	Formula
His	$C_6H_9N_3O_2$	Cys	C ₃ H ₇ NO ₂ S	Asn	$C_4H_8N_2O_3$
Ile	$C_6H_{13}NO_2$	Gln	$C_5H_{10}N_2O_3$	Asp	C ₄ H ₇ NO ₄
Leu	$C_6H_{13}NO_2$	Pyl	$C_{12}H_{21}N_3O_3$	Glu	C ₅ H ₉ NO ₄
Lys	$C_6H_{14}N_2O_2$	Orn	$C_5H_{12}N_2O_2$	Gly	C ₂ H ₅ NO ₂
Met	$C_5H_{11}NO_2S$	Pro	C ₅ H ₉ NO ₂	Aib	C ₄ H ₉ NO ₂
Phe	$C_9H_{11}NO_2$	Sec	$C_3H_7NO_2Se$	Cit	$C_6H_{13}N_3O_3$
Thr	C ₄ H ₉ NO ₃	Ser	C ₃ H ₇ NO ₃	Dha	C ₃ H ₅ NO ₂
Trp	$C_{11}H_{12}N_2O_2$	Tau	$C_2H_7NO_3S$	Gaba	C ₄ H ₉ NO ₂
Val	$C_5H_{11}NO_2$	Tyr	$C_9H_{11}NO_3$	Hcy	C ₄ H ₉ NO ₂ S
Arg	$C_6H_{14}N_4O_2$	Ala	C ₃ H ₇ NO ₂	Нур	C ₅ H ₉ NO ₃

Fig.	10.9:	Amino	acids
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• DNA is a string of pyridine bases (A=Ala; C=Cys; G=Gly; T=Thr)

Fig. 10.10: DNA sequence

• • •	CTTTT <mark>CA</mark> TT
	CT <mark>GA</mark> CT <mark>G</mark> CA
	<mark>ACGGG</mark> C <mark>AA</mark> T

Synthetic polymers include polyacrylonitrile, polypropylene, poly-1-butene, polystyrene, polyvinyl chloride, polyacrylic acid, polyvinyl acetate, alcohol polyvinyl, polyoxymethylene, polytetrafluo-roethylene, polydimethylsiloxane, polyethylene, poly(methyl methacrylate), polybutadiene, nylon 6 (Fig. 10.11):

- Polyacrylonitrile has applications in ultrafiltration membranes, hollow fibers for reverse osmosis, fibers for textiles, oxidized flame retardant fibers;
- Polystyrene has applications in disposable cutlery, casings; flows when heated above 100 °C, a behavior exploited for plastic patterns, molding, and extrusion;
- Polypropylene has applications in packaging and labeling, reusable containers, laboratory equipment, textiles, banknotes;
- Poly-1-butene has applications in pressure vessels, flexible packaging, water heaters, hot melt adhesives;

Fig. 10.11: Synthetic Polymers



- Polyvinyl chloride has applications in pipes for residential sewage and water supply systems;
- Polyacrylic acid has applications in disposable diapers and to thicken, disperse, suspend, and emulsify pharmaceutical and cosmetic products;
- Polyvinyl acetate is a component of a type of adhesive used on a wide scale (wood glue, white glue, carpenter's glue, school glue);
- Polyoxymethylene, with applications in precision parts that require high rigidity, low friction, and excellent dimensional stability;
- Polyethylene, with applications in packaging (plastic bags, plastic films, membranes, containers including bottles) Polytetrafluoroethylene (or Teflon) which water and water-containing substances do not wet it and has a very low coefficient of friction with any solid;
- Polydimethylsiloxane (silicones) which is inert, non-toxic and non-flammable; with applications in contact lenses, medical devices, elastomers; present in shampoos (makes hair shiny and slippery), lubricating oils and heat-resistant plates
- Polybutadiene with applications in synthetic rubber for automobile tires;
- Nylon 6 with applications in toothbrush bristles, surgical sutures, strings for acoustic and classical musical instruments (guitars, sitars, violins, violas and cellos), yarns, ropes, filaments, nets, tire cords and knitted garments and stockings;
- Poly(methyl methacrylate) which is a lightweight and shatter-resistant alternative to glass;



11. Organic chemistry and biochemistry

Organic compounds form the basis of all life on earth and constitute the majority of known chemical substances.

The skeleton of organic compounds is made up of C atoms. Together with them, H and O frequently appear. The name organogenic elements also includes N. Macroelements are N, P and K. Microelements (trace elements) are Fe, Mn, Zn, B, Cu, Mo and Si.

There is a strong connection between the structure of organic compounds and their functionality. A series of groups (called functional) are largely responsible for their chemical properties and biological activity.

• Alkanes have a structure made up of carbon and hydrogen atoms, with simple bonds being established between them. They can be defined by the expression R-H, where R denotes the structure of an alkane from which a hydrogen atom has been removed and is called an alkyl

Table 11.1: Examples of alkanes ($C_n H_{2n+2}$)

n	Formula	Alkane	Alkyl	Formula
1	CH_4	Methane	Methyl	$-CH_3$
2	C_2H_6	Ethane	Ethyl	$-C_2H_5$
3	C ₃ H ₈	Propane	<i>n</i> -Propyl <i>i</i> -Propyl	$\begin{array}{c} -CH_2-CH_2-CH_3\\CH_3\\-C-H\\CH_3\end{array}$
4	C_4H_{10}	<i>n</i> -Butane <i>i</i> -Butane		

The number of isomers increases very quickly with the number of carbon atoms. In addition to structural isomers, geometric isomers are also added. A representative example is the geometric conformers of n-Butane (see. Fig. 11.1)

- Substituted alkanes are defined by the expression |R-G|, where G is the functional group (or functional group). Examples include metal-alkyls: CH₃HgA A-methyl-mercury; CH₃HgCl chloro-methyl-mercury; CH₃HgCH₃ dimethyl mercury. [CH₃Hg]⁺ is a toxic bioaccumulative agent and CH₃HgCH₃ is one of the most potent known neurotoxins
- Haloalkanes are defined by the expression |R-X|, where X is a halogen (one of the elements F, Cl, Br, I, At). Examples include CH₄ derivatives obtained by substituting hydrogen atoms with chlorine atoms: CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄:





- CH₃Cl (methyl chloride) is toxic and extremely flammable, and is also an intermediate in the synthesis of silicone polymers.
- CH₂Cl₂ (methylene chloride) is widely used as a solvent; it is immiscible with water and miscible with many organic solvents. It also serves as a bleach and degreaser.
- CHCl₃ (chloroform) is a relatively unreactive solvent, miscible with most organic liquids, and slightly volatile.
- CCl₄ (carbon tetrachloride) is used as a dry cleaning solvent and as a refrigerant, but is also one of the most potent hepatotoxins (toxic to the liver, causing fulminant necrosis).
- Nitriles are defined by the expression |R-CN|. Examples include acetonitrile (CH₃CN, used in the purification of butadiene in refineries) and isobutylonitrile ((CH₃)₂CHCN) used as an organic solvent in the production of insecticides and as an additive to gasoline; also methyl cyanoacrylate and ethyl cyanoacrylate (see Fig. 11.2)

Fig. 11.2: Methyl and ethyl cyanoacrylates



- Amines are defined by the expression $|R-NH_2|$ having the nitrogen atom as the functional group. Examples include ammonia mono-, di-, and tri-substituted with methyl groups (-CH₃): methylamine (CH₃-NH₂), dimethylamine ((CH₃)₂NH), and trimethylamine ((CH₃)₃N). Methylamines are gases with a fishy odor; are used as building blocks in the synthesis of many compounds. Derivatives of triphenylamine ((C₆H₅)₃N) have applications in electrical conductivity and electroluminescence, being used in organic photodiodes (see Fig. 11.3).
- Alcohols are defined by the expression |R-OH|. Examples include methyl alcohol (CH₃OH)

Fig. 11.3: Triphenylamine derivatives



and ethyl alcohol (CH₃CH₂OH):

- Methanol is a natural product of the anaerobic metabolism of many varieties of bacteria. It is a common solvent in the laboratory. In industry, it is used to produce formaldehyde, which is then used in various products such as plastics, plywood, paints, explosives, and textiles. In addition to its direct use as a fuel (as an alternative to gasoline), it serves as a component in the transesterification of triglycerides to produce a form of biodiesel. The most common use of ethanol is as a motor fuel (as an alternative to gasoline) and as an additive to it. Ethanol is the main psychoactive constituent of alcoholic beverages, with depressant effects on the central nervous system. Long-term use can cause serious liver damage. It is used in medical wipes and antibacterial disinfectant gels. Ethanol kills most bacteria and fungi, and many viruses, by denaturing their proteins and dissolving their lipids, but is ineffective against bacterial spores
- Thiols are defined by the expression |R-SH|. Examples include methanethiol (CH₃SH), dimethyl sulfide (H₃CSCH₃), and dimethyl trisulfide (H₃CSSSCH₃).
 - Methanethiol is present in the blood and brain of humans and animals, as well as in plant tissue. Methanethiol is excreted in the feces and has an extremely strong and repulsive odor. It is toxic, affecting the respiratory system, lungs, and central nervous system
 - Dimethyl sulfide has a characteristic cabbage odor. It is present in low concentrations as a food additive to impart a savory flavor. Beets, asparagus, cabbage, corn, and seafood produce dimethyl sulfide when cooked
 - Dimethyl trisulfide is present in volatile compounds in onions, leeks, and broccoli when they are cooked, and is the unpleasant aroma of stale beer and aged Japanese sake.
- Carboxylic acids are defined by the expression R-COOH. Examples include formic acid (HCOOH, present in bee venom and ant stings), acetic acid (CH₃COOH, vinegar), oxalic acid ((COOH)₂, used as a mordant in the dyeing process and in bleaches, especially for cellulose), tartaric acid (present in grapes and bananas), citric acid (present in lemons, oranges, and limes), and acetylsalicylic acid (aspirin).

- Ethers, defined by the expression R-O-R' that can be obtained from a water elimination reaction (H₂O) between 2 alcohols (*R*-OH and HO-*R'*). Examples of ethers include:
 - Diethyl ether $(CH_3-CH_2-O-CH_2-CH_3)$ which is a solvent and an anesthetic;
 - polyethers, which are compounds with more than one ether group (Fig. 11.4)
- Esters, defined by the expression R-COO-R' that can be obtained from a water elimination reaction (H₂O) between an acid and an alcohol (*R*-COOH and HO-*R'*). An example is ethyl acetate (Et-O-Ac, where Et is CH₂-CH₃ and Ac is CH₃-C=O), which has a sweet smell

Fig. 11.4: Crown ethers



(like pear drops) and is used in glues, decaffeinated teas and coffees, and is the most common ester in wines. Related to organic esters are inorganic esters with applications including triphenyl phosphate (used as a plasticizer and flame retardant) and dioxalate boride (used in lithium-ion batteries).





• Anhydrides, defined by the expression R-COO-CO-R' that can be obtained from a water elimination reaction (H₂O) between 2 acids (*R*-COOH and HOOC-*R'*). Acetic anhydride (Ac₂O) is a reagent widely used in organic synthesis (see Fig. 11.6). The dimer of maleic

Fig. 11.6: Synthesis of aspirin (from salicylic acid and acetic anhydride)



anhydride (see Fig. 11.7) is used in the production of polyimides and as an alignment film for liquid crystal displays. The anhydride bonds in aromatic polyanhydrides are water regulators

Fig. 11.7: Maleic Anhydride Dimerization



- the polymer chain breaks at different positions at different reaction rates. The resulting

carboxylic groups are readily metabolized, making the polyanhydrides biocompatible. Their applications include the release of encapsulated drugs with well-defined kinetics (such as slowly over 24 h).

- Amides, defined by the expression |R-CO-NR'R''| can be obtained from a water elimination reaction (H₂O) between an acid and an amine (R-COOH and R'-HN-R''). Amides are used in nature and technology as structural materials (providing a strong framework). Examples:
 - DMF (dimethylformamide, (CH₃)₂NCHO) is a solvent with a low evaporation rate. It has numerous applications, including the production of acrylic fibers and plastics, a solvent for the coupling of peptides in drugs, the development and production of pesticides, the production of adhesives, synthetic leather, fibers, films, and surface coatings.
 - Acrylamide (CH₂=CH-CONH₂) is used in the synthesis of polyacrylamide. One of the properties of polyacrylamide is to flocculate solids in a liquid, finding applications in wastewater treatment, papermaking, pesticides, cosmetics, sugar, and soil treatment.

Fig. 11.8: DMF, acrylamide, and polyacrylamide

$$\begin{array}{ccccc} O & CH_3 & O & O \\ \parallel & \mid & \mid \\ HC-N & H_2N-C & \left[H_2N-C & \mid \\ H_2C+CH_3 & H_2C=CH & -\left[H_2C-CH & -\left[H_2C-CH & -\right] \right]_n \end{array} \right]$$

Aldehydes defined by the expression R-CHO and ketones defined by the expression R-CO-R' have the functional group O=C.

- Formaldehyde H₂CO is notable for its simplicity and is a precursor for a number of polymers including 1,3,5-trioxane and polyoxymethylene (a thermoplastic used in precision parts requiring high rigidity, low friction and dimensional stability).
- Acetaldehyde CH₃CHO is widely distributed in nature (coffee, bread, ripe fruit) being produced by plants as part of their natural metabolism and being produced on a large scale in industry.
- Paraldehyde is an anticonvulsant, hypnotic and sedative. It also has uses as a preservative (see Fig. 11.9).
- Metaldehyde is used as a pesticide against slugs, snails and other gastropods (see Fig. 11.9).
- Acetone (or propanone) (CH₃)₂CO is produced and eliminated by the human body as part of normal metabolic processes; it is present in blood and urine; it serves as a solvent for polystyrene, polycarbonate, and some polypropylenes.
- Acetylacetone (CH₃COCH₂COCH₃) undergoes rapid interconversions and is useful for the synthesis of some metal complexes (see Fig. 11.9).
- The alkenes defined by the expression $R^{I}R^{2}C = CR^{3}R^{4}$ have the functional group C = C.

With respect to the double bond, the substituents $R^1 - R^4$ can be positioned above and below the plane determined by the carbon and bond atoms, which causes cis-trans isomerism to occur (conformations on either side or the same side of the plane).

- 2-Butene is a petrochemical, produced by the catalytic cracking of crude oil or the dimerization of ethylene (see Fig. 11.10).
- Propene is produced naturally by vegetation, especially by certain tree species. It is a product of combustion, from forest fires and cigarette smoke to vehicle and aircraft exhaust. With a relatively short half-life, it is not bioaccumulative, so it has low acute toxicity by inhalation (see Fig. 11.10).

Fig. 11.9: Paraldehyde, metaldehyde, acetylacetone and the fixation of metal complexes (V complex)



- Ethylene is a colorless flammable gas with a faint sweet and musky odor and is an important natural plant hormone, used in agriculture to force fruit ripening with a niche use as an anesthetic (see Fig. 11.10).
- 1-Butene is highly flammable and readily forms explosive mixtures with air (see Fig. 11.10).

Fig. 11.10: 2-Butene (cis and trans), propene, ethylene and 1-butene



- Arenes (or aromatic compounds) are defined by the expression Ar-H or Ph-H with the aryl (or phenyl) functional group $-C_6H_5$. Examples:
 - Benzene (C_6H_6) is a natural component of crude oil; it is a highly flammable liquid with a sweet odor, with carcinogenic potential; approximately 80% is used for the production of ethylbenzene, cumene and cyclohexane.
 - Toluene (CH₃-C₆H₅) is a common solvent; it can be used as an octane booster in gasoline fuels used in internal combustion engines and for removing cocaine from coca leaves in the production of cola syrup.
 - Xylene (dimethyl benzene, $(CH_3)_2C_6H_4$) has three structural isomers (ortho-, meta-, and para-, see Fig. 11.11)
 - Polycyclic aromatic hydrocarbons include phenanthrene (phenanthrene is found in cigarette smoke) and anthracene (anthracene is a component of coal tar). Phenanthrene is more stable than anthracene.

Fig. 11.11: Xylene, Phenanthrene, and Anthracene



11.0.1 Biochemistry

Biochemistry is the study of chemicals and the chemistry of living organisms. Chemical compounds play an essential role in biological processes (see Fig. 11.12). Nutrition (see Fig. 11.13) uses solar



Fig. 11.12: Biological Processes

radiation to provide the energy needed to carry out chemical processes involving oxygen and/or carbon dioxide from the air as well as nutrients from the environment for survival, growth, copying, multiplication, signaling, and mutation. Replication uses the genetic code to make a copy of the

Fig. 11.13: Food pyramid



cell, multiplication separates the copied cell from the parent cell, and signaling uses chemicals to communicate between cells. A mutation is a wrong copy of the parent cell. It usually occurs with a very low probability ($< 1\%_0$). The mutant cell usually has a very low probability of surviving and adapting to the environment ($< 1\%_0$). Very rarely, however, it does, which can lead to the creation of a new, more potent, more environmentally adapted species.

Organisms that have developed specialized organs have also developed a complex feeding process in which enzymes are involved (see Fig. 11.14).

Such an enzyme has two cavities, one to accommodate the substrate S subject to the digestive





process and one to accommodate an allosteric effector A. The occupation of the 2 positions is mutually exclusive. Thus, the sensation of hunger is translated by an increase in the concentration of allosteric effectors that are released from the enzyme cavities. At this point, the enzyme is ready to fix the substrate in the cavity and thus significantly (usually by an order of magnitude) reduce the energy required to break it down and convert it into nutrients. The feeding process continues until the saturation process occurs, which is usually associated with reaching a critical concentration of nutrients resulting from the processing of substrates. At that point, allosteric effectors begin to fixate on the enzyme, no longer allowing substrates to fix.

Blue biotechnology (from the color of water) involves the artificial production of food in the form of carbohydrates ($(CH_2O)_n$) usually using the simplest organisms such as algae (see Fig. 11.15).





Such a system would have the advantage of using carbon dioxide from the air and water from the vessel to obtain the necessary food in a controlled environment.



See [102].



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