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Mineral Chemistry

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Chapter 3 :
Periodicity and In-Depth Study of the Properties of Elements

III.1. INTRODUCTION:

You can find all currently known and future chemical elements in their place according to the system proposed by Dmitri Mendeleev (1869) and represented today by the periodic table. He succeeded in finding a relationship between atomic weights and the chemical and physical properties of the elements. The elements were arranged in eight columns, numbered from I to VIII, according to their valency and divided into subgroups A and B. To respect the similarities between the elements, Mendeleev left many empty boxes, but he described in detail the properties of three of these unknowns and, in general, the properties of the others (1871). Other elements were added after their discovery:

- Gallium 1875
- Scandium 1879
- Germanium 1886
- L'argon l'hélium 1894 (Present in the atmosphere of the sun, and hence its name is derived from Helios, which means the sun in Greek)
- Le néon, le krypton et le xénon 1898
- Le radon 1900
- Over a somewhat extended period (1878-1907), dozens of chemical elements, similar to those already known but challenging to place in the periodic table, were discovered. These were called the rare earth elements, later classified in the same box as lanthanum.
- The study of radioactive materials led to the discovery of seven missing elements, all of which are radioactive: polonium and radium (1898), actinium (1899), radon, protactinium (1917), francium (1939), and astatine (1940).
  - In the early twentieth century, the atom began to reveal its secrets:
    - The nuclear model of the atom by Rutherford (1911-1912).
    - The emission of X-rays by Bohr (1913).

- The number of protons in atomic nuclei corresponds to the element's position in the periodic table.
- H.G.J. Moseley found a relationship to calculate the atomic number of an element by measuring its characteristic X-rays. This result led to the classification of elements in ascending order of their atomic number (A), eliminating the issue of atomic mass interference caused by isotopic masses.
- N. Bohr (1922) demonstrated that elements are chemically similar if the outer layers of their atoms have the same electronic distribution
- In 1929, Pauli introduced the Pauli Exclusion Principle, stating that in the atomic shell, one cannot find electrons with identical quantum numbers (n, l, m, s).
- In 1932, J. Chadwick successfully identified the particle in the nucleus responsible for the mass difference in isotopes of an element (the neutron).
- With the discovery of radioactivity (up to 2002), researchers were able to include almost all elements in the periodic table.

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		? Er = 56	La = 94		
		? Yt = 60	Di = 95		
		? In = 75,6	Th = 118?		

Д. Менделеев.

Figure 1: The first periodic table of Mendeleev Demiti

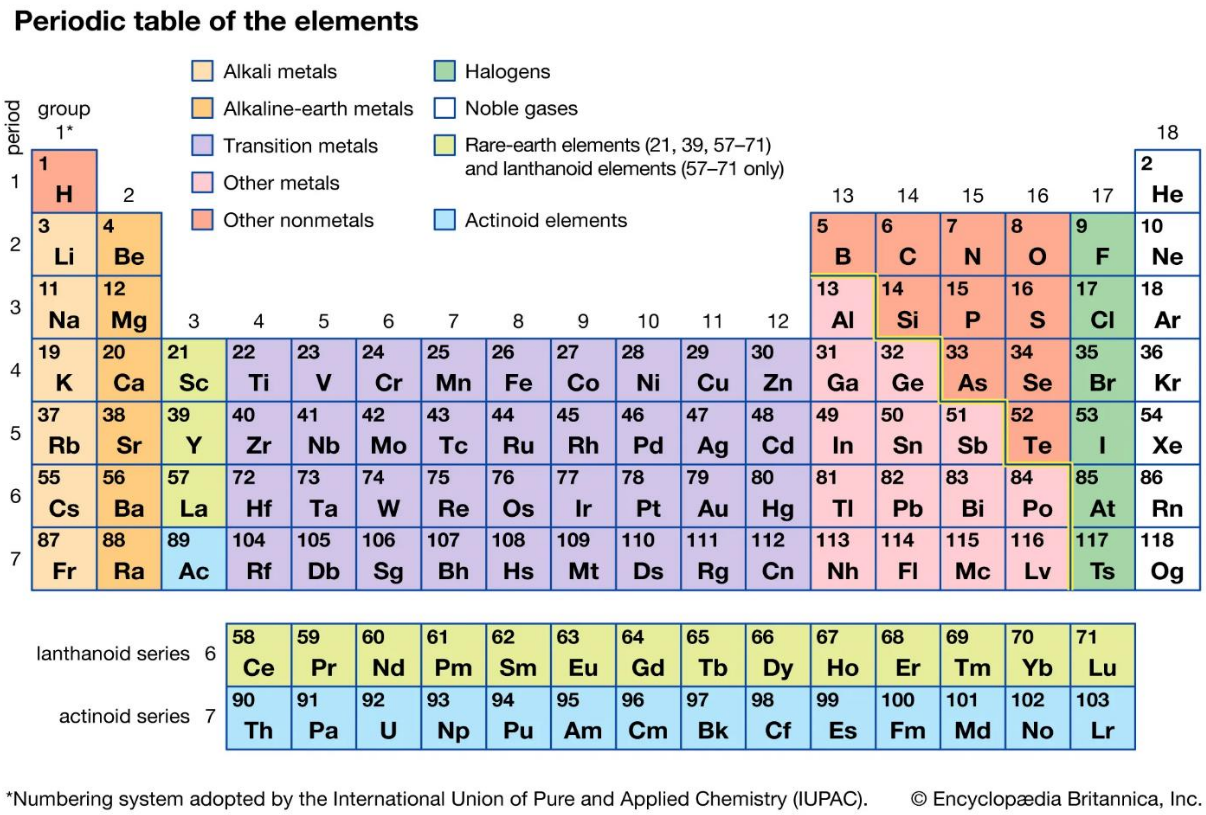
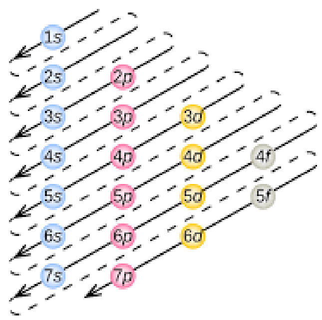


Figure 2: Current periodic table

III .2. PERIODIC CLASSIFICATION:

Studying the electron distribution in atoms provides a deeper understanding of the periodic classification of elements. The periodic classification relies on filling various sublevels (s, p, d, f) according to the Klechkowski rule.



- Each row begins by filling the ns sublevel and ends with the np sublevel, except for n = 1.
- Electrons in the atom are globally organized into energy levels in the same way for all atoms. These levels depend on the quantum numbers n (1, 2, ... 7) and l (s, p, d, f).
- Different columns are organized into groups s, p, d, and f based on the last sublevel to be filled.
- The horizontal rows constitute periods. Since the electrons of elements occupy the same principal quantum number (n), elements are arranged from left to right in ascending order of their atomic number (Z).

- . The columns form groups or families, and there are 18 of them. Elements belonging to the same group share certain properties since elements in the same group have the same number of electrons in their outermost energy level (also called the valence shell). • The groups are numbered "A" and are called "main" groups, ranging from IA to VIIIA, with the names listed below. Groups "B" are situated between groups IIA and IIIA and are called transition metals. Elements in the same group have the same number of valence electrons.

	period → colone ↓	1	2	13	14	15	16	17	18
K	1	H $1s^1$							He $1s^2$
L	2	Li $1s^2\ 2s^1$	Be $1s^2\ 2s^2$	B $1s^2\ 2s^2\ 2p^1$	C $1s^2\ 2s^2\ 2p^2$	N $1s^2\ 2s^2\ 2p^3$	O $1s^2\ 2s^2\ 2p^4$	F $1s^2\ 2s^2\ 2p^5$	Ne $1s^2\ 2s^2\ 2p^6$
M	3	Na $1s^2\ 2s^2\ 2p^6\ 3s^1$	Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$	Aℓ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	Si $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	P $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	S $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	Cℓ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	Ar $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
valece electrons		1	2	3	4	5	6	7	8
name		alcalins	alcalino-terreux					halogènes	gaz rares

Figure 3: Families Of Periodic Table

- Based on the number of valence electrons (or electrons in the outermost shell), we can predict the charge of the ion.

The groupe	The number of electrons in the outer shell	Possible ion	Tends to
IA	1	Cation +1	Lose 1 electron
IIA	2	Cation +2	Lose 2 electron
IB -> VIIIB	-	-	-
IIIA	3	Cation +3	Lose 3 electron
IVA	4	Cation or anion +4 to -4	Lose or win 4 electron
VA	5	Anon -3	Win 3 elctron
VIA	6	Anion -2	Win 2 electron
VIIA	7	Anoin -1	Win 1 electron
VIIIA	8		Stable

- Periodic table elements, numbering 103, are classified into three categories based on their properties: metals, metalloids, and nonmetals. However, most chemical elements are metals.

- Hydrogen is a special case, as it does not belong to any of these three categories. It tends to behave like a metal under certain conditions and like a nonmetal under others. It can act as an electron donor or acceptor, existing in the neutral form H2 or as a negative ion H-, or a positive ion H+.

- Metals are shiny, good conductors of heat and electricity, malleable, electron donors, react with acids, and generally solid under normal temperature and pressure conditions, except for mercury (Hg).

- Metalloids, meaning "metal-like," are intermediate elements between metals and noble gases. It's challenging to classify metalloids as either metallic or non-metallic; they lie along the borderline (the stepped line) that separates metals from nonmetals or metalloids. They resemble nonmetals in some properties but are weak electrical conductors (semiconductors).

- Nonmetals, or nonmetals, are non-metallic elements with a dull appearance, lacking luster. They are poor conductors of heat and electricity, often existing as gases or liquids.

The groups or families A in the periodic table, from left to right, are:

III.3.1. ALKALINE (IA):

These are monovalent reference reducing metals, tending to easily donate electrons from the outer ns1 shell to satisfy the energy level and form cations M+ (previous noble gas energy level). The reducing property increases from Li to Fr. In fact, ionization energy decreases from n = 1 to n = 7.

$$\boldsymbol{Li \rightarrow Li^{+} + e -}$$

Note: Ionization energy varies with the distance between the electron and the nucleus; the smaller the distance, the greater the ionization energy. During the periodic table rows (n), the distance between the nucleus and the electron decreases with Z (the number of protons in the nucleus), increasing the nucleus's attraction for electrons. Thus, the distance decreases, and ionization energy increases. As n increases, the distance between the nucleus and the electron increases, along with the shielding factor (the inner layer electrons acting as a screen shielding the outer electron from the nucleus), resulting in a decrease in ionization energy.

Alkali metals should be stored in oil because their contact with air or water can lead to violent reactions, producing alkaline hydroxides (heat-releasing reactions). Alkali metals are often used in medicine (pharmaceuticals) and in the manufacturing of explosives.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \uparrow$$

- Sodium and potassium are found in dissolved or solid states, in the form of halides, nitrates, or carbonates.
- Lithium, Rubidium, and Cesium are discovered in silicate minerals.
- Francium is a radioactive element ($T_{1/2}$ = 22 minutes) found as traces in Uranium and Thorium ores. It can be obtained through nuclear reactions from Actinium.

III.2.3. ALKALINE EARTH METALS:

These elements have valence electrons and are never found in a free metallic form in nature; they are highly reactive.

$$Mg \rightarrow Mg^{+2} + 2e\text{-}$$

- These elements have homogeneous properties and are relatively close to the properties of alkali metals (Group IA). However, the increase in their ionization ability affects the properties of their compounds, including solubility and tendency to form hydrates.
- Magnesium (Mg) and calcium (Ca) are the two most abundant elements in the group. They are also essential main group metals. In comparison to alkali metals, their reactivity does not allow them to exist in the free state.
- Beryllium is primarily found in silicate minerals (emerald: $\mathbf{Be}_3(Al,Cr)_2(SiO_3)_6$).
- Other metals are found in various salt forms (dissolved or crystallized), mainly chlorides, carbonates, or sulfates.
- Radium is a radioactive element ($T_{1/2}$ = 1600 years) associated with uranium in its ores.

III .3.3. BORE FAMILY (IIIA) :

The Group IIIA metals have three valence electrons in their highest-energy orbitals (ns^2p^1). They have higher ionization energies than the Group IA and IIA elements, and are ionized to form a 3+ charges.

$$B \rightarrow B^{+3} + 3e\text{-}$$

- It includes the metalloid boron (B), as well as the metals aluminium (Al), gallium (Ga), indium (In), thallium (Tl) and nihonium (Nh). Boron forms mostly covalent bonds, while the other elements form mostly ionic bonds.
- Group IIIA metals, silvery and good conductors of electricity, have lower melting points than Group 2A metals, with aluminium melting at 660ºC while gallium at

29.8ºC (A chunk of gallium would literally melt in your hand — that it, if you have the usual body temperature of 37ºC).

Element	Z	Isotopes	percent by weight of Earth's crust
Boron B	5	10 & 11	**0,001%**
Aluminum Al	13	22 isotopes 21-42 (only 27 is stable)	**8.2%**
Gallium Ga	31	31 isotopes 56-86 (only 6 and 71 are stable	**0.0018%**
Indium In	49	39 isotopes 97-135 only 113,115 are satable	**0.000005%**
Thallium Tl	81	37 isoptopes 176-212 only 203&205 are stable	**0.00006%**
Nihonium Nh	113	6radioisotopes278-286 286 Most stable	**synthetic**

Group 13 elements play biological roles in ecosystems, such as boron, which is essential for plants and can cause stunted growth. Aluminium is considered safe, while indium and gallium stimulate metabolism and can bind to iron proteins. Thallium, a highly toxic element, interferes with vital enzyme function and has been used as a pesticide.

Chemical and physical Characteristics:

The boron group exhibits distinct characteristics such as electron configuration trends, hardness, refractivity, and resistance to metallic bonding. Its tendency to form reactive compounds with hydrogen is an example of this trend.

	Electronic configuration	درجة الاكسدة	Ei1 kJ/mol	Ei2 kJ/mol	Ei3 kJ/mol	Melting point (K°)	Boiling point (K°)	Density g/cm^3	elecyron egativity
B	[He] $2s^22p^1$	-5,-1, 0, +1,+2	800.6	2427.1	3659.7	2349	4200	2.34	2.0
Al	[Ne] $3s^23p^1$	-2,-1, 0, +1,+2,+3	577.5	1816.7	2744.8	933.47	2743	2.70	1.5
Ga	[Ar] $3d^{10}4s^24p^1$	-5, -4, -3, -2,-1, 0, +1,+2, +3	578.8	1979.3	2963	302.9146	2676	5.90	1.6
In	[Kr] $4d^{10}5s^25p^1$	-5,-1, 0, +1,+2	558.3	1820.7	2704	429.7485	2345	7.31	1.7
Tl	[Xe] $4f^{14}5d^{10}6s^26p^1$	+5, -2,-1,+1,+2, + 3	703.3	1610	2466	577	1746	11.83	1.8
Nh	[Rn] $5f^{14}4d^{10}7s^27p^1$	-1,-3,+3,+5	704.9	2240	3020	700	1430	16	

- All the group IIIA elements form trihalides, although Tl does so reluctantly, preferring to remain in the +1 oxidation state. The general reaction is

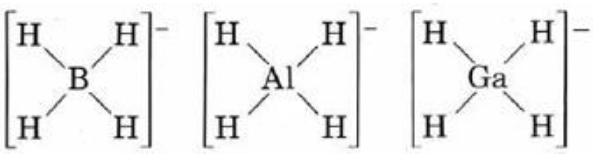
$$\mathbf{2M(s) + 3X_2 \rightarrow 2MX_3}$$

- The oxides and oxyanions of B and Al are commercially important compounds. B is primarily found in bauxite, a hydrous oxide with indeterminate water content. Al is the most abundant metal in the earth's crust, but is found in complicated aluminosilicates. The Bayer process is the first step in recovering Al, which is amphoteric due to the presence of $A1^{3+}$ and O^{2-} ions. Al^{3+} attracts H_2O molecules, while the oxide ion is a proton acceptor and strong base.

The Bayer process makes use of the acidic behavior of Al_2O_3 by dissolving it in strong base:

$$\mathbf{Al_2O_3(s)+3H_2O(l)+2OH^{-}(aq) \rightarrow 2Al(OH)^{-}_4(aq)}$$

- In contrast to groups IA and IIA, none of the elements in group IIIA react directly with hydrogen to produce hydrides. The halides of B, Al, and Ga, on the other hand, will react with sodium hydride to create tetrahydro anions:

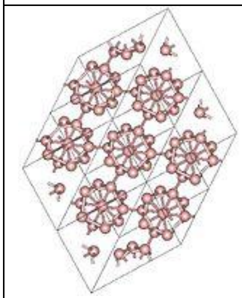
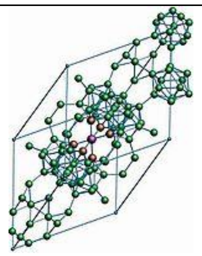
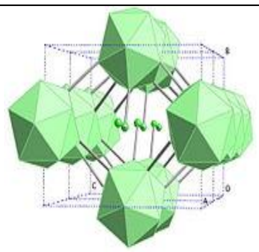
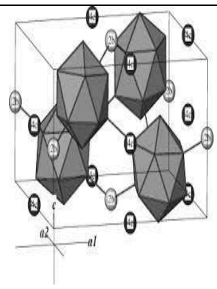
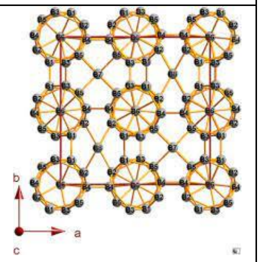


he tetrahydroaluminate and tetrahydrogallate ions react readily with H_2O, splitting the H_2O molecule so that the H ends up with another H to form H_2, while the OH ends up with the group IIIA atom:

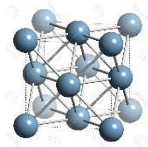
$$\mathbf{AlH^{-}_4(aq)+4HOH(l) \rightarrow Al(OH)_3(s)+OH^{-}(aq)+4H_2(g)}$$

<u>Alloptropes:</u>

- **Boron:** Boron can be prepared in several crystalline**:**

α-Rhombohedral	**β-rhombohedral**	**γ-rhombohedral**	**α-tetragonal**	**β- tetragonal**
				
Clear red	**Dark to shiny silver-grey**	**Dark grey**	**Black and opaque, with metallic lustre**	**Black/red**

- **Aluminium:** Aluminum in its pure form has a face centred cubic crystal structure, it is a soft metal and does not exist in different forms.



- **Gallium:** The unit cell is orthorhombic
- **Indium :** La maille de son système cristallin est isométrique et tétragonale.

III.3.4. CARBONE FAMILY (IVA)

The elements of this group share a common electron distribution in the outer shell (*ns^2np^2*), but they are heterogeneous in terms of their physical and chemical properties. For instance:

- Carbon is a non-metallic element that forms the skeletal structure of living molecules.
- Silicon is a semi-metallic element, the second most abundant element in the Earth's crust, and it forms the physical environment for life in association with oxygen (rocks, soil, clay, sand, etc.).
- Germanium is a semi-metallic element studied for its therapeutic properties.
- Tin and lead are poor metals with established toxicity.

These elements form negative ions when combined with elements of low electronegativity (s-block metals). For example, carbon ($\chi = 2.5$) forms ionic compounds like carbide anion (C_2^{2-}) in compounds such as CaC_2.

These elements also form covalent bonds, as seen in CO_2, SiO_2, GeH_4, $SnCl_4$, and PbO_2. The stability of tetravalent compounds in the group decreases down the column. Unstable compounds, especially those involving lead, act as oxidizing agents.

$$\mathbf{PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2}$$

Positive ions are also formed when these elements bond with elements having high electronegativity, such as **$SnCl_2$, $Pb(NO_3)_2$, $SiCl_2$**. The stability of compounds in the group increases in these cases. Unstable compounds act as reducing agents.

$$\mathbf{Sn^{2+}(aq) + 2Ag^{+}(aq) \rightarrow Sn^{4+}(aq) + Ag(s)}$$

III .3.5. NITROGEN FAMILY (VA)

Element	Z	Isotopes	percent by weight of Earth's crust
Nitrogen N	7	14,15	**0.0025%**
Phosphor P	15	23 isotopes 46-24	**0.01%**
Arsenic As زرنيخ	33	75	**1.8×10^{-5}%**
Antimony Sb	51	121, 123	**1.6×10^{-5}%**
Bismuth Bi	83	41 isotopes 224-184	**0.048×10^{-4}%**
Moscovium Mc	115	5 isotopes 290-286	**synthetic**

The appearance of elements in this group varies significantly due to the evolving metallic nature as one descends the column.

- Nitrogen and phosphorus are two essential elements found in a wide range of pharmaceutical compounds and fertilizers. Nitrogen exists in the diatomic form **N_2**, constituting 78% of the Earth's atmosphere and is a component of nitrates. Phosphorus is primarily found in the form of phosphates, especially in the natural mineral apatite **$Ca_5(PO_4)_3X$**, where **X** can be **OH^-**, **F^-**, or **Cl^-**.

- Arsenic, antimony, and bismuth predominantly exist in the form of sulfides, such as **As_2S_3, Sb_2S_3, Bi_2S_3**, often in association with other minerals.

<u>Physio-chemicals characteristics:</u>

	Electronic configuration	Oxidation state	Ei_1 kJ/mol	Ei_2 kJ/mol	Ei_3 kJ/mol	Density g/cm^3	electronegativity
N	[He] $2s^22p^3$	+3, -3	1402	2856	4578	1249,82	**3.04**
P	[Ne] $3s^23p^3$	+5, +3, -3	1012	1907	2914	1,82	**2,19**
As	[Ar] $3d^{10}4s^24p^3$	+5, +3	947.0	1798	2735	5,72	**2,18**
Sb	[Kr] $4d^{10}5s^25p^3$	+5, +3	830.6	1595	2440	6.697	**2,05**
Bi	[Xe] $4f^{14}5d^{10}6s^26p^3$	+3	703.3	1610	2466	9.78	**2,02**

- The elements of the group have a valence shell configuration of ns2np3, with 5 valence electrons. The valence electrons experience strong nuclear attraction, leading to high ionization energies (Ei). Consequently, these elements, especially the lighter ones, tend to form covalent bonds.
- N For nitrogen (N), being a very small atom, it cannot surround itself with 5 atoms, primarily exhibiting a trivalent valence: EO = -3, as seen in compounds like Li3N. However, it can form a fourth bond due to the presence of a lone pair, as in NH4+ (other oxidation states are possible, such as nitrogen oxides).
- Phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi) can form compounds with both three and five valence bonds, exemplified by PCl3 and PCl5. This is attributed to the presence of an empty d subshell belonging to the same principal quantum number (n).
- Nitrogen exists in the form of diatomic gas (**N_2**), colorless and odorless. In its liquid state, it is used as a coolant to ensure effective cooling (cryopreservation) and to maintain biological samples or substances (blood, DNA, organs, etc.). In its gaseous state, nitrogen serves as a carrier gas ("solvent" gas for transporting other gaseous species), as seen in gas chromatography, or to create an inert atmosphere (non-reactive environment when reactive substances are sensitive to air). Other elements in the group are solid substances.

<u>Allotropes</u>

Phosphorus, arsenic, and antimony have various allotropes:

- Phosphorus: It has several allotropes, with the most important being white phosphorus and red phosphorus.

Phosphorus has two types: α (cF, stable at normal temperatures) and β (h). It rapidly combusts in the air at temperatures below 50 °C, making it useful as an incendiary weapon, such as in phosphorus grenades. $P_4 + 5O_2 \rightarrow P_4O_{10}$ $P_4 + 5O_2 \rightarrow P_4O_{10}$	t has an amorphous non-crystalline structure obtained by heating white phosphorus at 240 °C. This substance is controlled due to its use in the production of amphetamines (controlled substances).	Having a monoclinic crystalline structure, it is obtained by heating red phosphorus at 530°C and oxidizing it using nitric acid to produce phosphoric acid.	It has a structure resembling that of graphite but crystallizes in an orthorhombic system. It is obtained by heating white phosphorus under a pressure of 12,000 atmospheres. It can be used to create electronic circuits, so scientists are exploring an element that is nearly equivalent to graphene but acts as a natural semiconductor and is cost-effective for the creation of transistors.

- **Arsenic:** It has three allotropes - gray, black, and yellow**.**

It is the most stable allotrope at room temperature with a rhombohedral structure, sparingly soluble. It is obtained by exposing yellow arsenic to light.	It is formed by the rapid condensation of arsenic vapor onto a cold surface, resulting in tetrahedral molecules (As4) similar to white phosphorus. This is the only known soluble form of arsenic. However, yellow arsenic, in the presence of light, rapidly decomposes to form gray arsenic.	Black arsenic (Asn) is manufactured by sublimating gray arsenic, followed by condensation onto a hot surface. It is believed to be the arsenic analogue of red phosphorus. However, in its crystalline stage, it resembles black phosphorus, adopting a layered structure built from As6 rings. It is a semiconductor..

Its products:

- **Hydrides**: All elements in Group 15 form hydrides with the formula EH_3

BiH3 Bismuthine	SbH3 Stibnine	AsH3 Arsénine	PH3 Phosphine	NH3 ammoniac	
-	−88	−117	−133.8	−77.7	**Melting point °C**
17	−18.4	−62.5	−87.8	−33.3	**Boiling point °C**
-	-	-	Weak base	Base	**acidity**

The unusually high boiling and melting points of ammonia (NH3), represented by FP (freezing point) and PE (boiling point), result from the formation of strong hydrogen bonds (due to the electronegativity difference between nitrogen and hydrogen). All hydrides are covalent, volatile compounds, and highly toxic.

- **Oxydes :**

	Bi	Sb	As	P	N		Element
Acidity increases with an increase in oxidation state.	-	-	-	-	N_2O	1+	**Oxidation state**
	-	-	-	-	NO	+2	
	Bi_2O_3	Sb_4O_6	As_4O_6	P_4O_6	N_2O_3	+3	
	-	-	-	-	NO_2 /N_2O_4	+4	
	-	Sb_2O_5	As_2O_5	P_4O_{10}	N_2O_5	5+	
	Base	Amphoteric			Acid		**Acidity**

Note: All nitrogen oxides are heat-absorbing compounds, dynamically unstable but kinetically stable. Their decomposition into N_2 and O_2 is an exothermic reaction.

III. 3.6. CHALCOGEN FAMILY: (VIA)

Element	Z	Electronic configutration	isotopes	percent by weight of Earth's crust
O oxygen	8	[He] $2s^2 2p^4$	16,17,18	**44,6%**
S sulfur	16	[Ne] $3s^2 3p^4$	25 Isotopes49-26	**0.042%**
Se selenium	34	[Ar] $3d^{10} 4s^2 4p^4$	30 isotopes94-65	**5×10^-6^%**
Te tellurium	52	[Kr] $4d^{10} 5s^2 5p^4$	552istopes142-105	**1×10^-7^%**
Po polonium	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	29 isotopes 218-190	**-**
Lv Livermorium	116	[Ra] $5f^{14} 6d^{10} 7s^2 7p^4$	290-291-292-293	**synthetic**

Tthe oxygen family, is called Chalcogens. Oxygen is the most abundant element on Earth. It is present in the form of diatomic gas molecules, **O_2**, constituting 21% of the Earth's atmosphere. Additionally, it is found combined with other elements such as **H_2O, CO_2**, oxides, carbonates, sulfates, silicates, salts, etc.

Sulfur exists both as a pure element (native sulfur) in volcanic areas (yellow lemony sulfur flowers) and in combined forms such as metal sulfides (**FeS** pyrite, **PbS** galena, **ZnS** blende), sulfates like gypsum (**$CaSO_4$**), and **H_2S** (impurities in petroleum products and natural gas).

Selenium and tellurium are found accompanying sulfur in their ores.

As for polonium, it is a radioactive and unstable element, with the isotope ^{210}**Po** having a half-life of 138 days; it was discovered by Marie Curie (Nobel Prize in 1911). Finally, Livermorium is one of the recently synthesized elements.

Physio-chemicals caracteristics:

- The elements of this group have a valence shell configuration of ns^2np^4, possessing 6 valence electrons: "4 p-electrons" and "2 s-electrons." The valence electrons experience strong nuclear attraction, leading to very high ionization energies that decrease down the column.
- The oxidation states (état d'oxydation EO) based on electronegativity (χ) for these elements are, in order: **O** (3.4), **S** (2.6), **Se** (2.6). **Te** (2.1), Oxygen is the second most electronegative element after fluorine (O < F). The other elements in the group have relatively high electronegativities and can form ionic compounds with less electronegative elements.
- **O.E : -2 w**ith weakly electronegative elements. The trend decreases down the group with decreasing electronegativity. This state is predominant in oxygen.
- **E.O: +2, +4, +6** with more electronegative elements. Oxygen has an oxidation state of **+2** with fluorine (**OF_2**)

Element	Physical state CNTP	conductivity	Metallic state	Ship
o	Gas with no color or smell	insulator	Non metal	-
S	Yellow crystal	insulator	Non metal	
Se	Gray solid	semiconductor	metalloid	
Te	Silver solid	semiconductor	metalloid	
Po	Crystal shiny gray	conductor	metal	

Its products :

- The bond energy of "**O - O**" is very low compared to the bond energy of oxygen with other elements. It stabilizes by bonding with other elements, including hydrogen (**H_2O,**

O_2H_2). Ozone (**O_3)** is a colorless gas with a blue tint and a strong, highly toxic smell. It is a very powerful oxidizer:

$$O_3(g) + H_2 \leftrightharpoons O_2(g) + H_2O$$

It strongly absorbs in the ultraviolet region, and its presence in the atmosphere is vital. It protects Earth's life from the harmful ultraviolet radiation emitted by the sun.

- While the bond energy of "**S - S**" approaches the sulfur bond energy with other elements, sulfur can stabilize by forming chains (**Cl - S - S - Cl**, disulfide bridge, etc.).
- Group 16 elements form binary compounds with many metals and nonmetals. While oxygen forms oxides (both metallic and non-metallic), sulfur, selenium, and tellurium form sulfides, selenides, and tellurides, respectively. These binary compounds can be ionic (with less electronegative metals) or covalent.
- Common compounds include

Element	O	S	Se	Te
With O	O_3	SO_2	SeO_2	TeO_2
Oxide nature	oxidant	acid	acid	amphoteric
With N	NO, NO_2	-	-	-
With halogen X	O_2F_2	SF_6, S_2Cl_2, S_2Br_2	SeF_6, SeX_4	TeF_6, TeX_4
With H_2	H_2O, H_2O_2	H_2S	H_2Se	-

III. 3.7. HALOGENS FAMILY (VIIA)

Halogens (from the Greek "Halos = salt and sea" and "génos = born"), are elements with relatively simple and homogeneous properties. They are highly reactive and are never found in nature in their elemental state.

Fluorine is found in the form of fluorite (**CaF_2**), cryolite (**Na_3AlF_6**), and fluapatite **($Ca_5(PO_4)_3F$)**. Chlorine, bromine, and iodine are generally found as dissolved salts in seawater and lakes or as salt deposits after the evaporation of water bodies. Astatine is a radioactive element ($t_{1/2}$ = 8.1 hours) and is considered the least abundant natural element on Earth. Tennessine is a recently discovered element obtained through nuclear synthesis.

Halogens exist as diatomic and nonpolar **molecules X_2**, and their polarity increases with an increase in the number of electrons (Z). The transition from the gaseous state (fluorine and chlorine) to the liquid state (bromine) and then the solid state (iodine) is observed.

Element	Z	Electronic configuration	aspect	Isotopes	percent by weight of Earth's crust
Fluorine F	9	F [He] $2s^22p^5$	Yellow gas	31-14 نظير14	**0.054%**
Chlorine Cl	17	[Ne] $3s^23p^5$	Greenish yellow gas	35, 37	**0.017%**
Bromine Br	35	Br [Ar] $3d^{10}4s^24p^5$	Red-brown oleic liquid	22 isotopes 66-97	**0.0003%**
Iodine I	53	[Kr] $4d^{10}5s^25p^5$	Purple-black solid	37 isotopes 108-144	**0.000049%**
Astatine At	85	[Xe] $4f^{14}5d^{10}6s^26p^5$	Metalloid black	32 radioisotopes 191-223	**synthetic**
Tennessine Ts	117	[Ra] $5f^{14}6d^{10}7s^27p^5$	Solid	117	**synthetic**

<u>Chemical and Physical caracteristics</u>:

- Valence shell type: ns^2np^5 tends to complete its outer shell either by forming ionic bonds with metals, such as halide anions (**X^-**), or by forming covalent bonds with nonmetals, such as **X-X, H-X, C-X**, etc.
- **Oxidation state**:
  - Fluorine: The most electronegative element in the periodic table, always in the oxidation state -1.
  - **Cl, Br,** and I usually have an oxidation state of **-1**. However, other oxidation states are possible when combined with more electronegative elements like F or **O**. Other oxidation states are possible for **Cl, Br**, and **I (+1, +3, +5, +7**).
- **Products:**
  - Fluorine has a very small atomic size, affecting properties like electron affinity and the strength of the **F-F** bond.
  - Fluorine is the most electronegative element in the periodic table (χ=4). Chlorine ranks third after oxygen (**χ=3.2**) and decreases down the group (**Br=3**, **I=2.7**). Thus, fluorine is the most oxidizing element in the periodic table (**E°= +2.87 V**) and reacts with most elements, including noble metals like **Au** and **Pt,** and some noble gases like **Kr, Xe,** and **Rn.** Fluorine attacks glass and is stored in containers previously fluorinated.
  - The oxidizing ability decreases down the group, allowing for reverse displacement reactions (used in the production of iodine and bromine).

$$\mathbf{F_2 + 2NaCl \rightarrow 2NaF + Cl_2}$$

$$\mathbf{Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2}$$

$$Br_2 + 2NaI \rightarrow NaBr + I_2$$

- The stability of "C-X" bonds explains the possibility of introducing halogen atoms into organic molecules through halogenation reactions (fluorination, chlorination, bromination, iodination).
- **With water :**

Element	F	Cl	Br	I
Reaction with water (CNTP)	**Violent**	**Speed**	**slow**	**Negligible**

-Fluorine does not dissolve in water. Its oxidizing strength oxidizes water, producing hydrogen fluoride and releasing oxygen.:

$$2\ F_2\ (g) + 2H_2O\ (l) \rightarrow O_2\ (g) + 4HF\ (aq)$$

- Chlorine, bromine, and iodine are weakly soluble in water. At CNTP (Conditions Near the Triple Point), they undergo dismutation reactions: Dismutation reaction is a type of redox reaction where two molecules of A react with each other, resulting in the appearance of molecule A' through oxidation and molecule A" through reduction.

$$X_2 \ + H2O \ \leftrightharpoons HXO + HX$$

E.O. 0 E.O. +1 E.O. -1

- During the reaction of Cl_2 **(E.O. 0)** in water, one chlorine atom will oxidize to form the hypochlorite ion (**ClO^-**, E.O. +1). The other chlorine atom is reduced to form the chloride ion (**Cl^-**, E.O. -1).
- The resulting products from the decomposition of chlorine in a basic medium are two acids: hypochlorous acid (**HClO**) and hydrochloric acid (**HCl**). These acids are then neutralized by hydroxide ions (**OH^-**) as follows:

$$Cl_2 + 2H_2O \leftrightharpoons HClO + H_3O^+ + Cl^-$$

$$HClO + OH^- \rightarrow ClO^- + H_2O$$

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

Therefore, the deviation reaction is favored (transition from a partial reaction "⇋" to a complete reaction "→"), and the equilibrium is shifted to the left.

The reaction equilibrium is written as follows:

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$

Dissolution of iodine in iodide solution: The solubility of iodine in water is negligible, but in the presence of iodide anion (**I^-**) such as in a solution of KI, the solubility increases with the formation of the triiodide anion (**I_3^-**)

$$I_2 + I^- \leftrightharpoons I_3^-$$

- **Hydrogen halides (HX):**

HX These are covalent and volatile compounds, except for **HF**, which is liquid at **CNTP** (normal Temperature and Pressure). Examination of the strength of the **H-X** bond indicates that stability decreases in the group. In aqueous solution, this affects the acidity strength, which increases in the group. **HF** is a weak acid (partial dissociation).

$$HF + H_2O \leftrightharpoons H_3O^+ + F^-$$

HCl, HBr, and **HI** are strong acids (complete dissociation).

$$HX\ (aq) + H_2O\ (l) \rightarrow X^-\ (aq) + H3O^+\ (aq)$$

- Oxides:

A. *For fluorine*: since fluorine is more electronegative than oxygen, it is called oxygen fluoride. We know two oxygen fluorides: **F_2O** (E.O O: +2) and **F_2O_2** (E.O. O: +1).

B. *As for chlorine, bromine, and iodine*: being less electronegative than oxygen, all oxidation states range from **+1** to **+7**. All oxides are heat-absorbing compounds and may be explosive (violently decompose) except **I_2O_5**, which is solid and stable at room temperature.

- **Oxoacids (HXO_n / XO_n^-):**

The oxidative acids have acidic and oxidizing properties. Their salts are basic (act as accompanying bases) and oxidizing agents. The acidity increases with:

Oxygen atom number: **$HClO < HClO_2 < HClO_3 < HClO_4$**

Halogen electronegativity: **$HClO > HBrO > HIO$**

Molecular stability:

$$HClO \rightarrow HClO_2 \rightarrow HClO_3 \rightarrow HClO_4$$

Decrease of oxidation power:

Hypochlorous acid is a strong oxidizing agent. In oxidation-reduction reactions, it is reduced to **Cl_2.**:

$$2HClO\ (aq) + 2H^+\ (aq) + 2e^- \rightarrow Cl_2\ (g) + 2H_2O\ (l)$$

The hypochlorite anion is a weaker oxidizing agent. In reactions, it is reduced to the chloride anion (**Cl^-).**

$$\mathbf{ClO^- (aq) + 2H_2O (l) + 2e^- \rightarrow Cl^- (aq) + 2OH^- (aq)}$$

Applications: The oxidizing power of **HClO** and hypochlorite (**NaClO**, **$Ca(ClO)_2$**) is used as a germicide. Hypochlorite is employed as disinfectants (bleach) or antiseptics (Dakin's solution).