

Part III Chapter I.

PROPERTIES OF ELEMENTS:

_ HALOGENS (F;Cl;Br;I et At)

_ CHALCOGENS (O;S;Se;Te;Po)

_ HYDROGEN (H)

_ NITROGEN (N)

_ PHOSPHORUS (P).

THE CHEMISTRY OF HYDROGEN

NATURAL STATE, PHYSICAL AND CHEMICAL PROPERTIES

Hydrogen is the most abundant element in the universe: 90% of the atoms in our universe are hydrogen atoms. Helium comes in second with about 9%. All the other elements share the remaining 1%.

There is very little molecular hydrogen (H_2) in the Earth's atmosphere. This is explained by its low density of 0.0899 g/L (about 14.5 times less dense than air). Since H_2 is a light gas, the Earth's gravitational attraction cannot retain it and it escapes naturally into the atmosphere.

Hydrogen isotopes

The best known isotopes of hydrogen are: protium (1H), deuterium (2H) and tritium (3H).

- 1) Protium 1H or light hydrogen: the most abundant ($\sim 99.98\%$ of natural hydrogen), its nucleus is made up of a proton and does not have a neutron. It is a stable isotope.
- 2) Deuterium 2H (or D): much less abundant ($\sim 0.015\%$ of natural hydrogen). The nucleus is made up of a proton and a neutron, it is a stable isotope. On Earth, it is mainly present in the form of deuterated water HDO (semi-heavy water).
- 3) Tritium 3H (or T): present in tiny quantities in natural hydrogen, its nucleus is made up of a proton and two neutrons. It is a radioactive isotope.

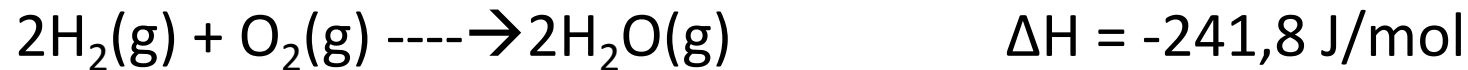
Note: there is also quadrium or tetradium 4H (or Q) the most unstable isotope of hydrogen its half-life is 1.39×10^{-22} seconds and hydrogen 7H the most neutron-rich isotope ever isolated, its half-life is 10^{-21} seconds.

Hydrogenated derivatives of non-metals

These are essentially covalent compounds. Example: HCl; NH₃; H₂O... the bond between hydrogen and the non-metal has a partial ionic character depending on the electronegativity of the non-metal. HCl more ionic than HI therefore HCl less stable than HI.

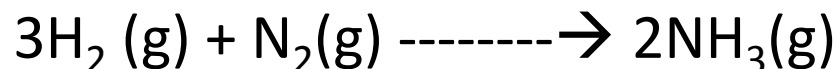
1. Reaction of hydrogen with oxygen (combustion)

The combustion of hydrogen is described by the following reaction:



2. Reaction with halogens Hydrogen reacts with each halogen to form a halide. The reaction with difluorine is explosive at room temperature and is still very lively with liquid dihydrogen (– 252°C).

3. Reaction with nitrogen The direct reaction between dihydrogen and dinitrogen allows the synthesis of ammonia NH₃ according to the reaction:



PREPARATION OR SYNTHESIS OF HYDROGEN

Industrially

Electrolysis of water An electric current is used to split water into oxygen and hydrogen. With appropriate equipment, oxygen is collected at the anode and hydrogen at the cathode.



This process is used to obtain very pure hydrogen. It is expensive because the reaction consumes a large amount of electricity.

USES OF HYDROGEN

- ☐ 50% hydrogen production for ammonia synthesis.
- ☐ 37% in hydrocarbon refining.
- ☐ 12% methanol synthesis.
- ☐ Hydrogenation of fats and oils, synthesis of alcohol and aldehydes from olefins and the manufacture of HCl.
- ☐ Deuterium ^2H is used in nuclear applications to slow down neutrons.

NATURAL STATE AND PHYSICAL PROPERTIES OF OXYGEN

NATURAL STATE In the universe, oxygen is the 3rd most abundant element, after hydrogen and helium (table below). On Earth, oxygen is the most abundant element. It constitutes 50% of the mass of the lithosphere (Earth's crust) and 88.8% of the mass of the hydrosphere.

PHYSICAL PROPERTIES

Oxygen in its natural state is a mixture of the three isotopes.

In the atmosphere, oxygen exists in three allotropic forms:

O: atomic oxygen (mon -atomic)
O₂: molecular oxygen (diatomic)
O₃: ozone (triatomic)

Dioxygen

Dioxygen O_2 is odorless and tasteless, colorless in the gaseous state and slightly blue in the solid and liquid state. Its solubility in water increases with decreasing temperature $30\text{cm}^3/\text{l}$ at 20°C and $21\text{cm}^3/\text{l}$ at 50°C under atmospheric pressure, allows aquatic life.

Table: Physical properties of dioxygen

Trioxygen or ozone

Trioxygen O_3 is a dangerous gas to breathe and is characterized by a strong pungent odor. Trioxygen O_3 is very slightly blue in the gaseous state, dark blue in the liquid state and blue-violet in the solid state.

CHEMICAL PROPERTIES

Oxygen belongs to the chalcogen family: 2nd period, group VIA; ${}^8\text{O}$: $1s^2 2s^2 2p^4$

☐ Oxygen can gain two electrons and form an oxide ion O^{2-} in ionic compounds.

☐ Formation of two single covalent bonds or a double covalent bond
Example: H_2O and CO_2 .

☐ Formation of a covalent bond with gain of an electron, Example: the hydroxide ion OH^- and the hydrogen carbonate ion HCO_3^- .

☐ Possibility of tricoordination example: H_3O^+ .

HALOGENS

GENERAL

The elements in column VIIA are called halogens, they are characterized by a fundamental electronic configuration $n(ns)^2(np)^5$, or 7 valence electrons.

We find successively:

$n = 2$: fluorine F, $(2s)^2(2p)^5$;

$n = 3$: chlorine Cl, $(3s)^2(3p)^5$;

$n = 4$: bromine Br, $(4s)^2(3d)^{10}(4p)^5$;

$n = 5$: iodine I, $(5s)^2(4d)^{10}(5p)^5$.

$n=6$: Astatine, At, $(6s)^2(5d)^{10} (4f)^{14}(6p)^5$,

Halogens exist in nature in a combined state.

Fluorine: it constitutes about 0.065% of the mass of the earth's crust and the main compounds in which it is found are: cryolite $AlNa_3F_6$, fluorite CaF_2 and fluoroapatite $Ca_5F(PO_4)_3$. As for the fluorine content of seawater, in which it is found in the form of fluoride ions F^- , it is about $6 \cdot 10^{-5} g/L$.

Chlorine: is the most widespread halogen, it constitutes about 0.19% of the mass of the earth's crust and seawater contains about 19g/L. Chlorine is mainly found in the form of sodium chloride NaCl.

Bromine: is the second most abundant halogen after chlorine with a content in seawater of 0.1 g/L, while the earth's crust contains about $2 \cdot 10^{-4}\%$.

Iodine: it is very rare in the earth's crust, about $6 \cdot 10^{-8}\%$ by mass, it is found mainly in the form of iodates $\text{Ca}(\text{IO}_3)_2$ and NaIO and in the form of iodide (I^-) in the brines that accompany oil wells. Sea water contains about $2.3 \cdot 10^{-3}\text{g/L}$ of iodine.

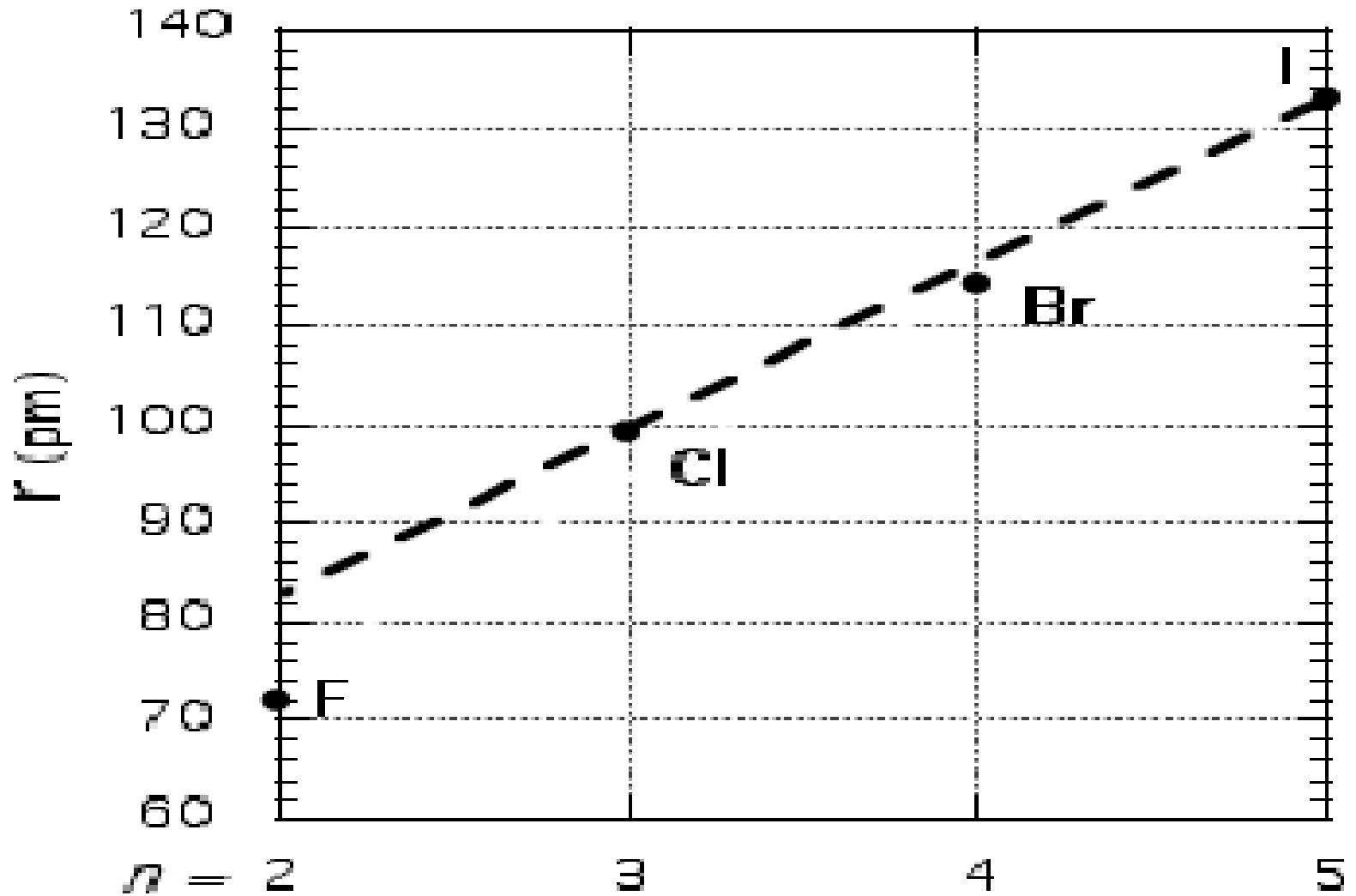
Astatine: it is radioactive as its name indicates (which means “unstable”).

•The atomic properties of the halogens, presented in tabular form below, are then discussed in more detail in graphical form.

X	F	Cl	Br	I
Z	9	17	35	53
Conf. élect.	[He]2s ² 2p ⁵	[Ne]3s ² 3p ⁵	[Ar]3d ¹⁰ 4s ² 5p ⁵	[Kr]4d ¹⁰ 5s ² 6p ⁵
Energie d'ionisation I, kJ mol ⁻¹ X(g) → X ⁺ (g) + e ⁻	1680,6	1255,7	1142,7	1008,7
Energie de fix. élect. -A, kJ mol ⁻¹ X(g) + e ⁻ → X ⁻ (g)	-332,6	-348,5	-324,7	-295,5
Electronégativité (Pauling)	3,98	3,16	2,96	2,66
r _{cov} (pm)	71	99	114	133
r _{X⁻} (pm)	133	184	196	220

Propriétés atomiques des éléments halogènes

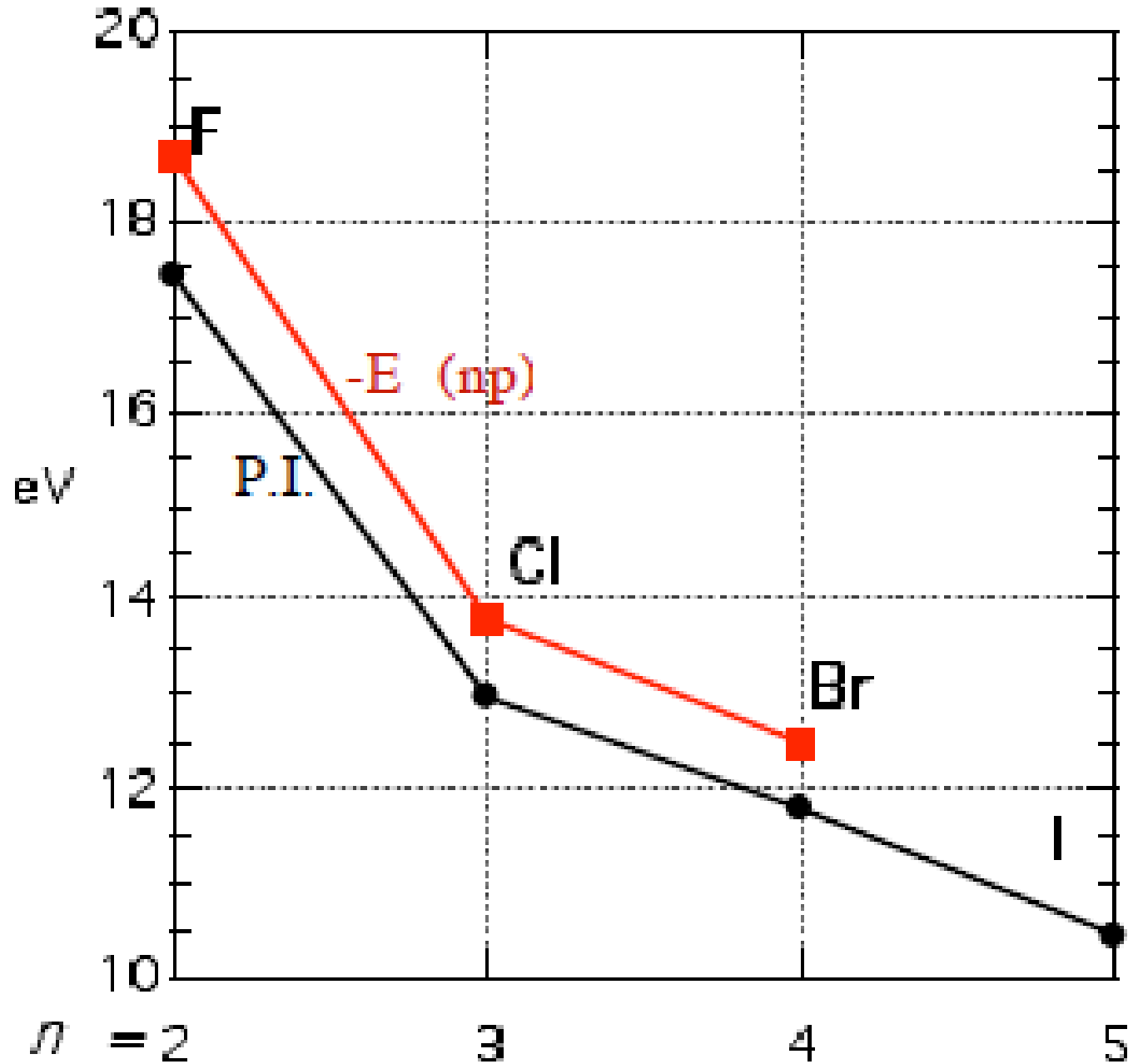
Size (atomic radius)



As expected, the atomic radius increases as one moves down the column.

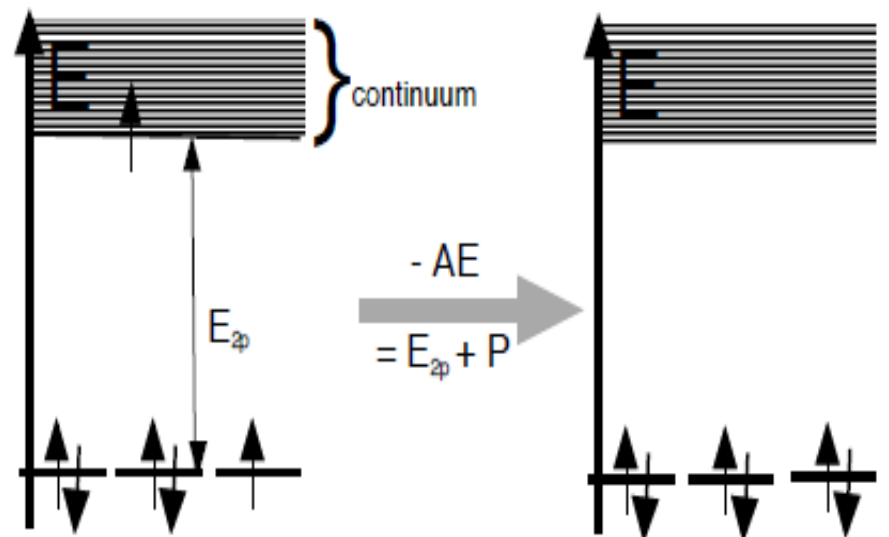
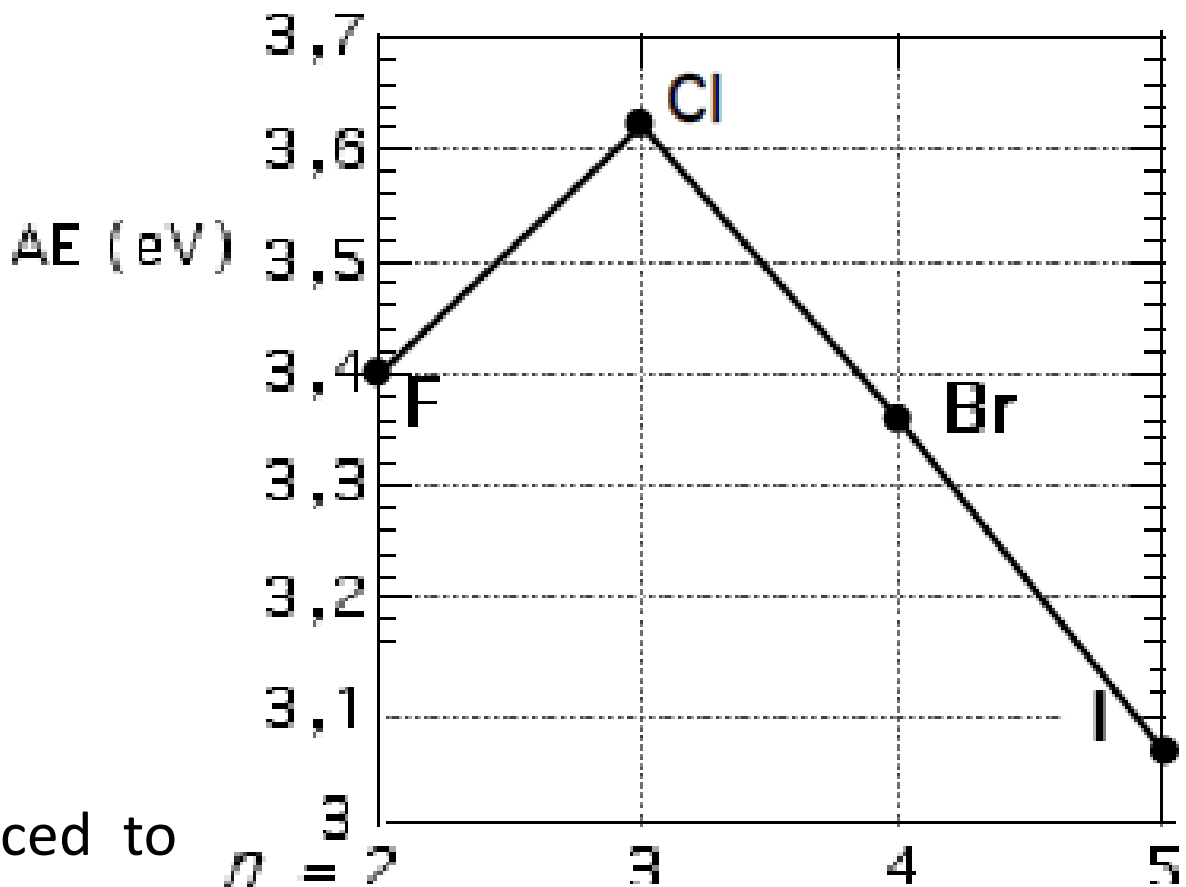
Ionization potential, electron affinity and orbital energies

•To ionize a halogen element, an electron must pass from the (np) level to the vacuum.



- The electronic affinities are much weaker than the P.I.s. Indeed, the capture of an electron results in passing from the $(np)5$ configuration of the halogen element to the $(np)6$ configuration of the corresponding anion.

- The extra electron is forced to occupy the second place in an already half-filled p orbital, which induces a considerable repulsion; in this case we will speak of a pairing energy, denoted P , positive and high.



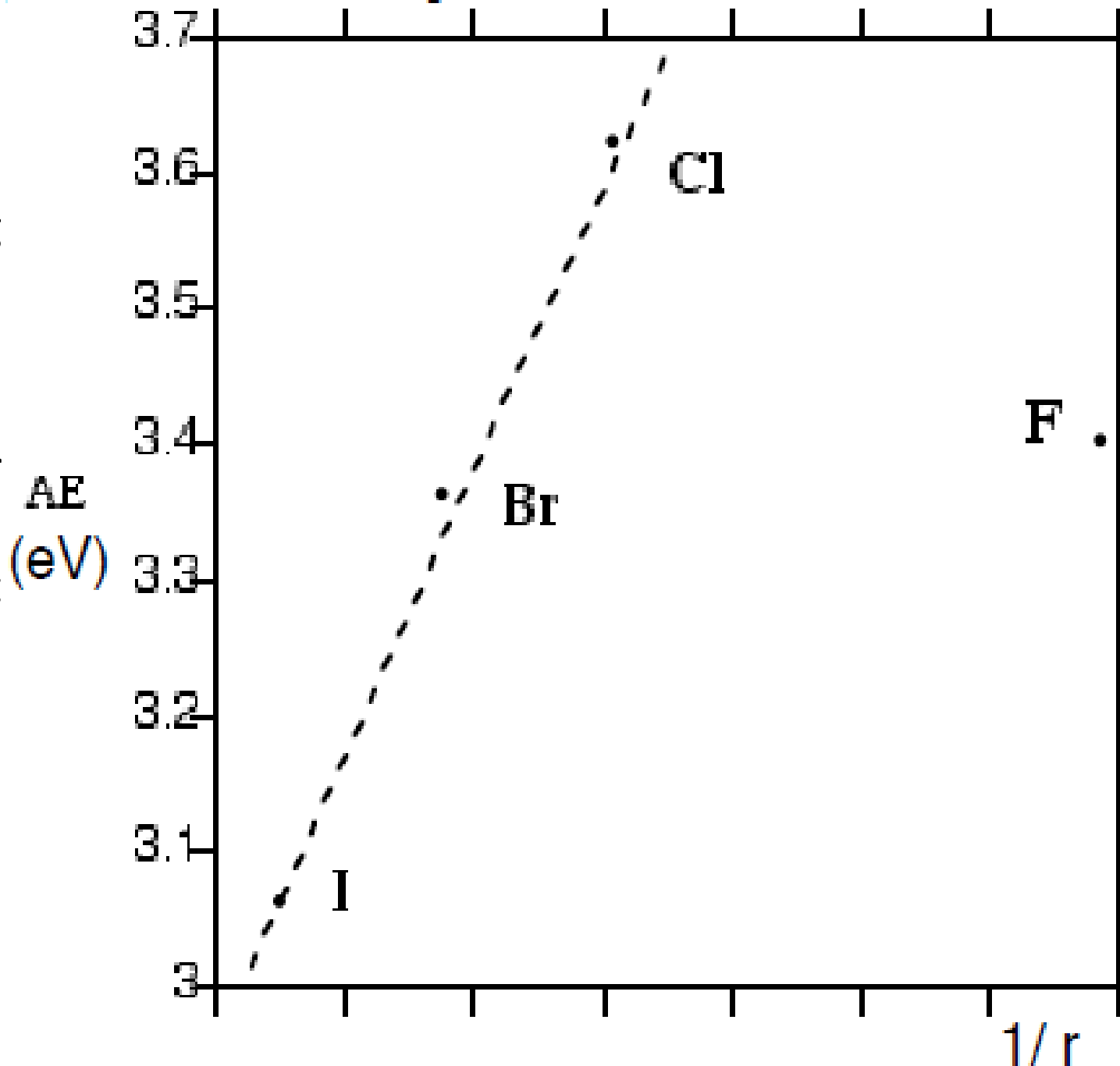
- For fluorine, the pairing energy will be particularly large because of the small size of the orbitals (2p), hence a fairly low electronic affinity.

- In this simplified model, the formation of the anion would amount to fixing an electron at a distance r_{at} from the nucleus; the potential energy of this additional electron should then be equal to:

$$\frac{-Z^* e^2}{4\pi\epsilon^0 r_{at}}$$

and the electron affinity, which is the opposite of this quantity, would therefore be proportional to $(1/r_{at})$.

The following diagram shows that this relationship is well obeyed for the I, Br, Cl series, but not for F, whose small size prohibits neglecting interelectronic repulsions.



PHYSICAL PROPERTIES

In the uncombined state, halogens consist of diatomic molecules F_2 , Cl_2 , Br_2 and I_2 .

Difluorine: is a gas with an irritating odor of extreme toxicity, its reactivity allows it to attack almost any material.

Dichlorine: is a very toxic gas with a suffocating and irritating odor, a content in the inspired air of about 0.01% causes death. In addition, it has a great bactericidal power and is used as a disinfectant, especially in water.

Dibromine: is very toxic and even though it is liquid under normal conditions, its vapors are excessively suffocating, it causes very painful burns on the skin that take a long time to heal and it is also used as a disinfectant.

Diiodine: is less reactive and less toxic than the others, it irritates the skin and stains it brown and in high doses, it causes vomiting and dizziness, it is used a lot as an antiseptic.

: Physical properties of dihalogen molecules

X₂	F₂	Cl₂	Br₂	I₂
Etat physique (conditions usuelles)	gaz incolore	gaz jaune- verdâtre	liquide rouge- orangé	solide violet foncé à l'éclat métallique
T f (°C)	-218,6	-101,0	-7,25	113,6
Téb (°C)	-188,1	-34,0	59,5	185,2
$\Delta H^{\circ}f$ (kJ mol ⁻¹)	0,51	6,41	10,57	15,52
$\Delta H^{\circ}éb$ (kJ mol ⁻¹)	6,54	20,41	29,56	41,95
$\Delta H^{\circ}diss$ (kJ mol ⁻¹) X ₂ (g) → 2X(g)	158,8	242,58	192,77	151,10
X-X (pm) (gaz)	143	199	228	266
X-X (pm) (solide)	149	198	227	272
plus courte distance intermoléculaire X...X (pm) (solide)	324	332	332	350

DIHALOGEN MOLECULES.

•The halogen elements, in their most stable state at 298K under pressure of 1 bar (standard thermodynamic state), are found in the form of diatomic molecules X_2 .

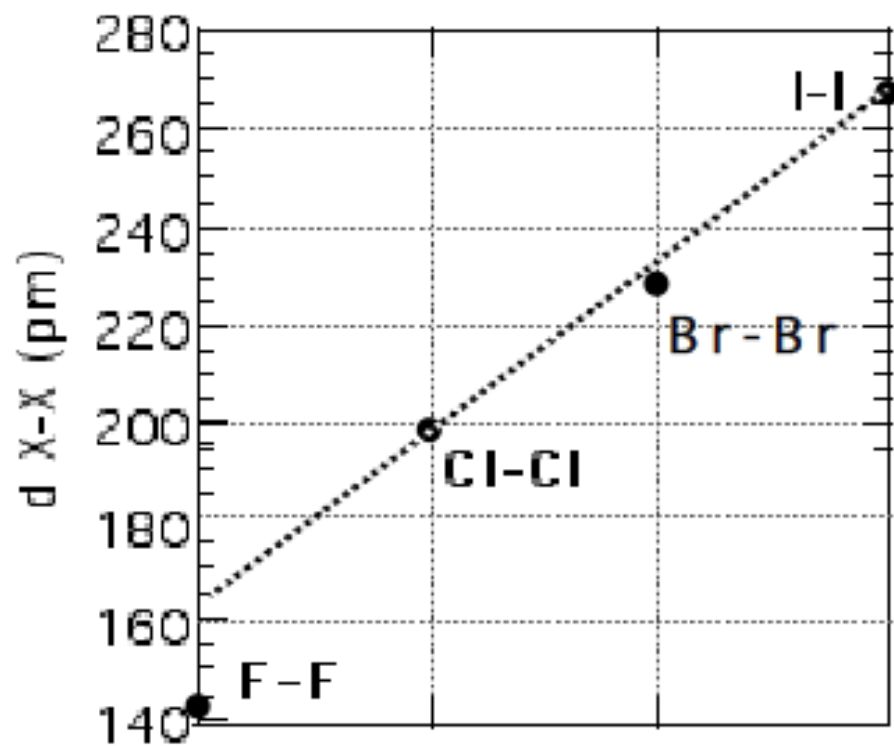
X_2	F_2	Cl_2	Br_2	I_2
Etat physique (conditions usuelles)	gaz incolore	gaz jaune-verdâtre	liquide rouge-orangé	solide violet foncé à l'éclat métallique
T_f (°C)	-218,6	-101,0	-7,25	113,6
$T_{éb}$ (°C)	-188,1	-34,0	59,5	185,2
ΔH_f^0 (kJ mol ⁻¹)	0,51	6,41	10,57	15,52
$\Delta H_{éb}^0$ (kJ mol ⁻¹)	6,54	20,41	29,56	41,95
ΔH_{diss}^0 (kJ mol ⁻¹) $X_2(g) \rightarrow 2X_g$	158,8	242,58	192,77	151,10
X-X (pm) (gaz)	143	199	228	266
X-X (pm) (solide)	149	198	227	272
plus courte distance intermoléculaire X...X (pm) (solide)	324	332	332	350

Propriétés physiques des molécules dihalogènes

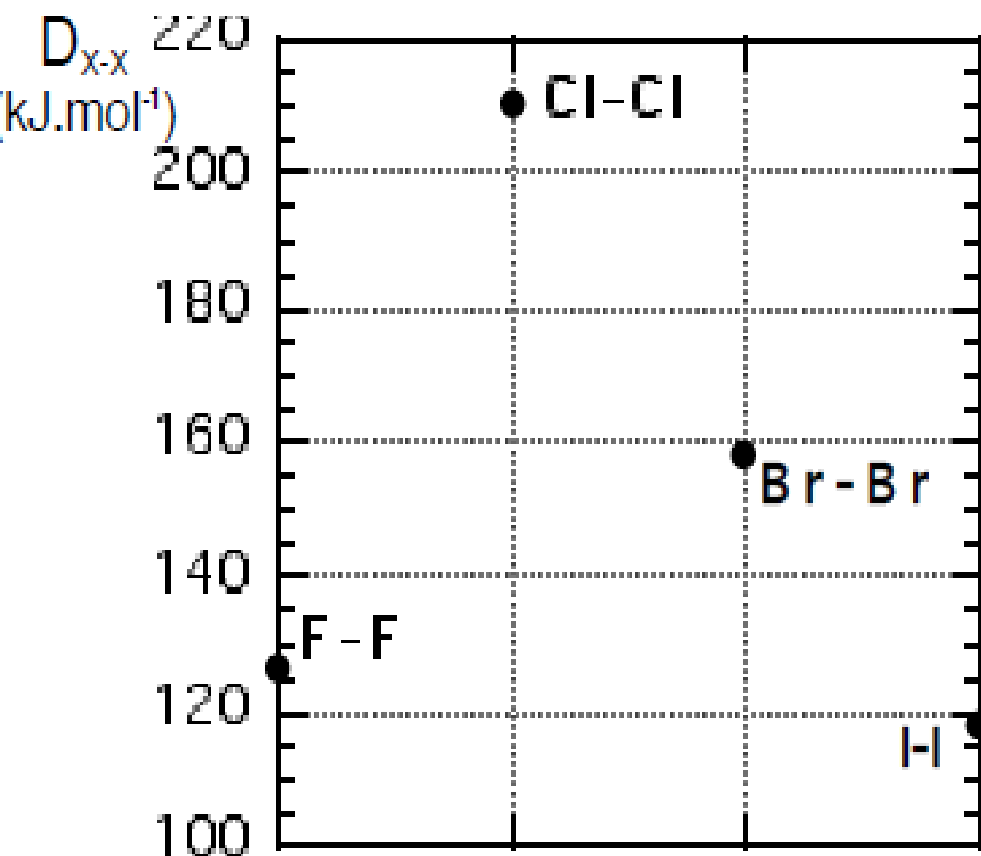
X	F	Cl	Br	I
$\frac{1}{2}X_2(g) \Rightarrow X(g)$ $\Delta_{\text{diss}}H^\circ$ (kJ mol ⁻¹)	79,4	121,29	146,37	75,55
$X(g) + e^- \Rightarrow X^-(g)$ -A (kJ mol ⁻¹)	-332,6	-348,5	-324,7	-295,5
$X^-(g) \Rightarrow X^-(aq)$ $\Delta_{\text{hyd}}H^\circ$ (kJ mol ⁻¹)	-515	-381	-347	-305
$X_2(aq) + 2e^- \Rightarrow 2X^-(aq)$ E^0 (V)	2,866	1,395	1,087	0,536

Quelques propriétés chimiques des molécules dihalogènes.

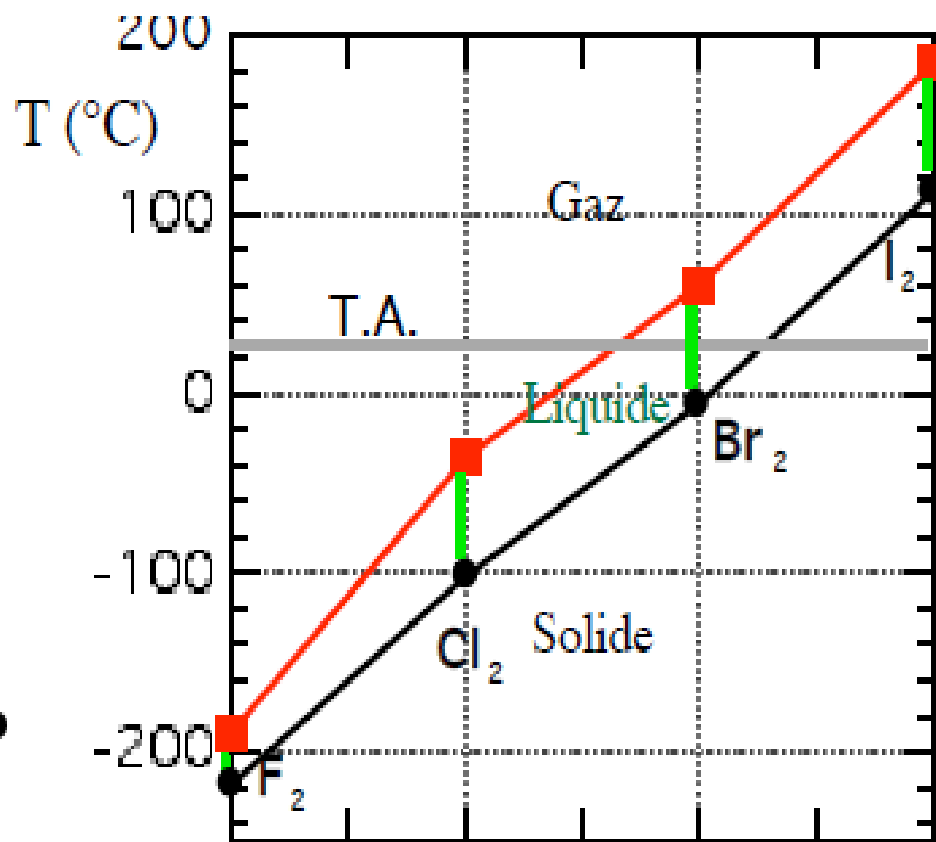
- Bond lengths: Note the small distance between the nuclei of the fluorine atoms in F_2 .*



- This intimate approach causes a repulsion between the lone pairs of the two fluorines (if we describe the molecule in the Lewis model framework), and is responsible for a lower binding energy than expected (left diagram below):



Enthalpies de dissociation de la liaison X-X

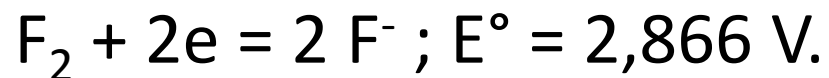


Températures de fusion et d'ébullition

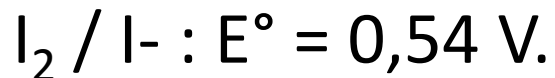
•Melting and boiling temperatures increase with atomic number. This appears to be due mainly to the greater polarizability of heavy elements, which increases intermolecular interactions of the dipole/induced dipole type (indeed, X₂ molecules interact with each other only by van der Waals-type interactions).

REACTIVITY OF DIHALOGENS

•Fluorine is the most reactive of the elements. It is also the most electronegative, which makes difluorine the only compound capable of oxidizing dioxygen. In aqueous solution, it behaves as a strong oxidant, following the half-reaction:



• This high value of E° indicates that difluorine can oxidize water to O_2 at any pH. The reactivity decreases as we go down the column. We then find less and less strong oxidants, which is related to a lower electronegativity of the corresponding elements. The standard potentials of the redox couples X_2 / X^- are respectively:

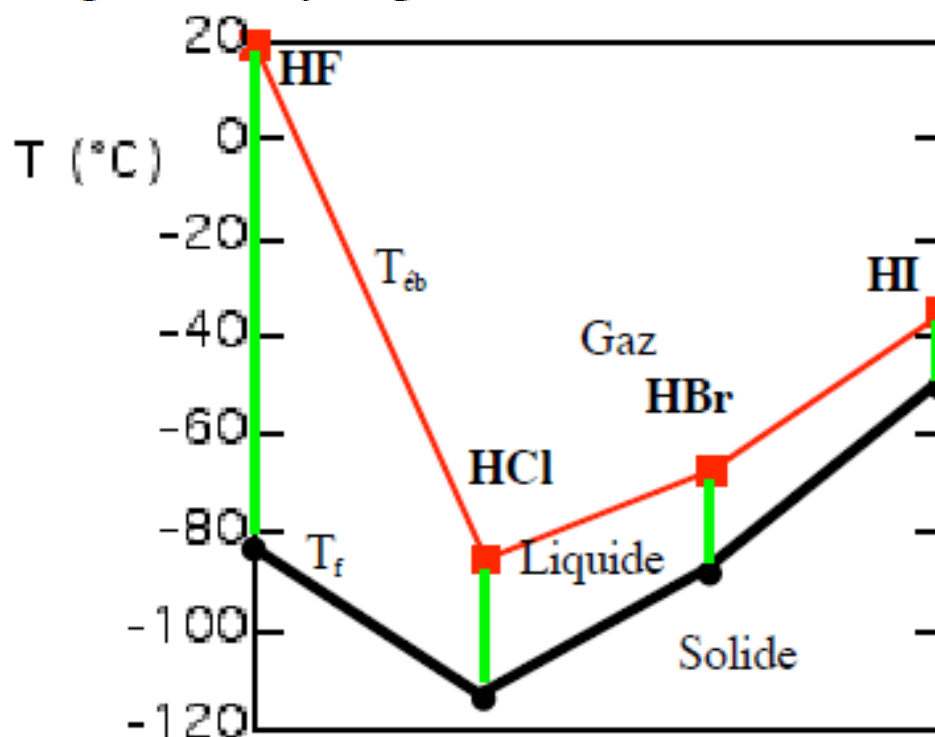
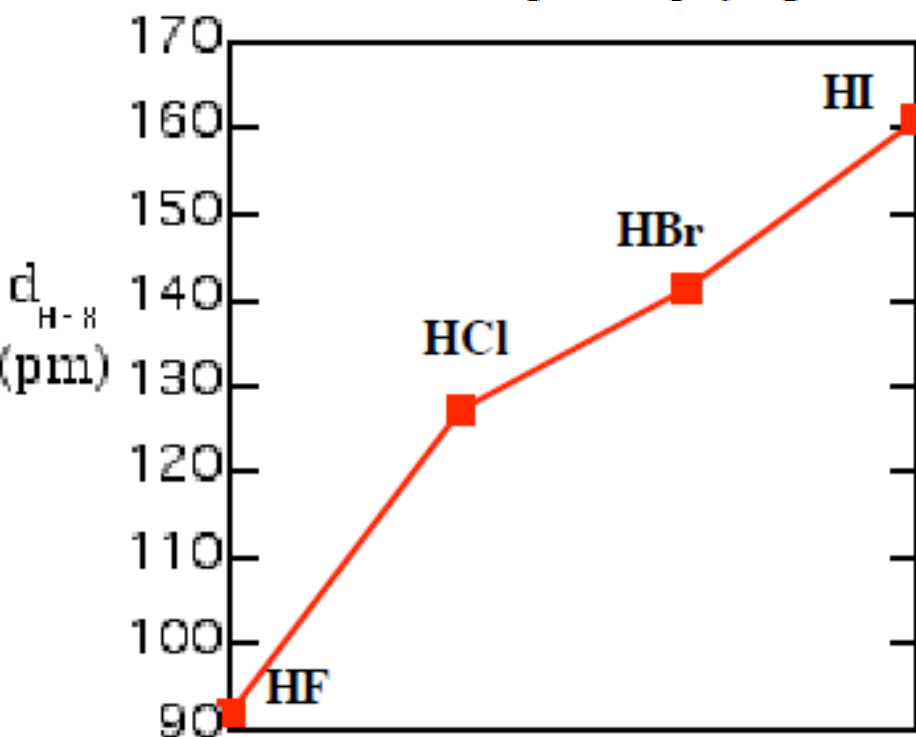


HYDROGEN HALIDES HX

Physical properties

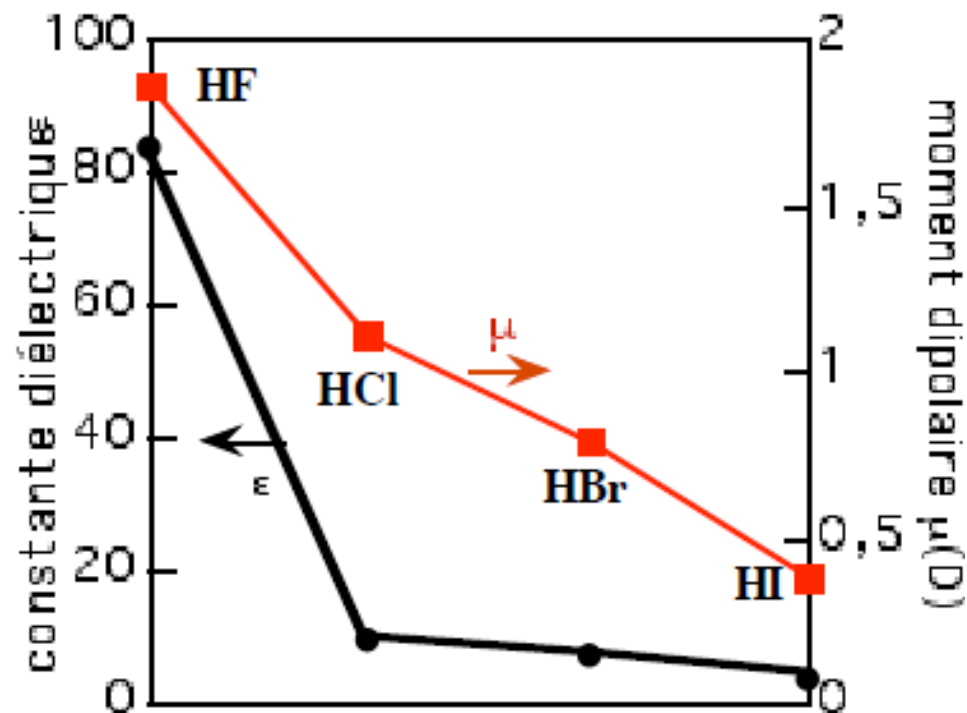
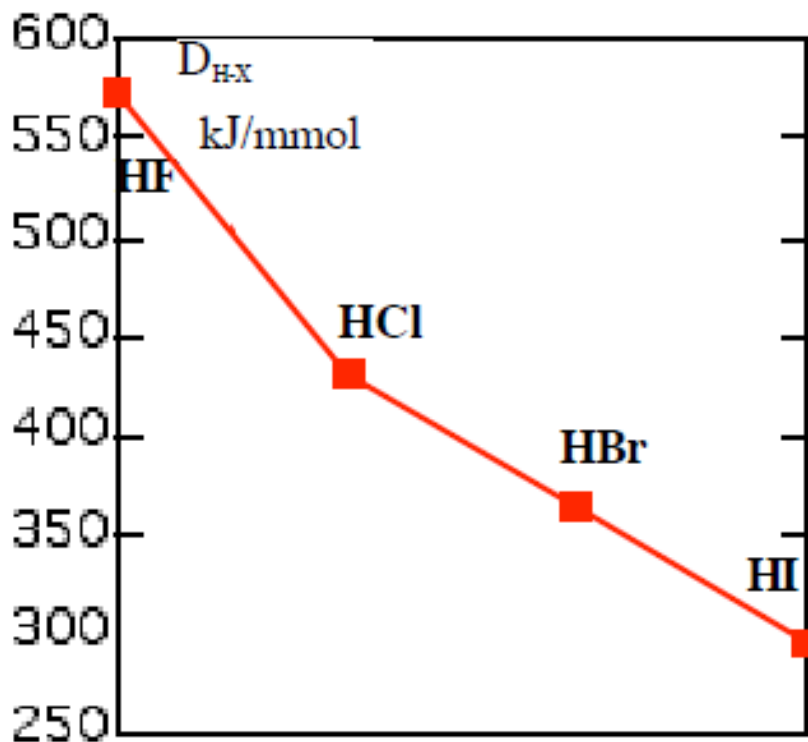
	HF	HCl	HBr	HI
T_f (°C)	-83,4	-114,7	-88,6	-51,0
T_{eb} (°C)	19,5	-84,2	-67,1	-35,1
H-X (pm)	91,7	127,4	141,4	160,9
moment dipolaire μ (Debye)	1,74	1,07	0,788	0,382

Propriétés physiques des halogénures d'hydrogène



- Note the wide range of existence of liquid HF.

- The following two diagrams represent the variation of the DH-X dissociation enthalpy, and of the dielectric properties of hydrogen halides. The higher we go in the column, the more polar the H-X bond is, which results in a high dielectric constant of the HX molecules in the liquid state (we have seen that for liquid HF, it is even higher than that of water).



CHALCOGENS

GENERAL INFORMATION ON THE ELEMENTS OF THE VIA GROUP

The elements of the VIA column are called chalcogens, they are characterized by a fundamental electronic configuration $(ns)^2(np)^4$, or 6 valence electrons.

We find successively:

$n = 2$: oxygen O, $(2s)^2(2p)^4$;

$n = 3$: sulfur S, $(3s)^2(3p)^4$;

$n = 4$: selenium Se, $(3d)^{10} (4s)^2 (4p)^4$;

$n = 5$: tellurium Te, $(4d)^{10} (5s)^2 (5p)^4$.

$n = 6$: Polonium Po, $(4f)^{14}(5d)^{10} (6s)^2(6p)^4$.

OXYGEN (O): Oxygen is the most widespread of these elements in both the lithosphere and the hydrosphere. In the lithosphere, it is found mainly in the form of silicates (Na_2SiO_3), oxides (Fe_2O_3), nitrates (NaNO_3), carbonates (MgCO_3), sulfates (Na_2SO_4)... in the hydrosphere, oxygen is found mainly in the form of H_2O or dissolved in water in the state of O_2 .

SULFUR (S): Sulfur represents approximately 0.05% of the lithosphere. It exists in nature in the state of a simple pure substance, in the form of hydrogen sulfides H_2S , in the form of metallic sulfides (CuS , ZnS , etc.) and in the form of sulfates (Na_2SO_4 , CuSO_4 , etc.). Oil, natural gas and coal contain significant quantities of sulfur from the decomposition of plants.

SELENIUM (SE) AND TELLURIUM: Selenium and tellurium exist in trace amounts in metal sulfide ores ($10^{-5}\%$ and $10^{-7}\%$ of the mass of the Earth's crust)

POLONIUM (PO): Polonium is a radioactive element that exists in trace amounts in uranium ores.

ATOMIC PROPERTIES

The atomic properties of chalcogens are shown in the table below: As expected, the atomic and anionic radius increase with the atomic number Z as one goes down the column. Whereas, the ionization potential and electronegativity decrease.

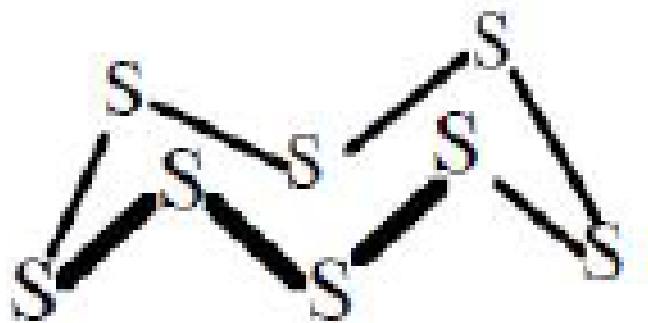
Oxygen and sulfur are nonmetals, selenium and tellurium are metallic-looking solids formed of long chains of atoms, and polonium is a metal.

Table: Atomic properties of chalcogen elements

X	O	S	Se	Te
Z	8	16	34	52
Conf. élect.	[He]2s ² 2p ⁴	[Ne]3s ² 3p ⁴	[Ar]3d ¹⁰ 4s ² 5p ⁴	[Kr]4d ¹⁰ 5s ² 6p ⁴
Energie d'ionisation I, kJ mol ⁻¹ X(g) → X+(g) + e ⁻	1314	999	941	869
Energie de fix. élect. -A, kJ mol ⁻¹ X(g) + e ⁻ → X ⁻ (g)	-141	-200	-195	-190
Electronégativité	3,5	2,44	2,48	2,01
r _c (pm)	73	102	117	135
r _x (pm)	126	170	184	207

SULFUR

By analogy with dioxygen, one could imagine a diatomic molecule S₂ with a fairly similar molecular orbital diagram. This species does indeed exist in the gaseous state, but the ordinary forms of sulfur that are solid at room temperature are based on different crystalline arrangements of cyclo-S₈ forming a “crown ring”:



Sulfur has a large number of cyclic molecules, we know of cyclo-S₆, cyclo-S₇, cyclo-S₁₂, cyclo-S₁₈, cyclo-S₂₀ and even “poly catena sulfurs”, infinite chains of sulfur atoms arranged in a helix (S_∞). The tendency of sulfur to form chains -S-S-S-... is called catenation. The allotropic forms (different crystal forms) α, β and γ of sulfur are based on the stacking of cyclo-S₈.

CHEMICAL PROPERTIES OF SULFUR

Sulfur belongs to the chalcogen family: 3rd period, group VIA. 16S:



☐ Sulfur can gain two electrons and form the sulfide anion S^{2-} .

☐ Formation of two single covalent bonds or a double covalent bond:

Example: H_2S hydrogen sulfide and CS_2 carbon sulfide.

☐ Formation of a covalent bond with gain of one electron: Example: the hydrogen sulfide anion HS^- and the disulfide S_2^{2-} (FeS_2).

☐ Other possibilities by using the d orbital: SF_4

THE DEGREES OF OXIDATION OF SULFUR

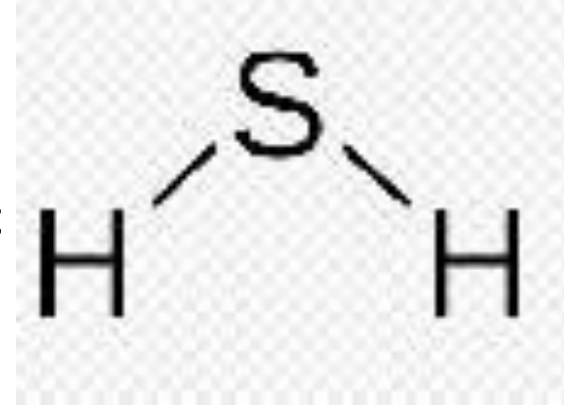
Sulfur can take the following oxidation states: -II, -I, 0, +I, +II, +IV, +V and +VI.

Oxidation degrees of sulfides

Sulfur in D.O (-II) can replace oxygen in a large number of compounds. With metals it forms analogues of oxides (Na_2S replaces Na_2O) and with hydrogen hydrogen sulfide H_2S the analogue of water.

The angle H \dot{S} H = 92.1°

Hydrogen sulfide H₂S: H₂S is a colorless gas, with an unpleasant odor (rotten egg smell), very toxic and slightly soluble in water.



H₂S acid: H₂S is a weak diacid, it dissociates in water.

H₂S reducer.

Preparation

H₂S can be obtained by extraction from certain natural gases or by the action of an acid on a metal sulfide. $MS + 2H^+ \rightarrow H_2S + M^{2+}(aq)$

H₂S toxicity: H₂S is a poison, a concentration of H₂S of the order of 10⁻³ mol/m³ produces dizziness, while a concentration of the order of 5.10⁻² mol/m³ can cause death by causing paralysis of respiration. The maximum level of H₂S that is considered acceptable is about 4.5.10⁻⁷ mol/m³ for a period of 1 hour.

GENERAL INFORMATION ON THE ELEMENTS OF THE VA GROUP

The elements of column VA are characterized by a fundamental electronic configuration $(ns)^2(np)^3$, or 5 valence electrons. We find successively:

$n = 2$: nitrogen N, $(2s)^2(2p)^3$;

$n = 3$: phosphorus P, $(3s)^2(3p)^3$;

$n = 4$: arsenic As, $(3d)^{10}(4s)^2(4p)^3$;

$n = 5$: antimony Sb, $(4d)^{10}(5s)^2(5p)^3$.

$n = 6$: Bismuth Bi, $(4f)^{14}(5d)^{10}(6s)^2(6p)^3$.

NITROGEN (N): In the form of N_2 molecules (dinitrogen), nitrogen represents approximately 78% of the volume of air. In the combined state, nitrogen represents approximately 0.03% by mass of the lithosphere and 3.0% of the human body.

PHOSPHORUS (P): it represents about 0.12% of the mass of the earth's crust and is found in a combined state in the form of apatite such as $Ca_5(PO_4)3OH$ (hydroxyapatite), $Ca_5(PO_4)_3F$ (fluorapatite), $Ca_5(PO_4)3Cl$ (chlorapatite). The human body contains 1.2% by mass of phosphorus, contained in bones, teeth, ADP, ATP and DNA.

ARSENIC, ANTIMONY AND BISMUTH: are elements present in trace amounts in the earth's crust. Arsenic ($5 \cdot 10^{-4}\%$), antimony ($10^{-4}\%$) and bismuth ($2 \cdot 10^{-5}\%$). They are found in the form of sulfides such as As_2S_3 , As_4S_4 , Sb_2S_3 , Bi_2S_3 , or oxides such as As_4O_6 , Sb_4O_6 , Bi_2O_3 .

ATOMIC PROPERTIES

The atomic properties of the elements of group VA are shown in the table below: As expected, the atomic radius increases with the atomic number Z as one goes down the column. Whereas, the ionization potential and electronegativity decrease. A progressive increase in metallic character is observed as Z increases.

Atomic properties of group VA elements

X	N	P	As	Sb	Bi
Z	7	15	33	51	83
Config. élect.	$[\text{He}]2s^2 2p^3$	$[\text{Ne}]3s^2 3p^3$	$[\text{Ar}]3d^{10} 4s^2 5p^3$	$[\text{Kr}]4d^{10} 5s^2 6p^3$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^3$
Energie d'ionisation I, kJ mol ⁻¹ $\text{X}(\text{g}) \rightarrow \text{X}^+(\text{g}) + \text{e}^-$	1402	1012	947	834	703
Electronégativité	3,07	2,06	2,20	1,82	1,67
rc (pm)	75	110	122	143	152

NITROGEN

CHEMICAL PROPERTIES OF NITROGEN

Nitrogen belongs to the 2nd period, group VA. $7N: [He] 2s^2 2p^3$

- ☐ Nitrogen can gain three electrons and form the nitride anion N^{3-} (Li_3N ionic bond).
- ☐ Formation of three single covalent bonds or one triple covalent bond
Example: NH_3 ammonia and N_2 dinitrogen.
- ☐ Formation of two covalent bonds with gain of one electron Example: the amide anion NH_2^-
- ☐ Formation of a covalent bond with gain of two electrons, Example: the imide anion NH^{2-} .
- ☐ Nitrogen can gain a proton and form the ammonium cation NH_4^+ .

Dinitrogen

Nitrogen is produced industrially by distillation of liquid air. Physical properties: Under normal conditions, nitrogen exists in the form of a diatomic gas N_2 which liquefies at $-195^\circ C$ and solidifies at $-209.9^\circ C$. This gas is colorless, odorless, tasteless and poorly soluble in water. The intermolecular interactions are of the extremely weak Van der Waals type because of the small size of the N_2 molecules.

Chemical properties:

The two nitrogen atoms are linked by a triple bond of length 109.76 pm and energy equal to -946 kJ/mol. The stability of the N₂ molecule and the absence of polarity makes dinitrogen chemically inert at room temperature, except for Li and Mg (nitride of Mg and Li) and explains its abundance in nature in the form of N₂. Note: Nitrogen is assimilated by plants only in the form of nitrate ions NO³⁻, ammonia NH₃ or NH⁴⁺.

PHOSPHORUS:

Elemental phosphorus exists in the solid state in amorphous or crystalline form. In the gaseous state, phosphorus exists in the form of diphosphorus and atomic phosphorus.

Preparation

Phosphorus is prepared by reduction in an electric furnace at around 1500°C of natural phosphate Ca₃(PO₄)₂ using a mixture of coke (C) and silicon dioxide (SiO₂) as a reducing agent. The oxidation number of phosphorus changes from +5 in Ca₃(PO₄)₂ to 0 in P₄.

$$2 \text{Ca}_3(\text{PO}_4)_2 + 6 \text{SiO}_2 + 10 \text{C} \rightarrow \text{P}_4 + 6 \text{CaSiO}_3 + 10 \text{CO}$$

Diphosphorus

The thermodynamically stable diphosphorus is obtained by decomposition of phosphorus P₄ at around 1200°C to 2000°C. Above 2000°C the diphosphorus molecules begin to dissociate into atomic phosphorus. $d(\text{P} \equiv \text{P}) = 189.5 \text{ pm}$.

Allotropic forms of phosphorus

Phosphorus has five crystalline forms and many amphiphilic phases. The most common allotropic forms are: white phosphorus and red phosphorus, there is also black and purple phosphorus. All forms give the same liquid and vapor of P₄ molecules (tetraphosphorus).

White phosphorus

White phosphorus or tetraphosphorus is formed of P₄ molecules (4 P atoms, $d(\text{P}-\text{P}) = 225 \text{ pm}$). It is a transparent waxy solid ($T_{\text{fus}} = 44.2^\circ\text{C}$, $T_{\text{eb}} = 280.5^\circ\text{C}$, $\rho = 1.82 \text{ g/cm}^3$) which turns yellow in the presence of light, toxic, unstable, highly flammable and pyrophoric (self-ignition) in contact with air.

White phosphorus is often stored in water because it is poorly soluble. However, it is soluble in benzene, oils, carbon disulfide and sulfur chloride.



White phosphorus

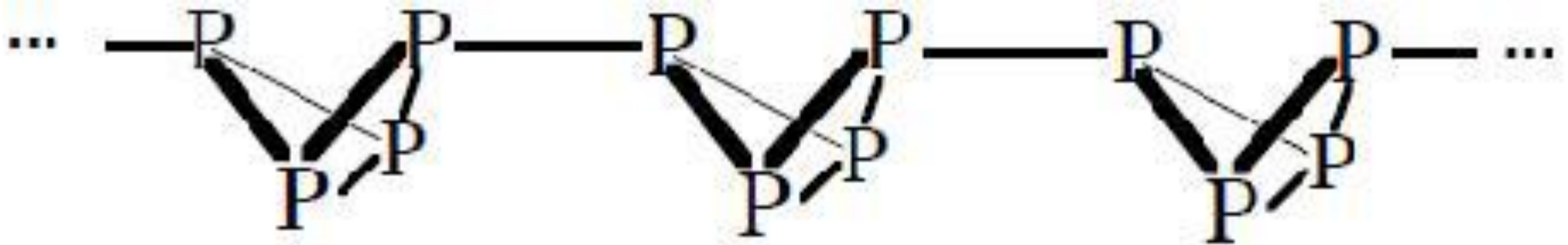
Note:

White phosphorus is a chemical weapon because it slowly oxidizes in air with chemiluminescence called phosphorescence and ignites spontaneously at around 35°C. This combustion leads to the creation of phosphorus pentoxide ($P_4^{+5} O_2 \rightarrow P_4O_{10}$) which absorbs moisture from the air and living tissues to form phosphoric acid, resulting in dissolution of living tissues ($P_4O_{10} + 6 H_2O \rightarrow 4 H_3PO_4$).

Red phosphorus

Red phosphorus is a thermodynamically stable amorphous allotrope of phosphorus ($T_{\text{fus}} = 600^{\circ}\text{C}$, $\rho = 2.16 \text{ g/cm}^3$) less flammable than white phosphorus and non-toxic (match striker contains red phosphorus). It can be obtained by gently heating white phosphorus to around 240°C or by exposure to sunlight.

Red phosphorus can be transformed into white phosphorus at 260°C .



Red phosphorus