Systematic Chemistry of elements s and p

I - s block metals

- Presence of cations A⁺ ou B²⁺ in minerals and natural water. Some are essential to life metabolism (ex: K⁺, Ca²⁺).

- Low ionization energies and vaporization enthalpies

  Labile valence electrons

- Strong reducing agents: vigorous reaction with H₂O(M +H₂O --> H₂)

- Oxydation degree: +1 for alcalins et +2 for earth-alcalin metal ions.

- In the absence of air and moisture, Na⁻ anions are accessible.

- The coordination of “hard » polydentate ligands (O- ou N-based) typically afford stable metal chelates.
Redox Reactions

Group 1: \[ \text{M(s)} + \text{H}_2\text{O} \rightarrow \text{M}^+(\text{aq}) + \text{OH}^-(\text{aq}) + 0.5 \text{H}_2(\text{g}) \]

Group 2: \[ \text{M(s)} + \text{H}_2\text{O} \rightarrow \text{M}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) \]

Why do these metal spontaneously inflame upon contact with H\textsubscript{2}O ?
- Low melting point metals, the liquid provides a clean surface, which is extremely favorable to the redox reaction to occur (highly exothermic).
- In the case of beryllium and magnesium, formation of a protecting layer of metal oxide.

☞ \( E^\circ \) all close to one another : -3 V (except for Be : -1.97V and Mg : -2.36 V: small cations). Such a uniformity arises from a compensation between the enthalpy of formation de \( \text{M}^+(\text{g}) \) and the enthalpy of hydratation de \( \text{M}^+ \). (see thermo cycles thermo on the next diapo).
Compensation between the energy of ionisation and the energy of hydration. (values give in KJ.mol$^{-1}$)
Potentiels standarts des éléments s
($E_0$ en volt)

Groupe 1
Groupe 2

Li, Na, K, Rb, Cs, Ba, Ca, Mg, Be
General Tendency: Example of group 2 metals

**First Ionisation Energy of the Group 2 elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st IE</td>
<td>900</td>
<td>800</td>
<td>700</td>
<td>600</td>
<td>500</td>
</tr>
</tbody>
</table>

(kJ mol⁻¹)

**Electronegativity of the Group 2 elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Melting Points of the Group 2 elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>1400</td>
<td>1200</td>
<td>1000</td>
<td>800</td>
<td>600</td>
</tr>
</tbody>
</table>
C) Composés binaires

Despite similar $E_0$ values, typical distinct behavior is observed for some alcalin and earth-alcalin metals. Example: the only stable nitride is $\text{Li}_3\text{N}$. Specific reactions are also observed with $\text{O}_2$.

Coordination: mostly octahedral coordination in aqueous medium, except for $\text{Li}^+$ (small cation) in some crystalline compounds ($\text{Li}_2\text{O}$, antifluorine-type structure). Cation $\text{Be}^{2+}$, small and highly charged (2+) affords compounds with some covalent character with typically four-coordinated Be centers.

Possibility of catenation (formation of chains)
Examples:
- $\text{Na}_2\text{O}_2$ (peroxyde ion $\text{O}_2^{2-}$), $\text{Li}_2\text{O}$ (oxyde ion $\text{O}^{2-}$), $\text{KO}_2$ (superoxyde ion $\text{O}_2^{-}$).
- Stabilisation of peroxydes et superoxydes by larger cations.
Complexes Formation

- Metallic ions of blocs (M⁺ et M²⁺) are considered as “hard” Lewis acids and can thus form complexes via Coulombian interactions with “hard” Lewis bases (small electronegative electron donors: O and N).

- Formation of remarquable complexes with polydentate ligands such as ether-crown and cryptand ligands.

These ligands are « sterically » selective for a given M⁺ ou M²⁺ cation

Necessary adequation between the size of M⁺ ou M²⁺ and that of the hosting cavity

Possibility of selective complexation
Formation Constants of cryptand complexes
As a function of cation size

![Graph and molecular structures]
**Alcalides anions M⁻**

**Conditions:** moisture- and oxygen-free environment

**First reported example:** Anion Na⁻ formed by reaction of Na(s) with cryptand [2.2.2]

\[
2 \text{Na} + N\{(\text{C}_2\text{H}_4\text{O})_2\text{C}_2\text{H}_4\}_3\text{N} \rightarrow \text{[Na N\{(C}_2\text{H}_4\text{O})_2\text{C}_2\text{H}_4\}_3\text{N]}^+ + \text{Na}^- \\
\text{cryptand[2.2.2]} \quad \text{[Na(cryptand[2.2.2])]}^+
\]

Full dissociation of the anion and cation

[Diagram of cryptand [2.2.2] and Na⁺-cryptand [2.2.2]]
Solutions of solvated electrons and Electrides

Alcalin metals are soluble in etheroxyde solvents and some amines to yield solutions of solvated electrons

Examples: Na is soluble in liq. NH$_3$ ($T_{eb} = -33^\circ$C) to afford une solution of electrons solvated by NH$_3$

\[
\text{Na} + x \text{NH}_3 \rightarrow \text{Na}^+ + e(\text{NH}_3)_x^-
\]

- Diluted solution (dark blue): excellent reducting properties
- Concentrated solution (bronze appearance): delocalized electrons like in a metal.

Electrides: Solid compounds containing solvated electrons. The complexation by crown-ethers of alcalin ions (ex: Cs$^+$) may allow the formation of stable electrides.
Electride consisting of Cs$^+$-[15-éther-5] anions and « free » electrons

Éther-couronne 5-15

X-ray determined molecular structure
These elements display diverse properties going from the more metallic elements (Al, Ga, In, Tl, Sn, Pb, Bi) to « metalloides » (Si, B, Te) and then non-metallic elements (noble gas, halogens)

Electrical resistivity of main group elements
Main group Metals of the p block

- Al, Ga, In, Tl (group 13)
- Sn et Pb (group 14)
- Bi (group 15)

Lower oxydation states are favored for heavier metals (complicated reasons: “Inert pair effect”).

- Common oxydation states: Tl(I), Pb(II) et Bi(III) (“Inert pair effect”)

Thus, Tl(III), Pb(IV) et Bi(V) compounds are readily reduced.
II - The groups of boron (13/III) and carbon (14/IV).

- Various physico-chimical properties.
- Great importance in industry and biosphere.

- **Carbone** (biosphere) → organic chemistry, binary compounds with metals and non-metals, organometallic chemistry

- **Bore** (earth’s crust) → combined with O and/or Al, it is an important component of the earth’s crust

**Other elements** (Al, Si, Ga, Ge, In, Sn, Tl, Pb) → high tech industry, semi-conductors

**A) General considerations**

- Going down each column:  → **non-metals** → **semi-conductors** → **metals**.

- Lighter elements have an electronegativity closer to that of hydrogen: they thus form numerous covalent compounds (hydrogenated and alkylated, for instance).
Group 13

Group 13 metals all display a shiny appearance.

\[ T_m {}^\circ\text{C} : \text{Al (660)} - \text{Ga (30)} - \text{In (157)} - \text{Tl (303)} \]

NB: In solid Ga, existence of Ga\(_2\) units that remain in the melted metal ⇒ \( T_m = 30 {}^\circ\text{C} \).

<table>
<thead>
<tr>
<th>Métal</th>
<th>Minéraux principaux</th>
<th>Méthode d'extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Groupe 13</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>Bauxite ( \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} )</td>
<td>Électrolyse (procédé Hall)</td>
</tr>
<tr>
<td>Gallium</td>
<td>Traces dans les minéraux d'aluminium et de zinc</td>
<td></td>
</tr>
<tr>
<td><strong>Groupe 14</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Étain</td>
<td>Cassitérite ( \text{SnO}_2 )</td>
<td>( \text{SnO}_2 + \text{C} \rightarrow \text{Sn} + \text{CO}_2 )</td>
</tr>
<tr>
<td>Plomb</td>
<td>Galène ( \text{PbS} )</td>
<td>( \text{PbS} + \text{O}_2 \rightarrow \text{PbO} + \text{SO}_2 ) suivi de: ( 2 \text{PbO} + \text{C} \rightarrow 2 \text{Pb} + \text{CO}_2 )</td>
</tr>
<tr>
<td><strong>Groupe 15</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bismuth</td>
<td>Traces dans les minéraux sulfurés de zinc, de cuivre et de plomb</td>
<td></td>
</tr>
</tbody>
</table>
Combining Boron with nitrogen: synthesis of boron nitride, an important material.

\[ B_2O_3(l) + 2NH_3(g) \xrightarrow{1200^\circ C} 2BN(s) + 3H_2O(g) \]

- Two types of structure for BN:
  1) Type graphite, with hexagonal planes facing one another.
  2) At high T and P, ‘diamond’ form or ZnS.

- Electrical insulator
- Used as lubricant

- Abrasive even at high T

Correlation between the toughness of metal and its reticular enthalpy.
2- **Boron Compounds with electronegative elements**

- Boron tri-halide species $\text{BX}_3$ (B(III): common oxidation state).
  6 electrons of valence at B(III) and a vacant orbital
  - Used as reagents and Lewis acids in catalysis.
  - Preparation: direct reaction of B with $X_2$ at high T/P.
  - Structure of $\text{BX}_3$: monomeric, trigonal plane geometry triangle plan at B(III).

- Boron halide compounds with B-B bonds are known.

- $\text{sp}^2$-hybridized B(III) center
* B-N and C-C bonds are isoelectronic.

\[
\frac{1}{2} B_2H_6 + N(CH_3)_3 \rightarrow H_3BN(CH_3)_3
\]

- Amino-borane species can be synthesized according to the reaction depicted below:

\[
((CH_3)_2CH)_2NH + BCl_3 \rightarrow \text{B-N} + \text{CH(CH}_3)_2 \text{Cl} + \text{HCl}
\]

- Despite some structural analogies, the properties/reactivity of amino-borane species is quite different from C-C bond species.
The example of Borazine

- Nucleophilic attack at the nitrogen centers
- Electrophilic attack at the boron centers

Reaction with HCl to form $(B_3H_3)(N_3H_6)Cl_3$

Borazine polymerizes upon heating (H$_2$ elimination)

Polyborazylene
**Borane Chemistry**

- **borane, BH₃**
  - trivalent, neutral, 6e
  - powerful LA

- **borohydride, BH₄⁻**
  - tetravalent, anionic, 8e
  - hydride donor

- **borane-THF, BH₃-THF**
  - tetravalent, neutral, 8e
  - borane chemistry

**hydroboration with BH₃-THF, simplified mechanism**

\[
BH₃-THF + \text{alkene} \rightleftharpoons \text{alkylborane} + THF \rightleftharpoons \text{alkane} + H₂B⁺H
\]
Amino- and Phosphino-Boranes: fundamental chemistry

**triethylamine-borane**

\[ \text{Et}_3\text{N}^-\text{BH}_3 \]

**pyridine-borane**

\[ \text{N}^-\text{BH}_3 \leftrightarrow \text{N}^-\text{BH}_3 \]

no self-reduction!

amine-boranes have two types of chemistries

\[ \text{Et}_3\text{N}^-\text{BH}_3 \leftrightarrow \text{Et}_3\text{N}^- + \text{BH}_3 \]

amine borane chemistry

borane chemistry

phosphine-boranes do not exhibit borane chemistry

\[ \text{Ph}_2\text{P}^-\text{BH}_3 + \equiv -\text{R} \rightarrow \text{Ph}_2\text{P}^+\equiv\text{BH}_3 \]

hydrophosphinylation, not hydroboration
**Groupe 13 metal species (Al, Ga, In): the most common oxidation state is +III**

Trihalido metal species MX₃ are strong Lewis acids. Al (metal) and Ga (metal) directly react with HCl ou HBr as follows:

\[
2 \text{Al(s)} + 6 \text{HCl(g)} \rightarrow 2 \text{AlCl}_3(s) + 3\text{H}_2(g)
\]

- AlF₃ et GaF₃ : hard solids, high Tₘ, low solubility. Formation of hypervalent coordination species: Na₃AlF₆ ou Na₃GaF₆

Relative to « hard » Lewis bases (O, N), the Lewis acidity decreases upon going down group 13 column

\[
\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3
\]

Relative to « soft » Lewis bases (S), the Lewis acidity increases upon going down group 13 column

\[
\text{GaX}_3 > \text{AlX}_3 > \text{BX}_3
\]

Hypervalent compounds are observed for Al(III) and heavier gp 13 elements

\[
\text{Cl}_3\text{AlN(CH}_3)_3 \text{ ou Cl}_3\text{Al(N(CH}_3)_3)_2
\]
AlF₃: Each Al center is hexa-coordinated. Each F coordinates to two Al centers.

AlCl₃, AlBr₃, AlI₃: dimeric in solution.

AlCl₃ commonly used as Lewis acid for the mediation of various organic reactions.
- A few Al(I) compounds are known to be stable at room temperature.

First example of X-ray determined Al(I) species (stable at RT)


- The stability of the +1 oxidation state increases going down the gp 13 column.
- Monohalides GaX, InX and TIX are known for X = Cl, Br, I.
A Monomeric Al(I) compound

First example of a monomeric Al(I) species


Lewis acidic and Lewis basic Al center

Amphoteric character

Al carbene analogue

Adduct of B(C₆F₅)₃
Oxydes et Jewelry

- $\text{Al}_2\text{O}_3$ ($\alpha$ alumine) is the most stable form of aluminum oxide.

- Hexagonal compact (HC) stacking in which the $\text{Al}^{3+}$ ions occupy 2/3 of the octahedral sites.

Also named Corundum--> sapphire (blue) : charge transfer from the $\text{Fe}^{2+}$ et $\text{Ti}^{4+}$ ions (impurities).

• Ruby : $\alpha$ Alumine in which part of the $\text{Al}^{3+}$ ions are replaced by $\text{Cr}^{3+}$.

• Other forms of Alumine $\alpha$ exist (obtained by dehydration of Al hydroxyde at 900°C): the majority of $\text{Al}_2\text{O}_3$ is used for the production of Al (metal) via the Hall-Héroult process.

- Amorphous $\text{Al}_2\text{O}_3$: metastable form with a large specific surface area. Presence de acidic and basic sites:--> widely used in heterogeneous catalysis.
<table>
<thead>
<tr>
<th>Élément</th>
<th>L/kJ.mol(^{-1})</th>
<th>(\chi^*)</th>
<th>(r_{cov}/\text{Å})</th>
<th>(r_{ion}/\text{Å})</th>
<th>Aspect et propriétés</th>
<th>Degrés d'oxydation courants</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>899</td>
<td>2,04</td>
<td>0,85</td>
<td></td>
<td>Sombre</td>
<td>3</td>
</tr>
<tr>
<td>Al</td>
<td>578</td>
<td>1,61</td>
<td>1,43</td>
<td>0,54</td>
<td>Semi-conducteur</td>
<td>3</td>
</tr>
<tr>
<td>Ga</td>
<td>579</td>
<td>1,81</td>
<td>1,53</td>
<td>0,62</td>
<td>Métal, F = 30°C</td>
<td>1, 3</td>
</tr>
<tr>
<td>In</td>
<td>558</td>
<td>1,78</td>
<td>1,67</td>
<td>0,80</td>
<td>Métal mou</td>
<td>1, 3</td>
</tr>
<tr>
<td>Tl</td>
<td>589</td>
<td>2,04</td>
<td>1,71</td>
<td>0,89</td>
<td>Métal mou</td>
<td>1, 3</td>
</tr>
<tr>
<td><strong>Groupe 13/III</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>C</strong></td>
<td>1086</td>
<td>2,55</td>
<td>0,77</td>
<td></td>
<td>Isolant dur (diamant)</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Semimétal (graphite)</td>
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<tr>
<td>Si</td>
<td>786</td>
<td>1,90</td>
<td>1,17</td>
<td>0,40</td>
<td>Semiconducteur dur</td>
<td>4</td>
</tr>
<tr>
<td>Ge</td>
<td>760</td>
<td>2,01</td>
<td>1,22</td>
<td>0,53</td>
<td>Métal</td>
<td>2, 4</td>
</tr>
<tr>
<td>Sn</td>
<td>708</td>
<td>1,96</td>
<td>1,40</td>
<td>0,69</td>
<td>Métal</td>
<td>2, 4</td>
</tr>
<tr>
<td>Pb</td>
<td>715</td>
<td>2,33</td>
<td>1,75</td>
<td>0,92</td>
<td>Métal mou</td>
<td>2, 4</td>
</tr>
<tr>
<td><strong>Groupe 14/IV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Group 14 elements

**Carbone:** extracted from mines as diamonds or graphite
Coke, black carbon: less pure forms

**Silicium:** produced in a pure form from the reduction of $\text{SiO}_2$ with $\text{C}$.

$$\text{SiO}_2 + 2 \text{C} \xrightarrow{\text{HT}} \text{Si(s)} + 2 \text{CO}$$

**Si:** widely used in modern semi-conductor industry
(small band gap = 1.12 eV)
Silicon compounds: Silanes

- \( \text{SiH}_4 \): tetrahedral structure, stable but less than \( \text{CH}_4 \)

\( \text{Si}_n\text{H}_{2n+2} \) (silanes) are much less stable than alkanes

**Pourquoi?**

- The Si-Si bond is less strong than the C-C bond
- Si est less electronegative and larger than C

**More reactive towards nucleophiles**

**Silanes decomposition**

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{Si} \quad \text{Si} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{Si} \quad \text{Si} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{Si} \\
\text{H} & \quad \text{H} \\
\text{Si} & \quad \text{H}_2 \\
\text{Si} & \quad \text{H}_2
\end{align*}
\]

\[ \text{Si} + \text{H}_2 \]
Tin and Lead (Group 14)

Sn:

- Sn exists in two allotropic forms:
  - a “diamond” form ($\alpha$) stable at $T < 13 \, ^\circ\text{C}$
  - a metal form ($T > 13 \, ^\circ\text{C}$), much more stable

- Oxidation state: $+2$ ou $+4$

In aqueous medium, Sn$^{2+}$ (which bears a lone pair of electrons) is a soft reducting agent.

$$Sn^{2+}(aq) + \frac{1}{2}O_2(g) + 2H^+(aq) \xrightarrow{E^\circ=1.08 \, \text{V}} Sn^{4+}(aq) + H_2O$$

- Sn$X_4$ compounds ($X = \text{Cl, Br, I}$) exhibit a covalent character.

- Sn (II) et Sn (IV) have a rich coordination chemistry
SnCl₂

Stereochemically active lone pair

SnCl₃⁻

Pt₃Sn₈Cl₂₀
Pb :
Lead oxide compounds are technologically important…..but also very toxic

Oxidation state: +2 (the most stable) and +4

--> The structure de PbO also features a stereochemically active lone pair on Pb. Pb²⁺ tetra-coordinated (by O).

--> Mixed Valence Oxides: Pb₃O₄ ‘minium’
Structure of Pb₃O₄

Despite its toxicity, this red-orange pigment is produced industrially and used in the painting industry.

Sn and Pb :
- Oxidation +2 et +4 possible for various Sn and Pb compounds.
- Pb(IV) is very oxydant.
- Sn(II) et Pb(II) both display a stereoactif lone pair
Illustrate the role of kinetics and thermodynamics at work in electrochemical cells

Charged state: cathode = PbO₂ et anode = Pb. In diluted H₂SO₄, PbO₂ et Pb are insoluble.

**Cathodic reduction and anodic oxidation**

While working: at the cathode Pb(IV) --> Pb(II) (PbSO₄)

\[
PbO_2(s) + H_2SO_4 + 2H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O \quad (E^\circ = 1.69 \text{ V})
\]

At the anode Pb(0) --> Pb(II) (PbSO₄)

\[
Pb(s) + H_2SO_4 \rightarrow PbSO_4(s) + 2H^+(aq) + 2e^- \quad (E^\circ = -0.356 \text{ V})
\]

Global Reaction:

\[
PbO_2(s) + 2H_2SO_4 + Pb(s) \rightarrow 2PbSO_4(s) + 2H_2O
\]

Difference of potential: 2 volts. (>> to that of H₂O : 1.23 V)

Explanation: slow reaction with H₂O (slow kinetics)

**Lead-based Battery**