Systematic Chemistry
of elements s and p

I - s block metals

- Presence of cations A\(^+\) ou B\(^{2+}\) in minerals and natural water. Some are essential to life metabolism (ex: K\(^+\), Ca\(^{2+}\)).

- Low ionization energies and vaporization enthalpies

  Labile valence electrons

- Strong reducing agents: vigorous reaction with H\(_2\)O(M +H\(_2\)O --> H\(_2\))

- 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: \( M(s) + H_2O \rightarrow M^+(aq) + OH^-(aq) + 0.5 H_2(g) \)

Group 2: \( M(s) + H_2O \rightarrow M^{2+}(aq) + 2OH^-(aq) + H_2(g) \)

Why do these metal spontaneously inflame upon contact with \( H_2O \)?

- 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 \( M^+(g) \) and the enthalpy of hydratation de \( M^+ \). (see thermo cycles thermo on the next diapo).
Compensation between the *energie of ionisation* and the *energie of hydration*. (values given in KJ.mol⁻¹)
Potentiels standards des éléments s
($E_0$ en volt)

- Groupe 1
- Groupe 2
General Tendency: Exemple of group 2 metals

First Ionisation Energy of the Group 2 elements

Electronegativity of the Group 2 elements

Melting Points of the Group 2 elements
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 blocks ($M^+ \text{ et } M^{2+}$) 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 remarkable complexes with polydentate ligands such as ether-crown and cryptand ligands.

These ligands are « sterically » selective for a given $M^+$ ou $M^{2+}$ cation

Necessary adequation between the size of $M^+$ ou $M^{2+}$ and that of the hosting cavity

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

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

Full dissociation of the anion and cation

Cryptand [2.2.2]  
\[\text{Na}^+ - \text{Cryptand [2.2.2]}\]
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. NH₃ \((T_{eb} = -33^\circ \text{ C})\) to afford a solution of electrons solvated by NH₃

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

- 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

15-crown-5 rings (sandwich)

Cs⁺

Electron-Trapping Cavity

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

- Common oxidation 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).
**IA) Group 13**

Group 13 metals all display a shiny appearance.

\[ T_m (°C) : \text{Al (660)} - \text{Ga (30)} - \text{In (157)} - \text{TI (303)} \]

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

<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>Cassitèrite ( \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 ) suivie 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 ou ZnS.

- Electrical insulator
- Used as lubricant

Ablasive 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 $\text{X}_2$ 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.

[Diagram showing sp$^2$ hybridization of 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:

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, BH₃  Borohydride, BH₄⁻  Borane-THF, BH₃-THF

<table>
<thead>
<tr>
<th>Borane, BH₃</th>
<th>Borohydride, BH₄⁻</th>
<th>Borane-THF, BH₃-THF</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td><img src="image2.png" alt="Structure" /></td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Trivalent, neutral, 6e powerful LA</td>
<td>Tetravalent, anionic, 8e hydride donor</td>
<td>Tetravalent, neutral, 8e borane chemistry</td>
</tr>
</tbody>
</table>

Hydroboration with BH₃-THF, simplified mechanism:

\[
\text{BH₃-THF} + \text{R} = \text{BH₃} + \text{THF} \rightarrow \text{R}_2\text{B=}-\text{H}
\]
Amino- and Phosphino-Boranes: fundamental chemistry

triethylamine-borane

pyridine-borane

\( \text{Et}_3\text{N}^-\text{BH}_3 \)  \( \text{py}-\text{BH}_3 \)

no self-reduction!

amine-boranes have two types of chemistries

heat

\( \text{Et}_3\text{N}^-\text{BH}_3 \)  \( \text{Et}_3\text{N} + \text{BH}_3 \)

amine borane chemistry
borane chemistry

phosphine-boranes do not exhibit borane chemistry

\( \text{Ph}_2\text{PH}^-\text{BH}_3 \)  \( \equiv\text{R} \)  \( \text{heat} \)

\( \text{Ph}_2\text{Ph}^+\text{BH}_3 \)

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

Trihalido metal species $MX_3$ are strong Lewis acids. Al (metal) and Ga (metal) directly react with HCl ou HBr as follows:

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

- $\text{AlF}_3$ et $\text{GaF}_3$: hard solids, high $T_m$, low solubility. Formation of hypervalent coordination species: $\text{Na}_3\text{AlF}_6$ ou $\text{Na}_3\text{GaF}_6$

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

$$\text{Cl}_2\text{AlN(CH}_3)_2\text{ou Cl}_2\text{Al(N(CH}_3)_2\text{o}}$$
Structure of Aluminum halides

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


- The stability of the +I oxidation state increases going down the gp 13 column

- Monohalides GaX, InX and TlX 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

- $\text{Al}_2\text{O}_3$ (α 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>I/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><strong>Groupe 13/III</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<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>Semiconducteur</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, $F = 30^\circ\text{C}$</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 14/IV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1086</td>
<td>2,55</td>
<td>0,77</td>
<td></td>
<td>Isolant dur (diamant)</td>
<td>4</td>
</tr>
<tr>
<td>Si</td>
<td>786</td>
<td>1,90</td>
<td>1,17</td>
<td>0,40</td>
<td>Semimétal (graphite)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>760</td>
<td>2,01</td>
<td>1,22</td>
<td>0,53</td>
<td>Semiconducteur dur</td>
<td>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>
</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 SiO$_2$ with 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

- **SiH₄**: tetrahedral structure, stable but less than CH₄

  \[ \text{Si} \text{H}_2 \text{Si} \text{H}_2 \text{Si} \text{H}_2 \text{Si} \text{H}_2 \]  (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**

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

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

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

\[
\text{SiH}_2 \\
\text{Si} + \text{H}_2
\]
**Sn:**

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

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

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

\[
\text{Sn}^{2+} (aq) + \frac{1}{2} \text{O}_2 (g) + 2 \text{H}^+ (aq) \xrightarrow{E^\circ=1.08 \, \text{V}} \text{Sn}^{4+} (aq) + \text{H}_2 \text{O}
\]

- \( \text{SnX}_4 \) compounds (X = Cl, Br, I) exhibit a covalent character.

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

Stereochemically active lone pair

\[ \text{SnCl}_2 \]

\[ \text{SnCl}_3^- \]

\[ \text{Pt}_3\text{Sn}_8\text{Cl}_{20} \]
**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. Pb$^{2+}$ tetra-coordinated (by O).

--> **Mixed Valence Oxides:** Pb$_3$O$_4$‘minium’
Structure of Pb$_3$O$_4$

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
**Lead-based Battery**

_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)_

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

At the anode Pb(0) --> Pb(II) (PbSO₄)

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

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)
The Specific case of Calcium

Organocalcium Overview

Nucleophilicity

\[
R^- \quad Na^+ \quad Ca^{2+} \quad R^-
\]

Electrophilicity

Nucleophilicity

\[
R^- \quad Al^{3+} \quad R^-
\]

Electrophilicity

Harder, S.; Chem. Rev. 2010, 110, 3852–3876
Advantages of Calcium

• Abundant: 3.4% of Earth’s crust (one of the cheapest commercially available metals, <$4/kg)
• Non-toxic: Human tolerance of Ca is high (∼1 g/day is considered safe)
• Associated environmental hazards are low: easily convertible to limestone (CaCO₃) and slaked lime (Ca(OH)₂) for disposal

Harder, S.; Chem. Rev. 2010, 110, 3852–3876
Characteristics of Calcium compounds

- Large coordination numbers of calcium leads to insoluble aggregates
- Low reactivity of Ca metal, compared to very high reactivity of C-Ca bonds

- Highly reactive and sensitive reagents (reacts with O₂ and H₂O)
- Increased ionic character of the Ca-C bond (versus the Mg-C bond)
- Inorganic and organometallic Ca compounds may readily undergo ligand exchange reactions in solution
- First discovered with organomagnesium derivatives

The nature of the R and X substituents, solvent and the presence of Lewis bases influence the Schlenk equilibrium
An example of the Schlenk equilibrium with organocalcium compounds

The presence/absence of THF directly influences the $K_{eq}$ of the Schlenk equilibrium.
Preparation of OrganoCalcium compounds

1) Direct route from metal

\[
Ca + Arl \rightarrow ArCal \quad (a)
\]

\[
Ca + 2 (\text{Me}_3\text{Si})_2\text{NH} \rightarrow Ca[\text{N}((\text{SiMe}_3)_2]_2 + H_2 \quad (b)
\]

\[
Ca + \text{Sn}[\text{N}((\text{SiMe}_3)_2]_2 \rightarrow Ca[\text{N}((\text{SiMe}_3)_2]_2 + \text{Sn} \quad (c)
\]

\[
Ca + \text{COT} \rightarrow Ca^{2+} \text{COT}^{2-} \quad (d)
\]

2) Salt metathesis

\[
CaI_2 + 2 \text{KBN} \rightarrow Ca\text{BN}_2 + 2 \text{KI} \quad (e)
\]

3) Deprotonation (acid-base reaction)

\[
Ca\text{BN}_2 + 2 \text{Ph}_3\text{CH} \rightarrow Ca(\text{CPh}_3)_2 + 2 \text{BnH} \quad (f)
\]