

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_2O ($M + H_2O \rightarrow H_2$)

- 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

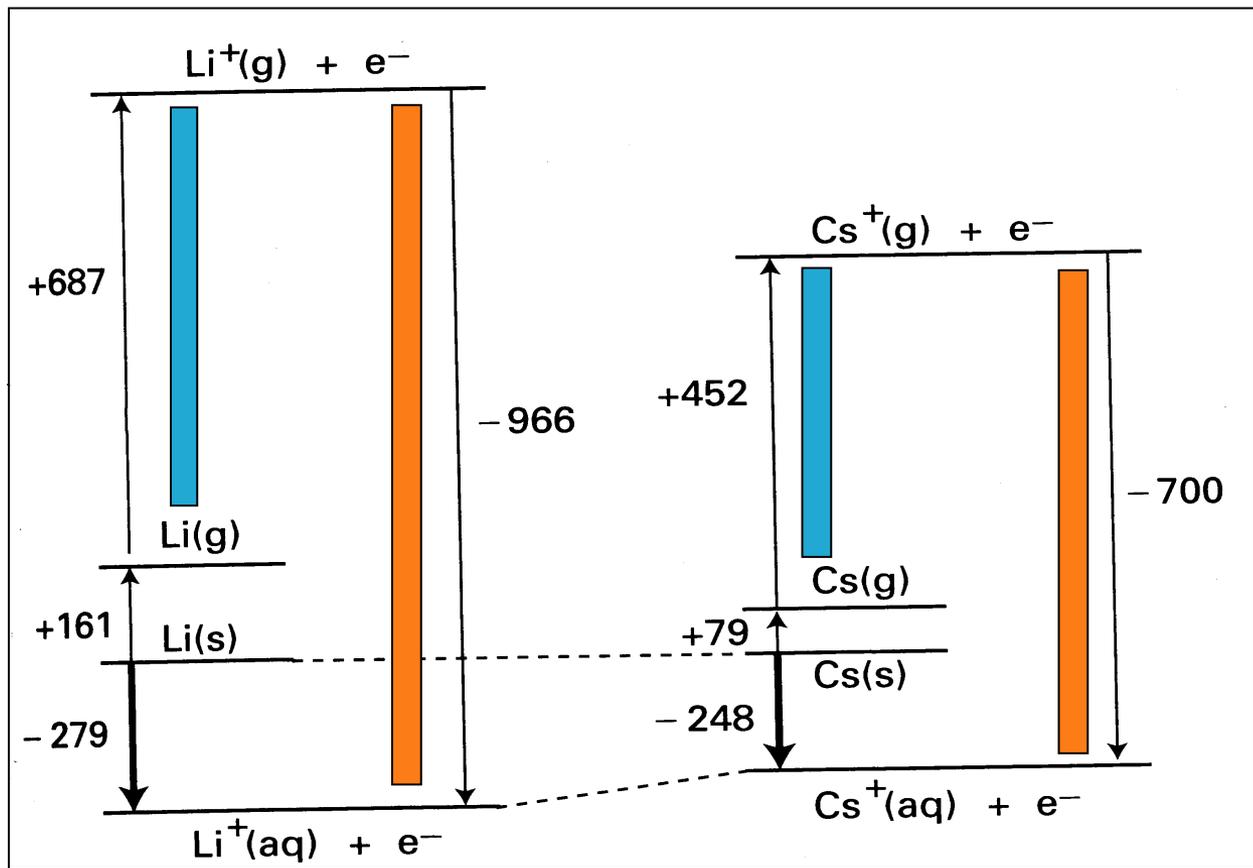


Why do these metal spontaneously inflame upon contact with H_2O ?

- Low melting point metals, the liquid provides a clean surface, which is extremely favorable to the redox reaction to occur (highly exothermic).

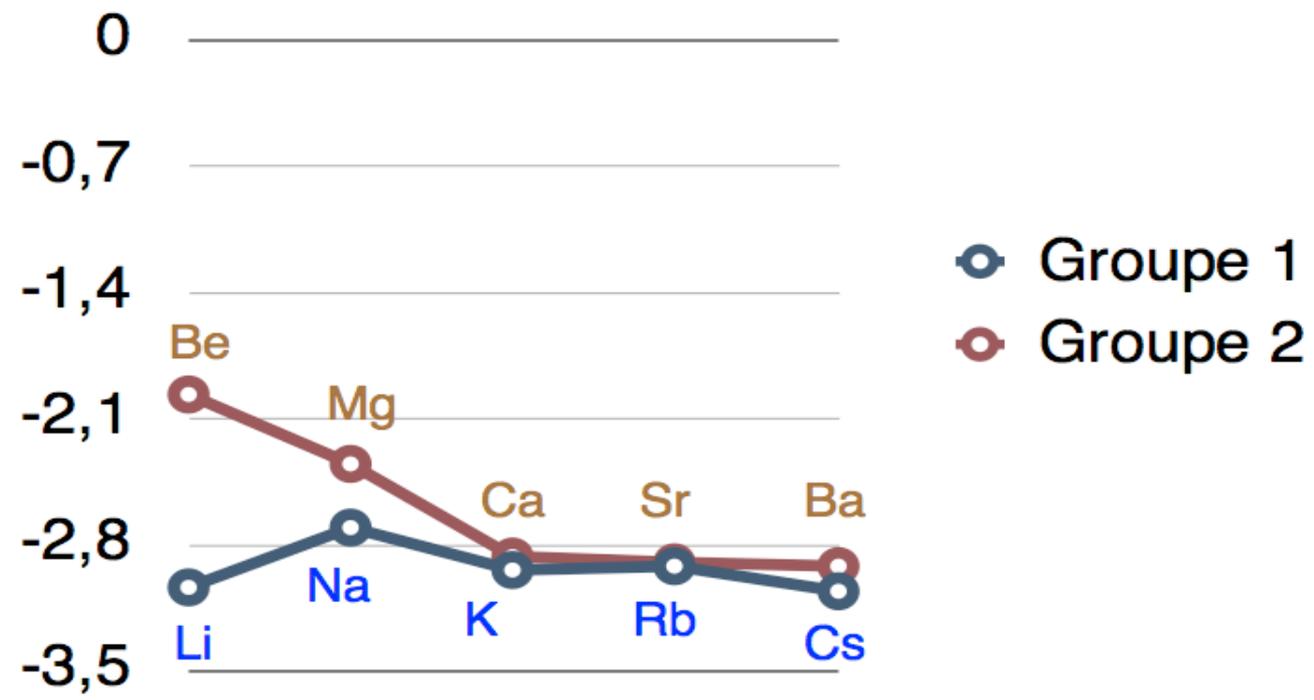
- In the case of beryllium and magnesium, formation of a protecting layer of metal oxide.

👉 E° 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 enthalpie of formation de $M^+(g)$ and the enthalpie of hydratation de M^+ . (see thermo cycles thermo on the next diapo).



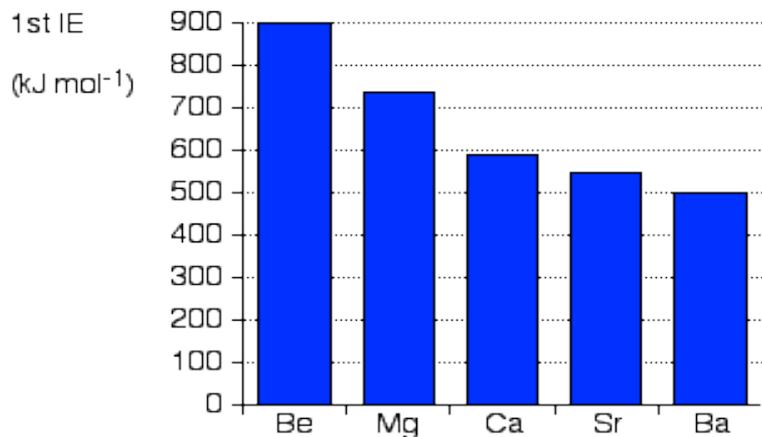
Compensation between the **energie of ionisation** and the **energie of hydratation**. (values give in $\text{Kj}\cdot\text{mol}^{-1}$)

Potentils standards des éléments s
(E_0 en volt)

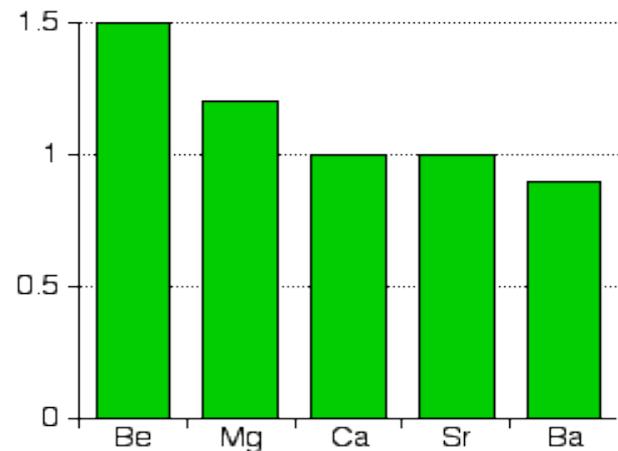


General Tendency: Exemple of group 2 metals

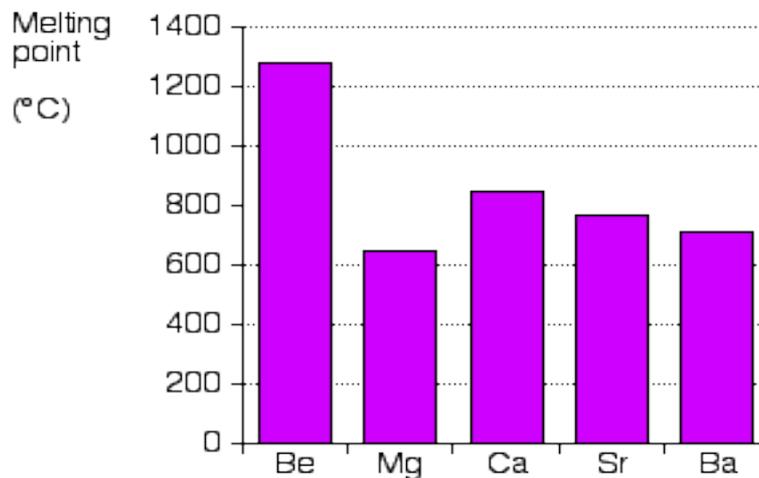
First Ionisation Energy of the Group 2 elements



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 Li_3N . Specific reactions are also observed with O_2 .

Coordination : mostly octahedral coordination in aqueous medium, except for Li^+ (small cation) in some crystalline compounds (Li_2O , antifluorine-type structure). Cation Be^{2+} , small and highly charged (2+) affords compounds with some covalent character with typically four-coordinated Be centers.

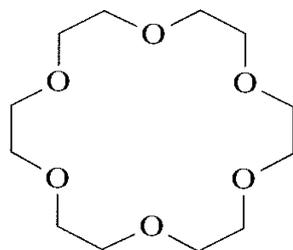
Possibility of catenation (formation of chains)

Examples :

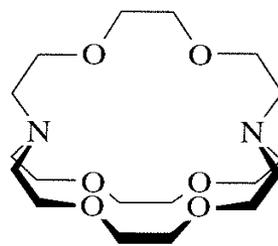
- Na_2O_2 (peroxyde ion O_2^{2-}), Li_2O (oxyde ion O^{2-}), KO_2 (superoxyde ion O_2^-).
- Stabilisation of peroxydes et superoxydes by larger cations.

Complexes Formation

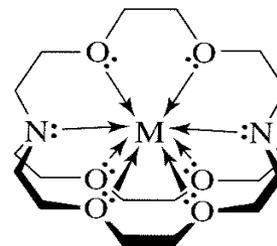
- Metallic ions of bloc s (M^+ et M^{2+}) are considered as “hard” Lewis acids and can thus form complexes via Coulombian interactions with “hard” Lewis bases (small electronegative electron donors: O and N)
- Formation of remarquable complexes with polydentate ligands such as ether-crown and cryptand ligands.



18-crown-6
or
18C6



Cryptand [2.2.2]
or
C222



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

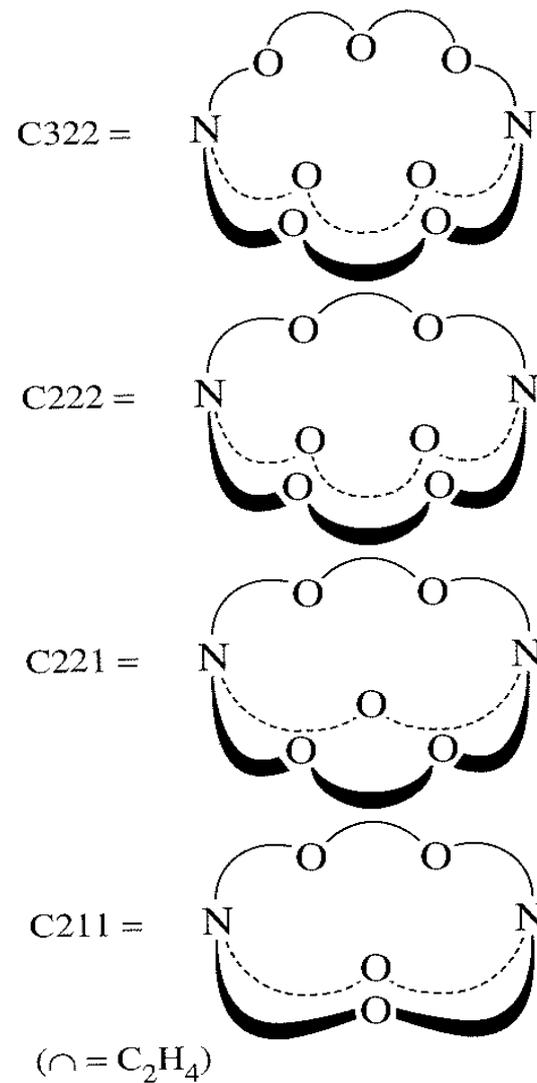
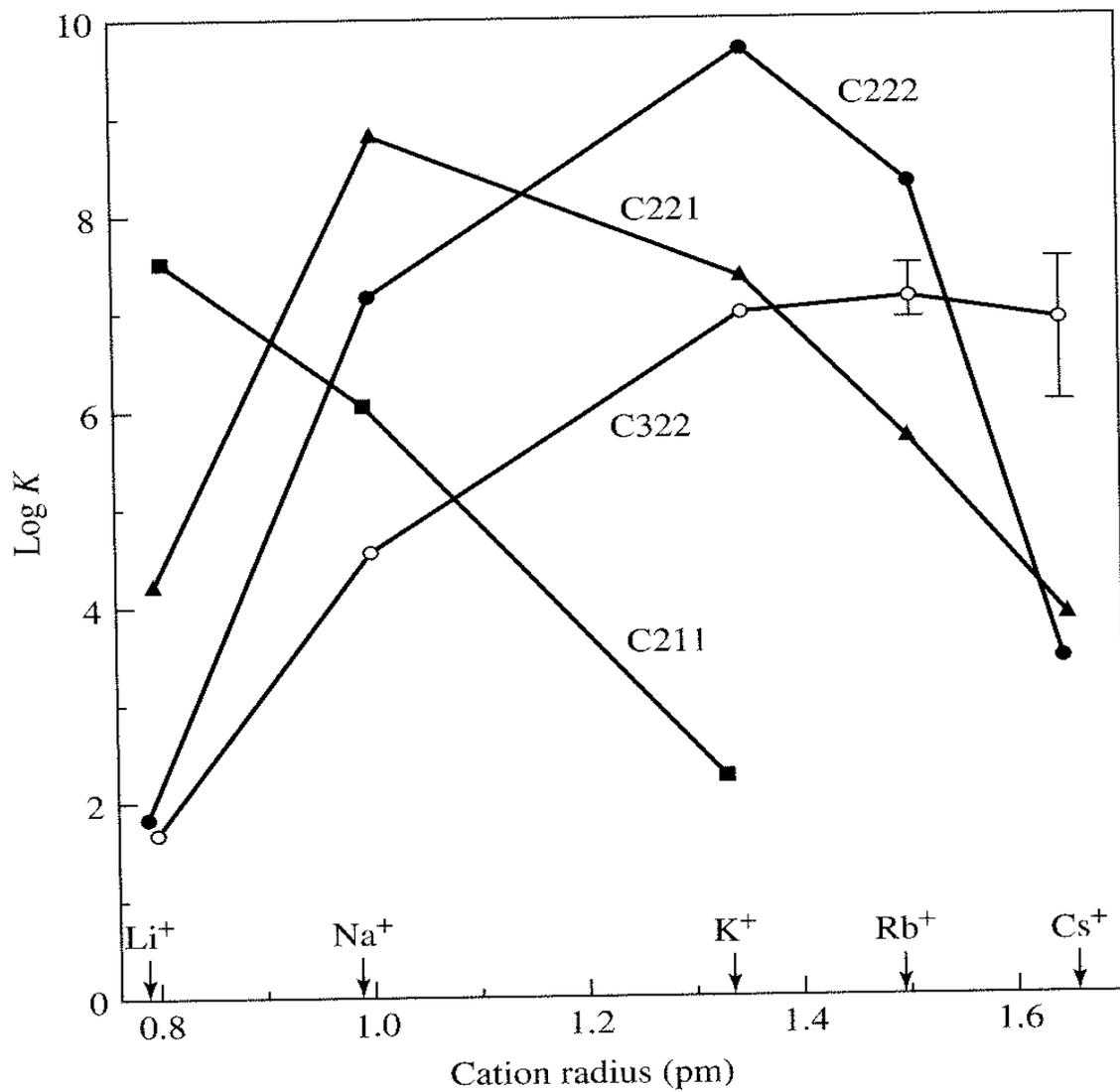


Necessary adequation between the size of M^+ ou M^{2+} and that of the hosting cavity



Possibility of selective complexation

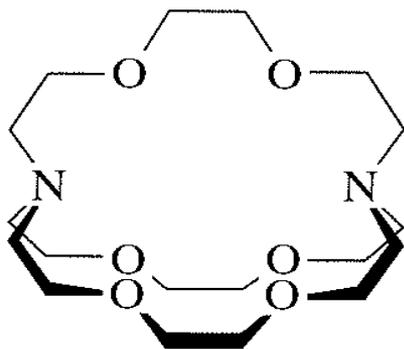
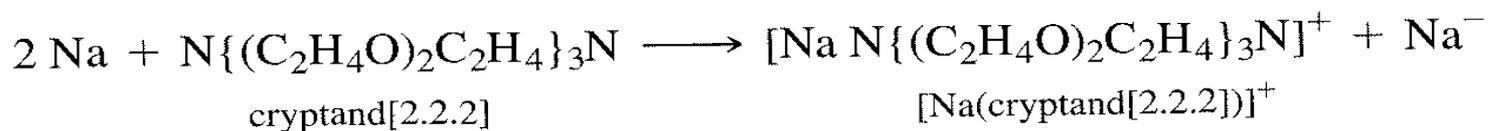
Formation Constants of cryptand complexes As a function of cation size



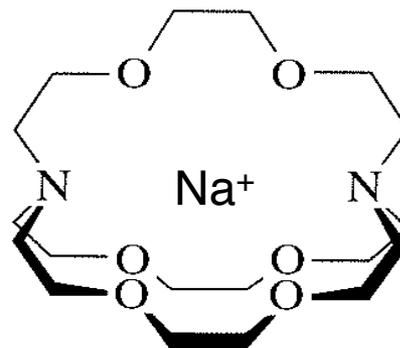
Alcalides anions M⁻

Conditions: moisture- and oxygen-free environment

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



Cryptand [2.2.2]



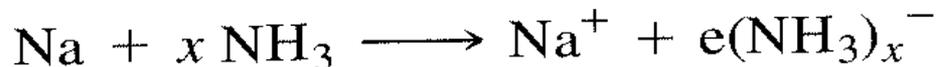
Na⁺- Cryptand [2.2.2]

Full dissociation
Of the anion
and cation

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 ($T_{\text{eb}} = -33^\circ\text{C}$) to afford a solution of electrons solvated by NH_3



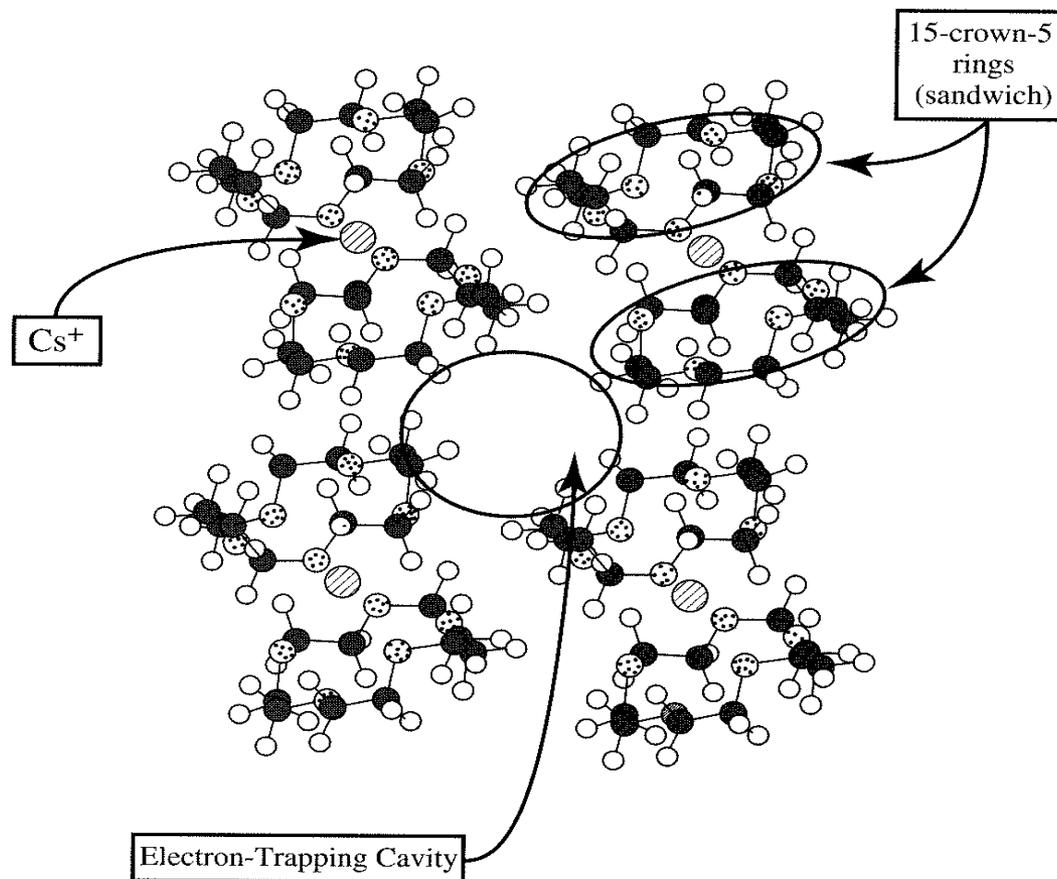
- Diluted solution (dark blue): excellent reducing properties
- Concentrated solution (bronze appearance): delocalized electrons like in a metal.

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-éter-5] anions and « free » electrons



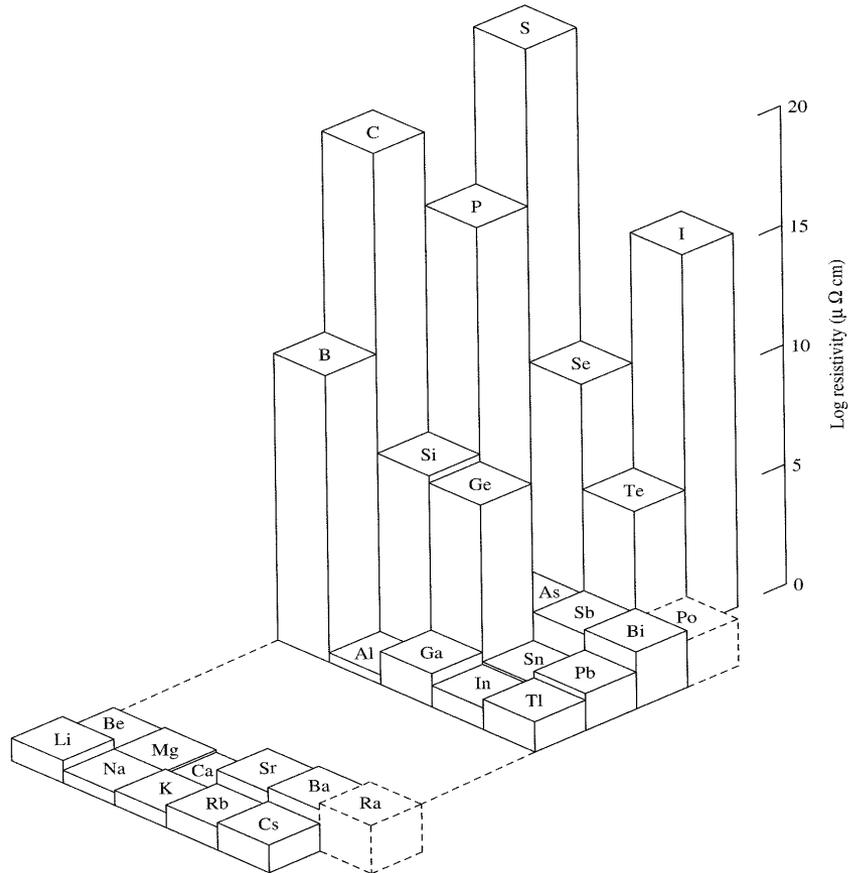
Éther-couronne 5-15



X-ray determined molecular structure

Main group Elements of Group p

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-chemical 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

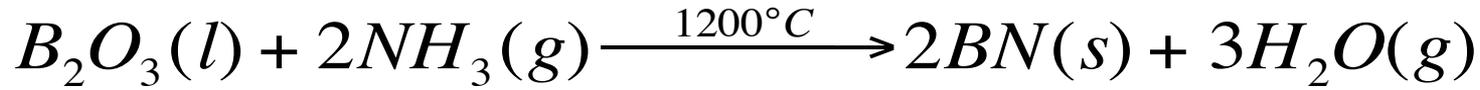
Group 13 metals all display a shiny appearance.

T_m (°C) : Al (660) - Ga (30) - In (157) - Tl (303)

NB: In solid Ga, existence of Ga_2 units that remain in the melted metal
 $\Rightarrow T_m = 30^\circ$.

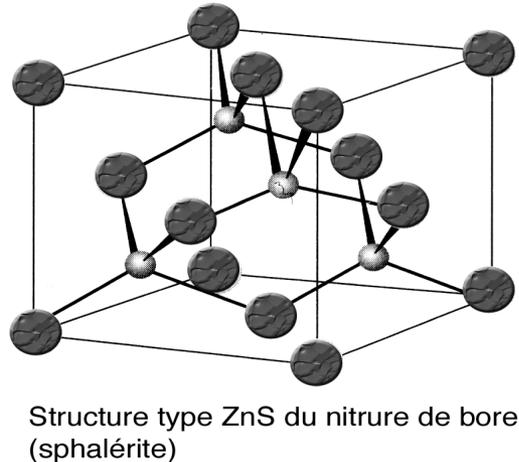
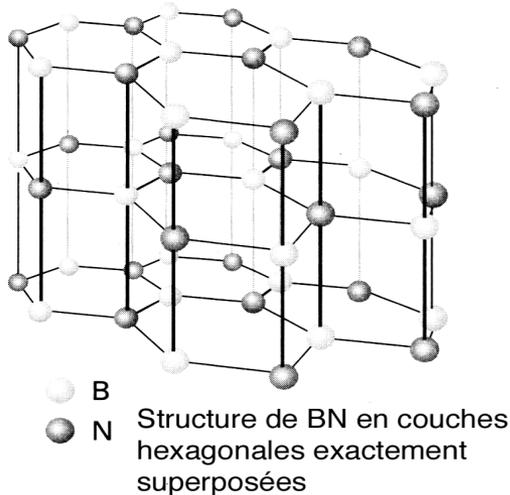
Métal	Minéraux principaux	Méthode d'extraction
<i>Groupe 13</i>		
Aluminium	Bauxite $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	Électrolyse (procédé Hall)
Gallium	Traces dans les minerais d'aluminium et de zinc	
<i>Groupe 14</i>		
Étain	Cassitérite SnO_2	$\text{SnO}_2 + \text{C} \longrightarrow \text{Sn} + \text{CO}_2$
Plomb	Galène PbS	$\text{PbS} + \text{O}_2 \longrightarrow \text{PbO} + \text{SO}_2$ suivi de : $2 \text{PbO} + \text{C} \longrightarrow 2 \text{Pb} + \text{CO}_2$
<i>Groupe 15</i>		
Bismuth	Traces dans les minerais sulfurés de zinc, de cuivre et de plomb	

Combining Boron with nitrogen: synthesis of boron nitride, an important material.



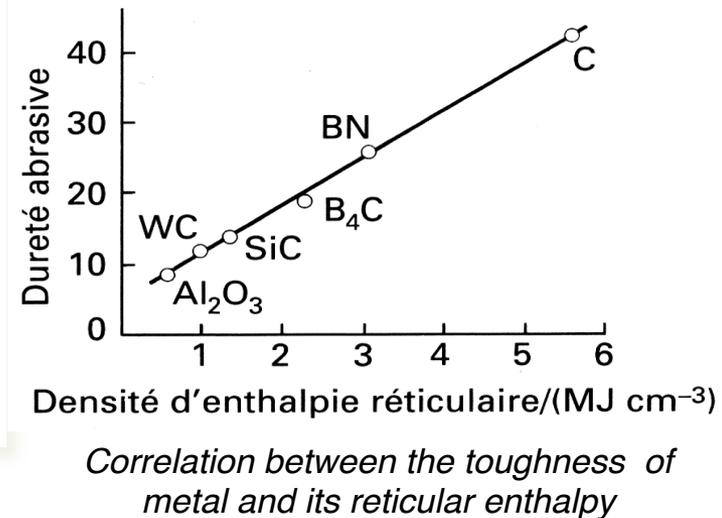
- **Two types of structure for BN :**

- 1) Type graphite, with hexagonal planes facing one another.
- 2) At high T and P, 'diamond' form ou ZnS.



Abrasive even at high T

- Electrical insulator
- Used as lubricant

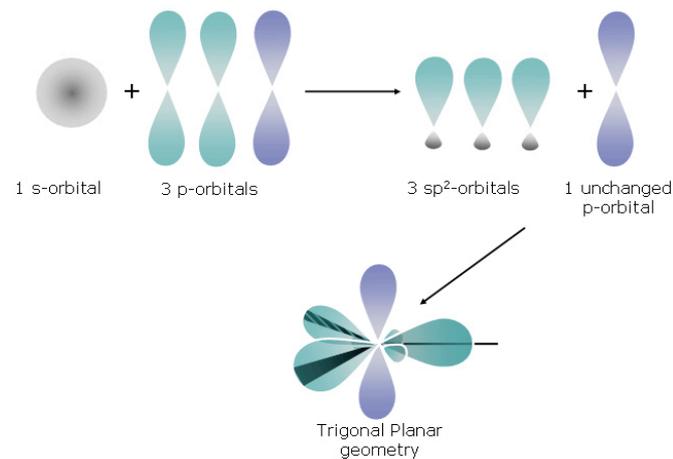


2- Boron Compounds with electronegative elements

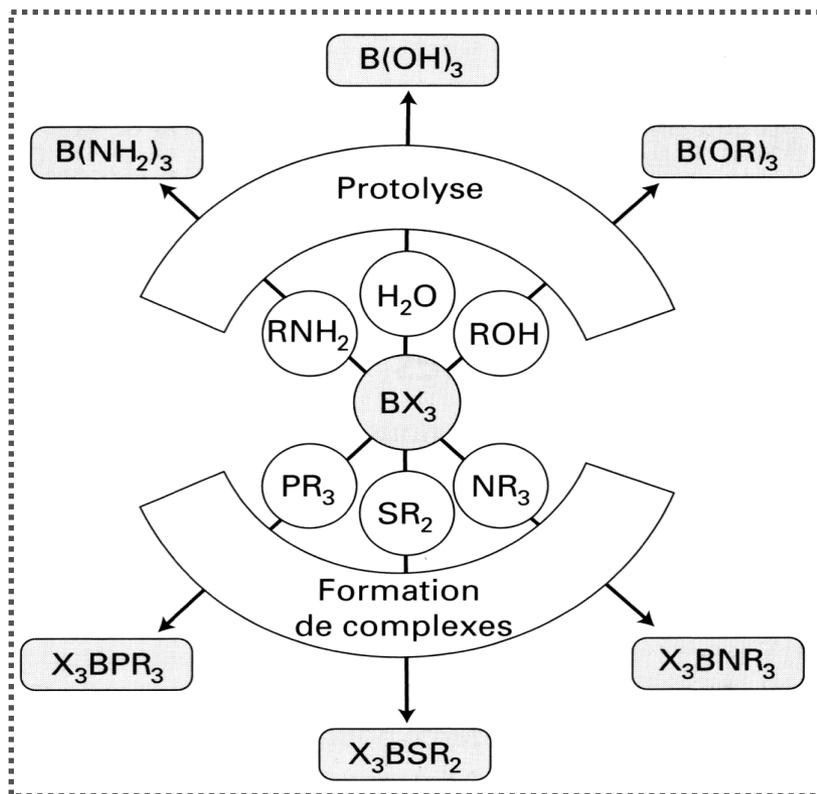
- Boron tri-halide species BX_3 (B(III): common oxidation state).

6 electrons of valence at B(III) and a vacant orbital

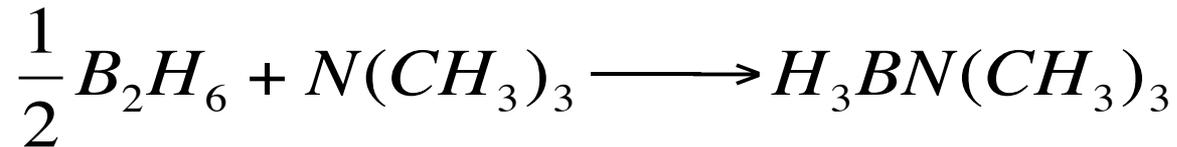
- Used as reagents and Lewis acids in catalysis.
- Preparation: direct reaction of B with X_2 at high T/P.
- Structure of BX_3 : monomeric, trigonal plane geometry triangle plan at B(III).
- Boron halide compounds with B-B bonds are known.



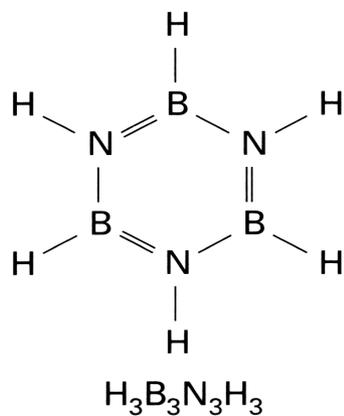
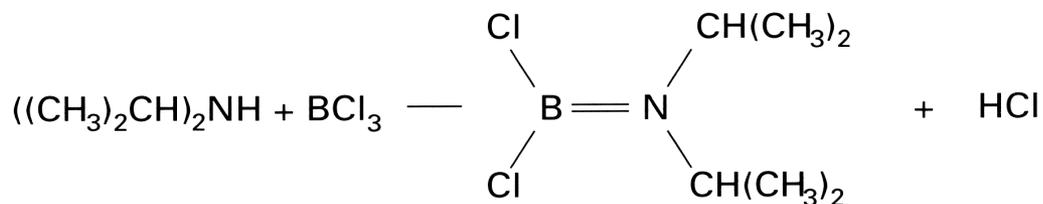
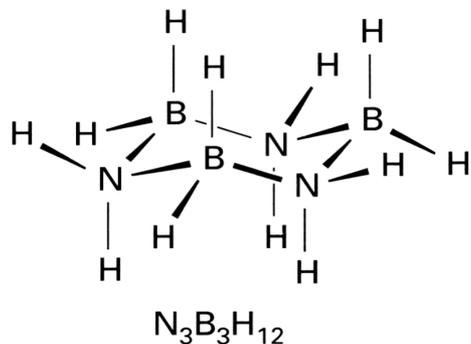
sp^2 -hybridized B(III) center



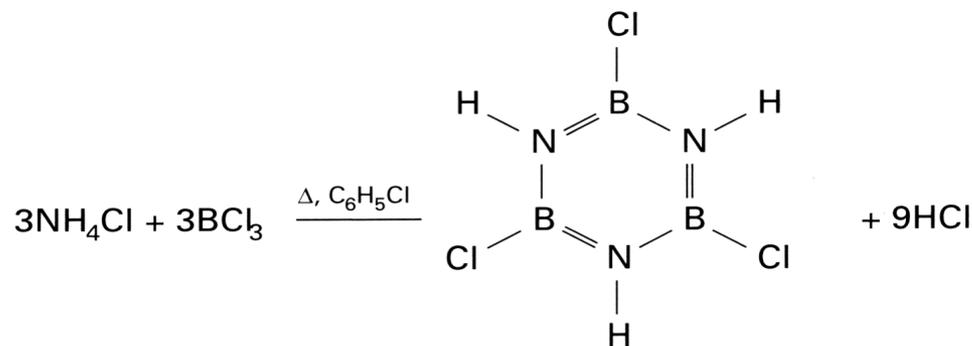
* B-N and C-C bonds are isoelectronic.



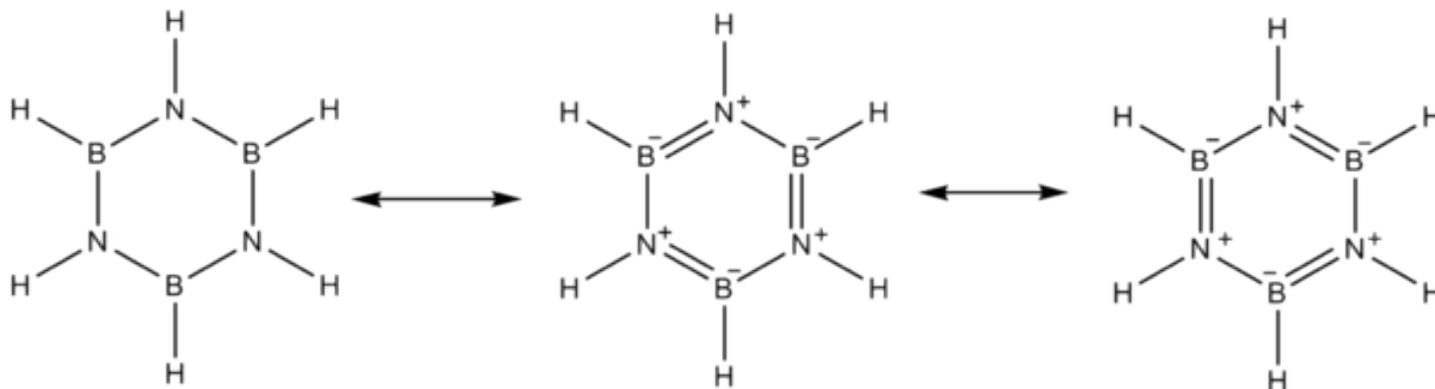
- Amino-borane species can be synthesized according to the reaction depicted below:



Borazine



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



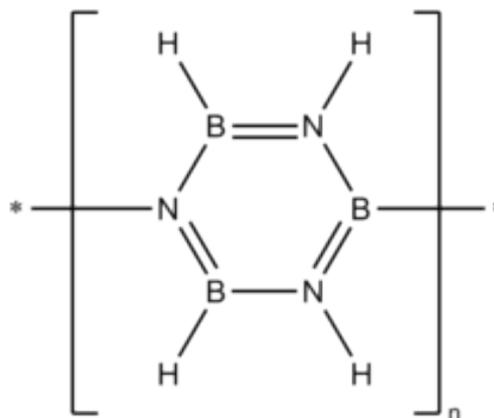
- ***Nucleophilic attack at the nitrogen centers***
- ***Electrophilic attack at the boron centers***



Reaction with HCl to form (B₃H₃)(N₃H₆)Cl₃



Borazine polymerizes upon heating (H₂ elimination)



Polyborazylene