# Inorganic chemistry of elements

Inorganic compounds hold most world records and can display unique physical and chemical properties, structures, reactivities and bonding situations that are not encountered in organic chemistry

**In inorganic chemistry**
**EVERYTHING is super….**

**super expensive**
Gold
Platinum
Iridium
Diamonds

**super-corrosive**
Ozone (O3)
Fluorine
ClF3
$NO_2$

**super-explosive**
$NI_3$
Fulminates
$XeO_3$
Azides

**super-complicated**
Unusual bonding in inorganic compounds is the rule rather then the exception.

**super-complicated**
High coordination numbers
$IF_7$ (CN = 7)
$[ReH_9]^{2-}$ (CN = 9)

**super-hard**
**Diamond** (5600 Vickers)
Cubic boron nitride (γ-BN)
Ti-B-C-N (6000 Vickers)

**super-conducting**
**Hg**
$Nb_3Ge$
$YBa_2La_3CuO_7$

**super-high melting**
**TaC**, m. p. = 3780 $^{o}$C (the highest in 2007)
The race is still continuing

**super-clean**
Si 99.999999 %
Semiconductors

# History line

**500** bce: Term "atom" is first used by the Greek philosopher ***Empedocles*** (atomos = a-tomos, "no-cut").
**500 bce. - 1600** empirical work by alchemists in Europe and especially Arabia. Important contribution of Arabic Alchemists : translation and thereby preservation of Greek philosophy. many Greek manuscripts are only known through their Arabic translations because the originals were lost or willfully destroyed by religious zealots.
**1300 - 1600** systematic development of mining technology especially in Germany and Austria. The elements Ag, Cu, Au, Pb and Sn are in widespread use. ***Georgius Agricola*** (latinized for *Georg Bauer*) writes "*De Re Metallica*" the first fundamental treatise of metallurgy and in many ways the first modern chemical publication. Some element names are derived from the language of the early German miners: *Bismuth* (Ger.: white earth), *Cobalt* (Ger.: goblin), *Nickl* (Ger.: devil), *Wolfram* (Ger.: hungry wolf). The English translation of the book is still in press and was done by the mining engineer and later US president Hoover.
**1661** ***Robert Boyle*** (England) writes his landmark treatise "*The Sceptical Chymist*" For the first time, the experimental approach is specifically advocated and the distinction of elements from compounds recognized as an important task of chemistry.
**1789** "*Traite Elementaire de Chimie*" by ***Antoine Lavoisier*** (France) identifies 30 elements, ***Lavoisier*** starts to give the precision to chemical experiments by weighing the starting materials and products of each reactions. ***Dalton*** formulates his law of multiple proportions: elements react in constant proportions to give compounds of defined composition. The modern way of writing formulas like "$H_2SO_4$" is introduced by ***Dalton***.
**1868** ***Lothar Meyer*** (Karlsruhe, Germany), uses the first modern periodic table in his textbook.
**1869** ***Dimitrii Mendeleev*** (Kazan, Russia) publishes the modern version of the periodic table. Mendeleev concludes that Boron is the lighter version of Al (and not Be as was assumed before). M. makes precise predictions about the then unknown elements (Ga, Ge).
1900 80 elements have been discovered. The only missing elements are the radioactive elements, Rhenium (Re) and hafnium (Hf). Rhenium and Hafnium escape discovery because they have no specific minerals and are also quite rare. Re accompanies Mo in its principal ore, $MoS_2$. Hf is constant ingredient (1 %) of any Zirconium ore (main ore: ZrO2).

# Course structure

1. Concept of the oxidation state and valence

2. Source and implications of the periodicity of properties.

3. Chemistry of elements in the following order:

a) Hydrogen, water, rules of water solubility water-based acids and basis. Chemical reaction aqueous solutions;

b) Chemistry of elements 1A-8A;

c) Transition metals 1B-8B;

d) Lanthanides 1B-8B;

c) Actinides outline (Th, U, Pu)

Note: chemistry of element includes: preparation, chemical properties, and practically important reactions.

**Reminder:** **the source of chemical reactivity**

**Basic facts:**

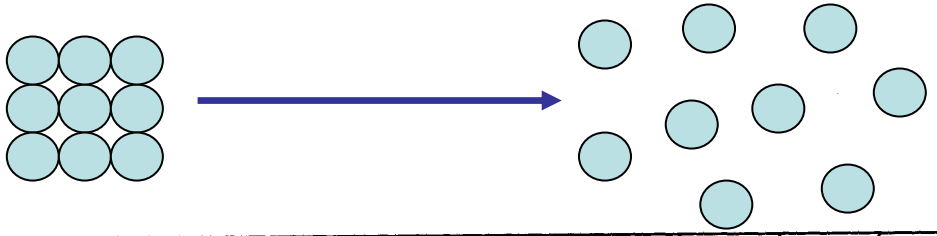
**1. Any chemical reaction is redistribution of the electrons**

**2. The driving force for the redistribution of electrons is the dependence of electron energy on: the presence of other electrons and nucleolus**

# Simple examples

## Cohesive Energies $\Delta H_c$ (kJ/mol and eV/atom) of the Elemental Solids at $T = 0$ K

***Cohesive energy=standard enthalpy of formation of the consistent atoms form a solid phase.***

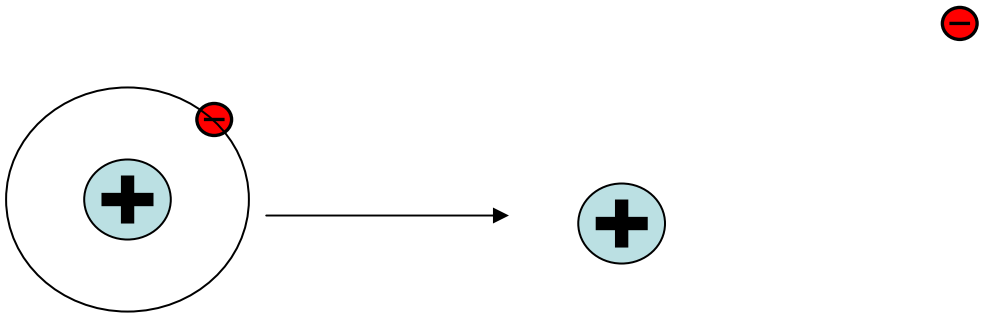


| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H<br>218.0<br>2.24 | | | | | | | | | | | | | | | | | He |
| Li<br>157.7<br>1.64 | Be<br>319.8<br>3.31 | | | | | | | | | | | B<br>559.9<br>5.80 | C<br>711.2<br>7.37 | N<br>470.8<br>4.88 | O<br>246.8<br>2.56 | F<br>76.9<br>0.80 | Ne<br>1.92<br>0.020 |
| Na<br>107.8<br>1.12 | Mg<br>145.9<br>1.51 | | | | | | | | | | | Al<br>327.6<br>3.40 | Si<br>451.3<br>4.68 | P<br>315.7<br>3.27 | S<br>274.9<br>2.85 | Cl<br>120.0<br>1.24 | Ar<br>7.74<br>0.080 |
| K<br>89.9<br>0.93 | Ca<br>177.3<br>1.84 | Sc<br>376.0<br>3.90 | Ti<br>470.3<br>4.87 | V<br>511.0<br>5.30 | Cr<br>394.5<br>4.09 | Mn<br>279.4<br>2.90 | Fe<br>414.0<br>4.29 | Co<br>423.1<br>4.39 | Ni<br>427.7<br>4.43 | Cu<br>336.2<br>3.49 | Zn<br>129.9<br>1.35 | Ga<br>276.0<br>2.86 | Ge<br>369.2<br>3.83 | As<br>301.4<br>3.12 | Se<br>226.4<br>2.35 | Br<br>117.9<br>1.22 | Kr<br>11.2<br>0.116 |
| Rb<br>82.2<br>0.85 | Sr<br>164.0<br>1.7 | Y<br>420.5<br>4.36 | Zr<br>607.5<br>6.30 | Nb<br>722.8<br>7.49 | Mo<br>656.6<br>6.81 | Tc<br>680.0<br>7.0 | Ru<br>641.0<br>6.64 | Rh<br>555.6<br>5.76 | Pd<br>377.4<br>3.91 | Ag<br>285.4<br>2.96 | Cd<br>111.9<br>1.16 | In<br>243.7<br>2.53 | Sn<br>301.3<br>3.12 | Sb<br>262.0<br>2.72 | Te<br>197.0<br>2.04 | I<br>107.2<br>1.11 | Xe<br>15.9<br>0.16 |
| Cs<br>78.0<br>0.81 | Ba<br>180.7<br>1.87 | La<br>431.3<br>4.47 | Hf<br>618.9<br>6.42 | Ta<br>781.4<br>8.10 | W<br>848.1<br>8.79 | Re<br>769.0<br>7.97 | Os<br>790.0<br>8.2 | Lr<br>664.3<br>6.89 | Pt<br>564.4<br>5.85 | Au<br>365.9<br>3.79 | Hg<br>64.5<br>0.67 | Tl<br>182.8<br>1.90 | Pb<br>195.9<br>2.03 | Bi<br>207.4<br>2.15 | Po<br>145.0<br>1.5 | At | Rn<br>19.5<br>0.202 |
| Fr | Ra<br>159.0<br>1.6 | Ac<br>406.0<br>4.2 | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce<br>423.4<br>4.39 | Pr<br>356.7<br>3.70 | Nd<br>328.6<br>3.41 | Pm | Sm<br>206.1<br>2.14 | Eu<br>177.1<br>1.84 | Gd<br>398.9<br>4.14 | Tb<br>390.6<br>4.05 | Dy<br>293.1<br>3.04 | Ho<br>302.6<br>3.14 | Er<br>318.3<br>3.30 | Tm<br>233.4<br>2.42 | Yb<br>152.8<br>1.58 | Lu<br>427.8<br>4.43 |
| Th<br>602.2<br>6.24 | Pa<br>606.0<br>6.3 | U<br>523.9<br>5.52 | Np | Pu<br>384.0<br>4.0 | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

# First and Second Ionization Energies of the Atoms (eV)

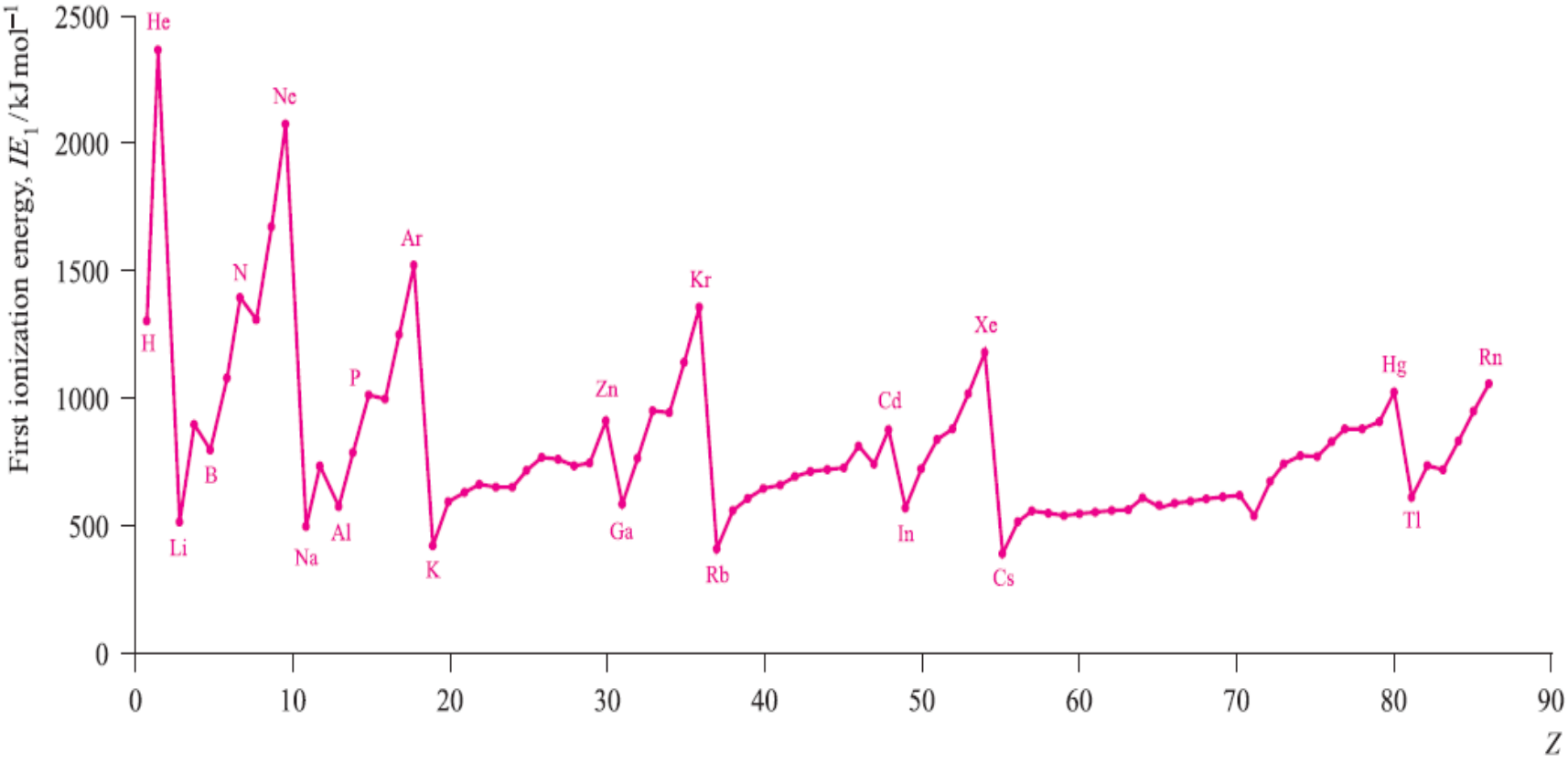
***The work (energy) required to remove the most weakly bound (outermost) electron from an isolated atom is known as the "ionization energy".***



| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 13.60 — | | | | | | | | | | | | | | | | | 2 He 24.59 54.42 |
| 3 Li 5.39 75.64 | 4 Be 9.32 18.21 | | | | | | | | | | | 5 B 8.30 25.15 | 6 C 11.26 24.38 | 7 N 14.53 29.60 | 8 O 13.62 35.12 | 9 F 17.42 34.97 | 10 Ne 21.56 40.96 |
| 11 Na 5.14 47.29 | 12 Mg 7.65 15.04 | | | | | | | | | | | 13 Al 5.99 18.83 | 14 Si 8.15 16.35 | 15 P 10.49 19.77 | 16 S 10.36 23.34 | 17 Cl 12.97 23.81 | 18 Ar 15.76 27.63 |
| 19 K 4.34 31.63 | 20 Ca 6.11 11.87 | 21 Sc 6.56 12.80 | 22 Ti 6.83 13.58 | 23 V 6.75 14.66 | 24 Cr 6.77 16.49 | 25 Mn 7.43 15.64 | 26 Fe 7.90 16.19 | 27 Co 7.88 17.08 | 28 Ni 7.64 18.17 | 29 Cu 7.73 20.29 | 30 Zn 9.39 17.96 | 31 Ga 6.00 20.51 | 32 Ge 7.90 15.93 | 33 As 9.82 18.63 | 34 Se 9.75 21.19 | 35 Br 11.81 21.8 | 36 Kr 14.00 24.36 |
| 37 Rb 4.18 27.29 | 38 Sr 5.69 11.03 | 39 Y 6.22 12.24 | 40 Zr 6.63 13.13 | 41 Nb 6.76 14.32 | 42 Mo 7.09 16.16 | 43 Tc 7.28 15.26 | 44 Ru 7.36 16.76 | 45 Rh 7.46 18.08 | 46 Pd 8.34 19.43 | 47 Ag 7.58 21.49 | 48 Cd 8.99 16.91 | 49 In 5.79 18.87 | 50 Sn 7.34 14.63 | 51 Sb 8.64 16.53 | 52 Te 9.01 18.6 | 53 I 10.45 19.13 | 54 Xe 12.13 21.21 |
| 55 Cs 3.89 23.16 | 56 Ba 5.21 10.00 | 57 La 5.58 11.06 | 72 Hf 6.83 14.9 | 73 Ta 7.89 — | 74 W 7.98 — | 75 Re 7.88 — | 76 Os 8.7 — | 77 Ir 9.1 — | 78 Pt 9.0 18.56 | 79 Au 9.23 20.5 | 80 Hg 10.48 18.76 | 81 Tl 6.11 20.42 | 82 Pb 7.42 15.03 | 83 Bi 7.29 16.69 | 84 Po 8.42 — | 85 At | 86 Rd 10.75 — |
| 87 Fr | 88 Ra 5.28 10.15 | 89 Ac 5.17 12.1 | | | | | | | | | | | | | | | |

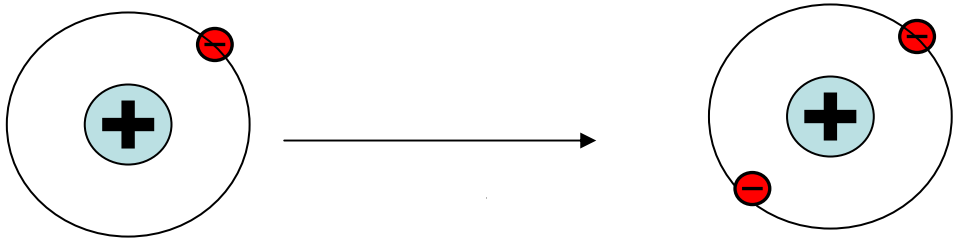
| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 Ce 5.54 10.85 | 59 Pr 5.46 10.55 | 60 Nd 5.53 10.73 | 61 Pm 5.55 10.90 | 62 Sm 5.64 11.07 | 63 Eu 5.67 11.24 | 64 Gd 6.15 12.09 | 65 Tb 5.86 11.52 | 66 Dy 5.94 11.67 | 67 Ho 6.02 11.80 | 68 Et 6.11 11.93 | 69 Tm 6.18 12.05 | 70 Yb 6.25 12.18 | 71 Lu 5.43 13.9 |
| 90 Th 6.08 11.5 | 91 Pa 5.89 — | 92 U 6.19 — | 93 Np 6.27 — | 94 Pu 6.06 — | 95 Am 5.99 — | 96 Cm 6.02 — | 97 Bk 6.23 — | 98 Cf 6.30 — | 99 Es 6.42 — | 100 Fm 6.50 — | 101 Md 6.58 — | 102 No 6.65 — | 103 Lr |

# Periodicity of the first ionization energy



## Electron Affinities EA of the Atoms up to $Z = 87$ (eV)

*The amount of energy released on acquisition of an electron is called the electron affinity.*



| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 0.754 | | | | | | | | | | | | | | | | | 2 He <0 |
| 3 Li 0.618 | 4 Be <0 | | | | | | | | | | | 5 B 0.280 | 6 C 1.26 | 7 N <0 | 8 0 1.46 | 9 F 3.40 | 10 Ne <0 |
| 11 Na 0.548 | 12 Mg <0 | | | | | | | | | | | 13 Al 0.433 | 14 Si 1.39 | 15 P 0.747 | 16 S 2.08 | 17 Cl 3.61 | 18 Ar <0 |
| 19 K 0.501 | 20 Ca 0.025 | 21 Sc 0.188 | 22 Ti 0.084 | 23 V 0.525 | 24 Cr 0.676 | 25 Mn <0 | 26 Fe 0.151 | 27 Co 0.663 | 28 Ni 1.16 | 29 Cu 1.24 | 30 Zn <0 | 31 Ga 0.41 | 32 Ge 1.23 | 33 As 0.81 | 34 Se 2.02 | 35 Br 3.36 | 36 Kr <0 |
| 37 Rb 0.486 | 38 Sr 0.052 | 39 Y 0.307 | 40 Zr 0.426 | 41 Nb 0.893 | 42 Mo 0.747 | 43 Tc 0.55 | 44 Ru 1.05 | 45 Rh 1.14 | 46 Pd 0.562 | 47 Ag 1.30 | 48 Cd <0 | 49 In 0.404 | 50 Sn 1.11 | 51 Sb 1.05 | 52 Te 1.97 | 53 I 3.06 | 54 Xe <0 |
| 55 Cs 0.472 | 56 Ba 0.145 | 57 La 0.47 | 72 Hf ≈ 0 | 73 Ta 0.322 | 74 W 0.815 | 75 Re 0.15 | 76 Os 1.08 | 77 Ir 1.56 | 78 Pt 2.13 | 79 Au 2.31 | 80 Hg <0 | 81 Tl 0.377 | 82 Pb 0.364 | 83 Bi 0.942 | 84 Po 1.9 | 85 At 2.8 | 86 Rd <0 |
| 87 Fr 0.46 | 88 Ra — | 89 Ac — | | | | | | | | | | | | | | | |

***Electronegativity is a concept used to guess roughly the character of the bonds.***

***There is more than one concept of electronegativity.***

$$E(A\text{-}B) = \frac{E(A\text{-}A) + E(B\text{-}B)}{2} + (X_A - X_B)^2$$

***E is bond energy, calculated from cohesive energy. $X_A$ is relative electronegativity. $X_A$-$X_B$ is roughly proportional to the number of electrons transferred from A to B.***

**Ionicities of Some Crystals**

| Crystal | Group Number | Local Atomic Bonding Unit | $f_i^a$ |
|---|---|---|---|
| C, Si, Ge | IV | $A-A_4$ | 0.00 |
| SiC | IV–IV | $A-B_4$ | 0.18 |
| BN | III–V | $A-B_4$ | 0.26 |
| GaAs | III–V | $A-B_4$ | 0.31 |
| InAs | III–V | $A-B_4$ | 0.36 |
| AlN | III–V | $A-B_4$ | 0.45 |
| MgTe | II–VI | $A-B_4$ | 0.55 |
| ZnS | II–VI | $A-B_4$ | 0.62 |
| CdTe | II–VI | $A-B_4$ | 0.72 |
| HgS | II–VI | $A-B_4$ | 0.79 |
| AgCl | I–VII | $A-B_6$ | 0.86 |
| NaCl | I–VII | $A-B_6$ | 0.94 |

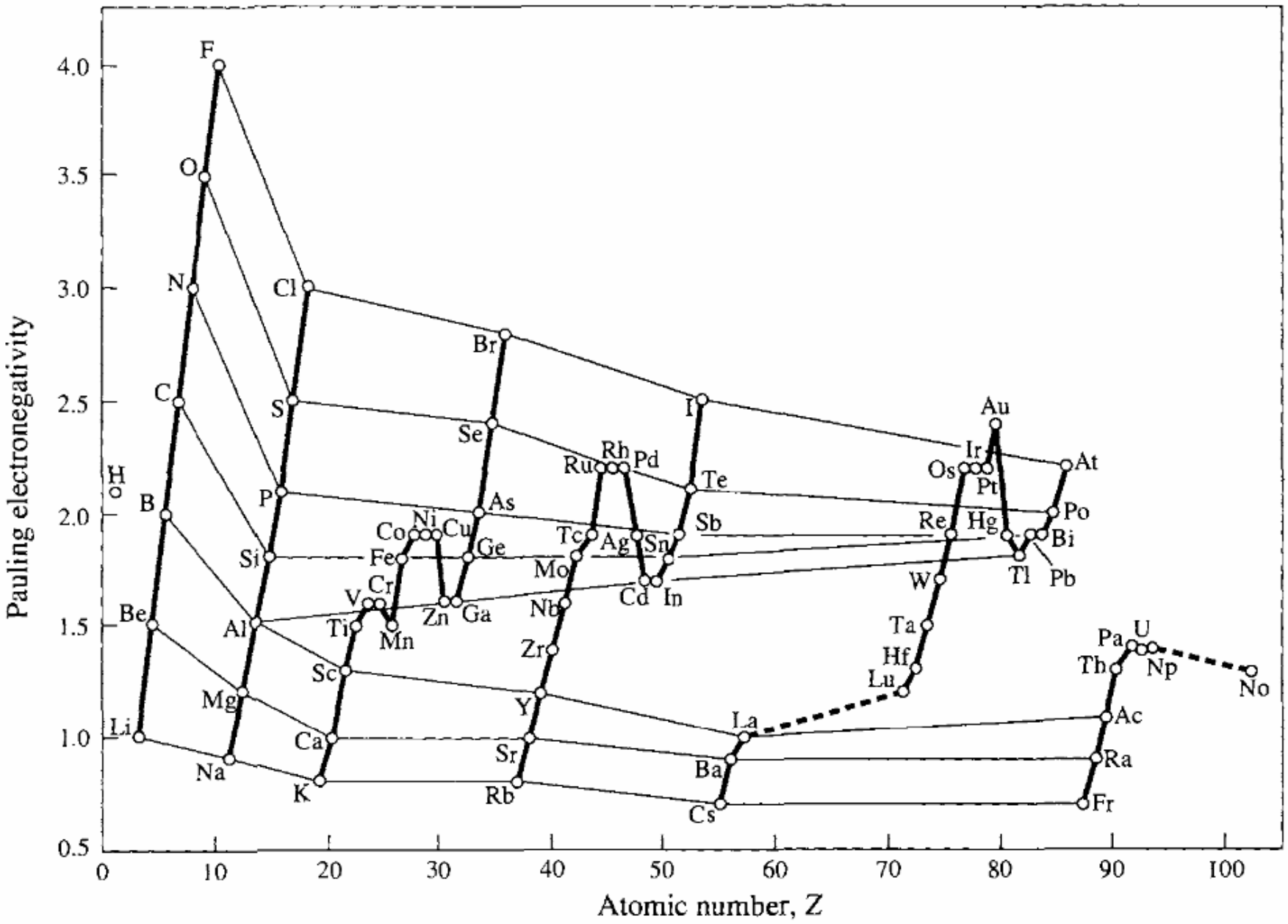
***Predictions based on electronegativity values are very approximate!***

**Electronegativity, was introduced by Pauling as 'the power of an atom to attract electrons to itself '.**

# *The electronegativity values for the elements.*

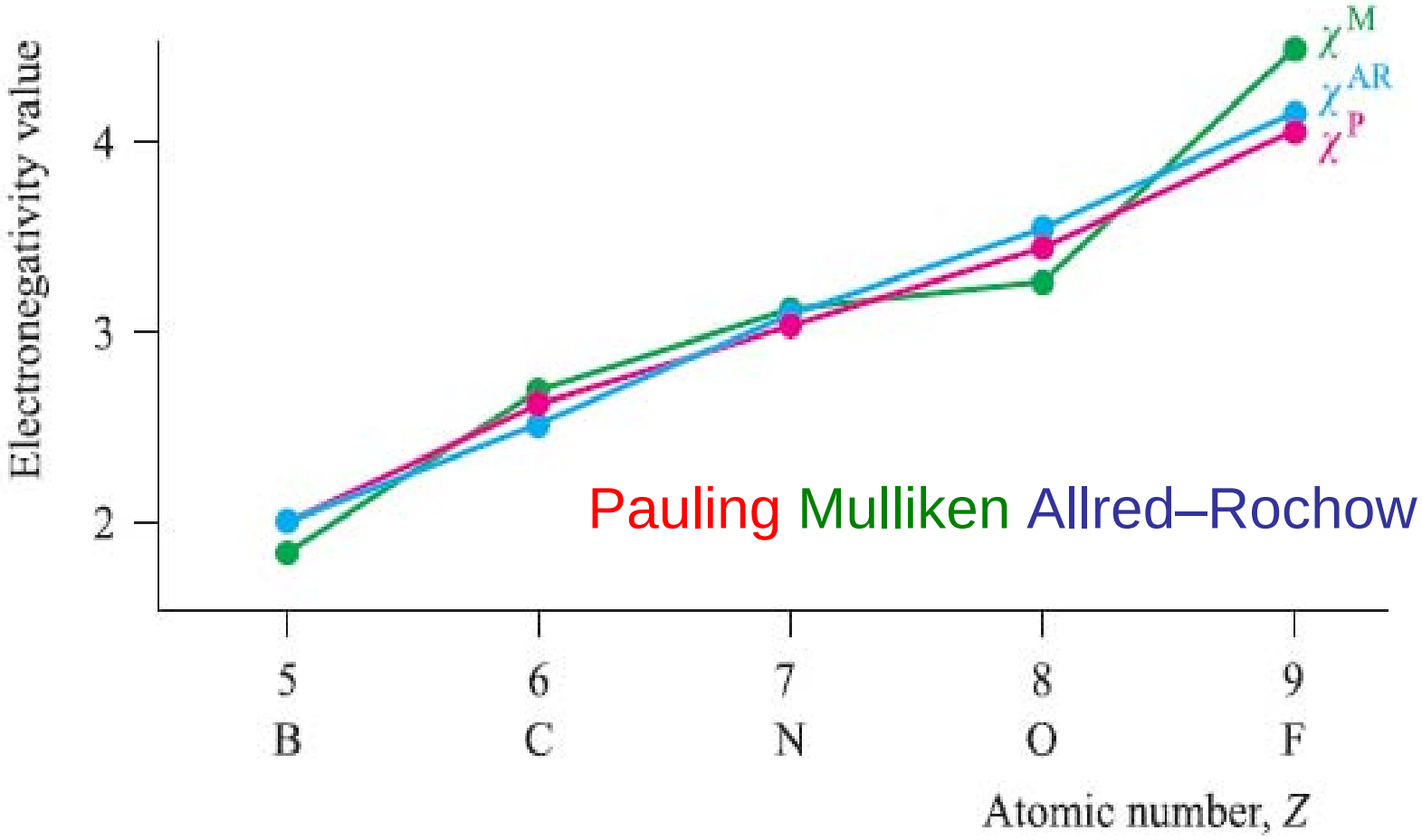
| IA | IIA | IIIB | IVB | VB | VIB | VIIB | VIII | | | IB | IIB | IIIA | IVA | VA | VIA | VIIA | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1<br>H<br>2.1 | | | | | | | | | | | | | | | | | 2<br>He<br>– |
| 3<br>Li<br>1.0 | 4<br>Be<br>1.5 | | | | | | | | | | | 5<br>B<br>2.0 | 6<br>C<br>2.5 | 7<br>N<br>3.0 | 8<br>O<br>3.5 | 9<br>F<br>4.0 | 10<br>Ne<br>– |
| 11<br>Na<br>0.9 | 12<br>Mg<br>1.2 | | | | | | | | | | | 13<br>Al<br>1.5 | 14<br>Si<br>1.8 | 15<br>P<br>2.1 | 16<br>S<br>2.5 | 17<br>Cl<br>3.0 | 18<br>Ar<br>– |
| 19<br>K<br>0.8 | 20<br>Ca<br>1.0 | 21<br>Sc<br>1.3 | 22<br>Ti<br>1.5 | 23<br>V<br>1.6 | 24<br>Cr<br>1.6 | 25<br>Mn<br>1.5 | 26<br>Fe<br>1.8 | 27<br>Co<br>1.8 | 28<br>Ni<br>1.8 | 29<br>Cu<br>1.9 | 30<br>Zn<br>1.6 | 31<br>Ga<br>1.6 | 32<br>Ge<br>1.8 | 33<br>As<br>2.0 | 34<br>Se<br>2.4 | 35<br>Br<br>2.8 | 36<br>Kr<br>– |
| 37<br>Rb<br>0.8 | 38<br>Sr<br>1.0 | 39<br>Y<br>1.2 | 40<br>Zr<br>1.4 | 41<br>Nb<br>1.6 | 42<br>Mo<br>1.8 | 43<br>Tc<br>1.9 | 44<br>Ru<br>2.2 | 45<br>Rh<br>2.2 | 46<br>Pd<br>2.2 | 47<br>Ag<br>1.9 | 48<br>Cd<br>1.7 | 49<br>In<br>1.7 | 50<br>Sn<br>1.8 | 51<br>Sb<br>1.9 | 52<br>Te<br>2.1 | 53<br>I<br>2.5 | 54<br>Xe<br>– |
| 55<br>Cs<br>0.7 | 56<br>Ba<br>0.9 | 57–71<br>La–Lu<br>1.1–1.2 | 72<br>Hf<br>1.3 | 73<br>Ta<br>1.5 | 74<br>W<br>1.7 | 75<br>Re<br>1.9 | 76<br>Os<br>2.2 | 77<br>Ir<br>2.2 | 78<br>Pt<br>2.2 | 79<br>Au<br>2.4 | 80<br>Hg<br>1.9 | 81<br>Tl<br>1.8 | 82<br>Pb<br>1.8 | 83<br>Bi<br>1.9 | 84<br>Po<br>2.0 | 85<br>At<br>2.2 | 86<br>Rn<br>– |
| 87<br>Fr<br>0.7 | 88<br>Ra<br>0.9 | 89–102<br>Ac–No<br>1.1–1.7 | | | | | | | | | | | | | | | |

# Periodicity of the electronegativity



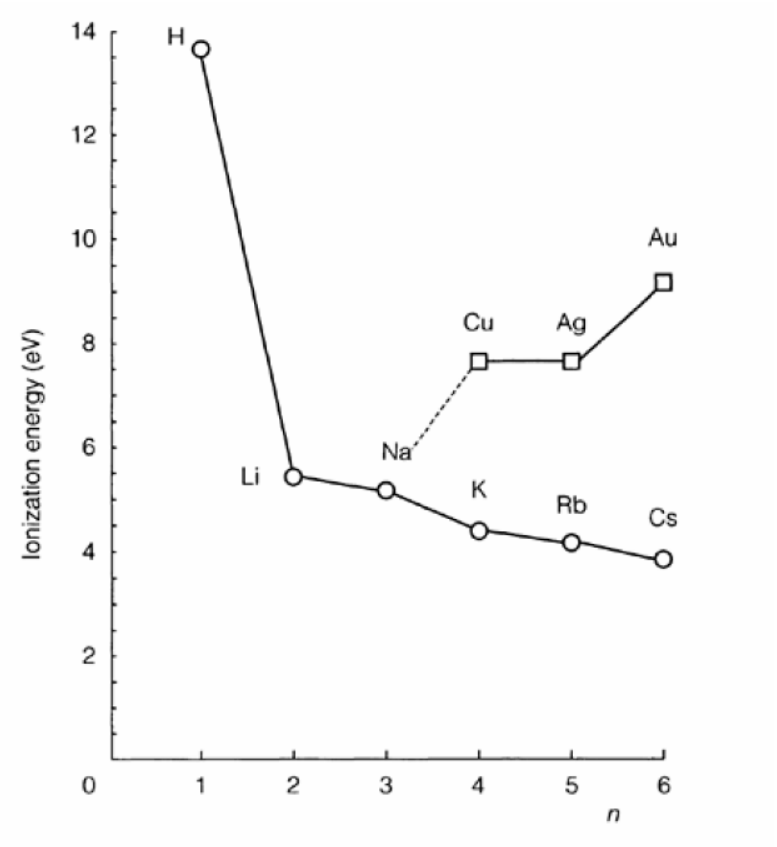
# Horizontal trends in chemical properties

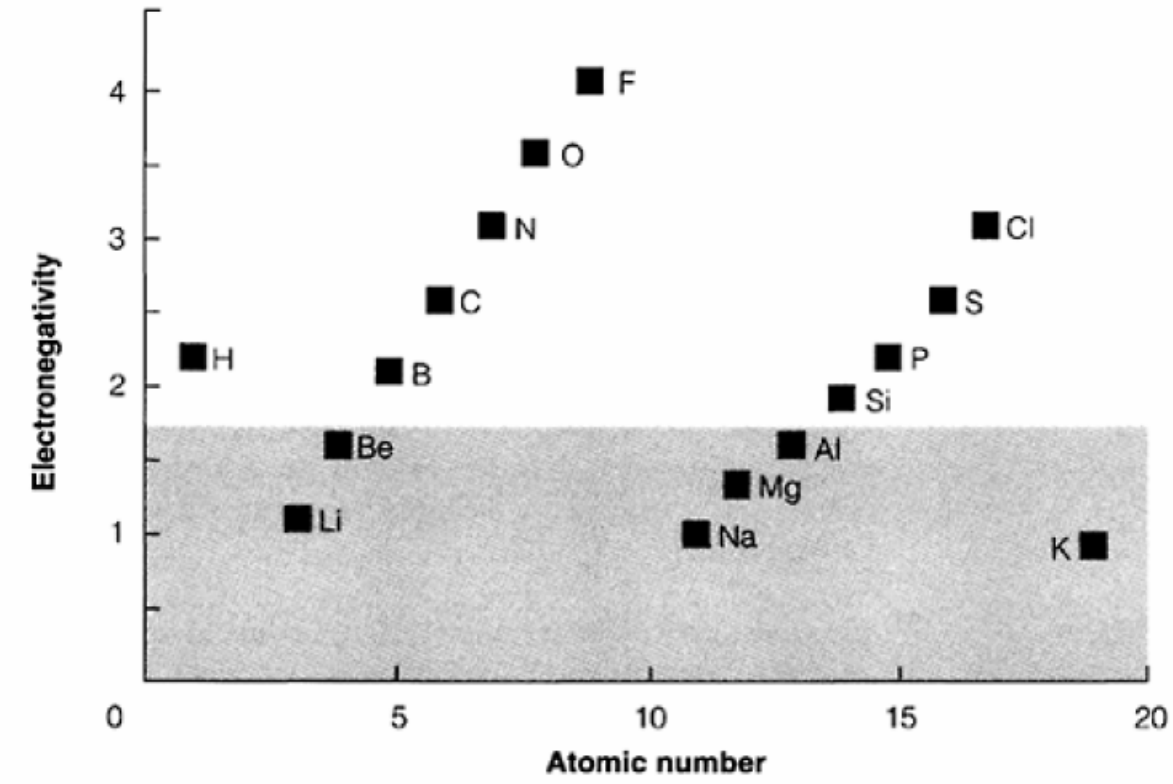
**A) Left to right EN increases in MAIN period;**
**B) For D-elements EN reaches maximum at d8-d9**



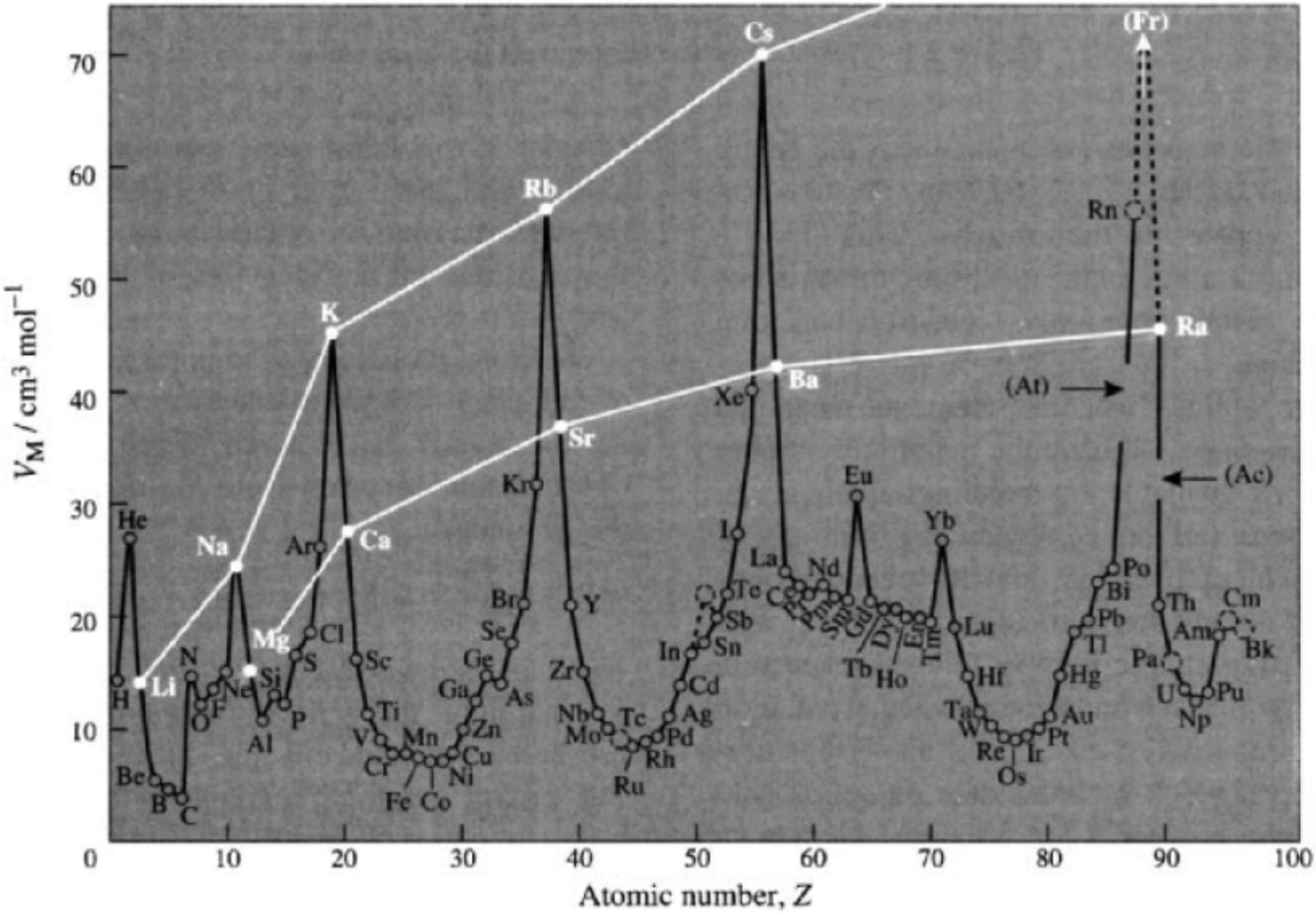
# Vertical trends in chemical properties

**A) Main groups: IE and EN decrease with increasing Z**
**B) For D-elements EN increase with increasing Z**

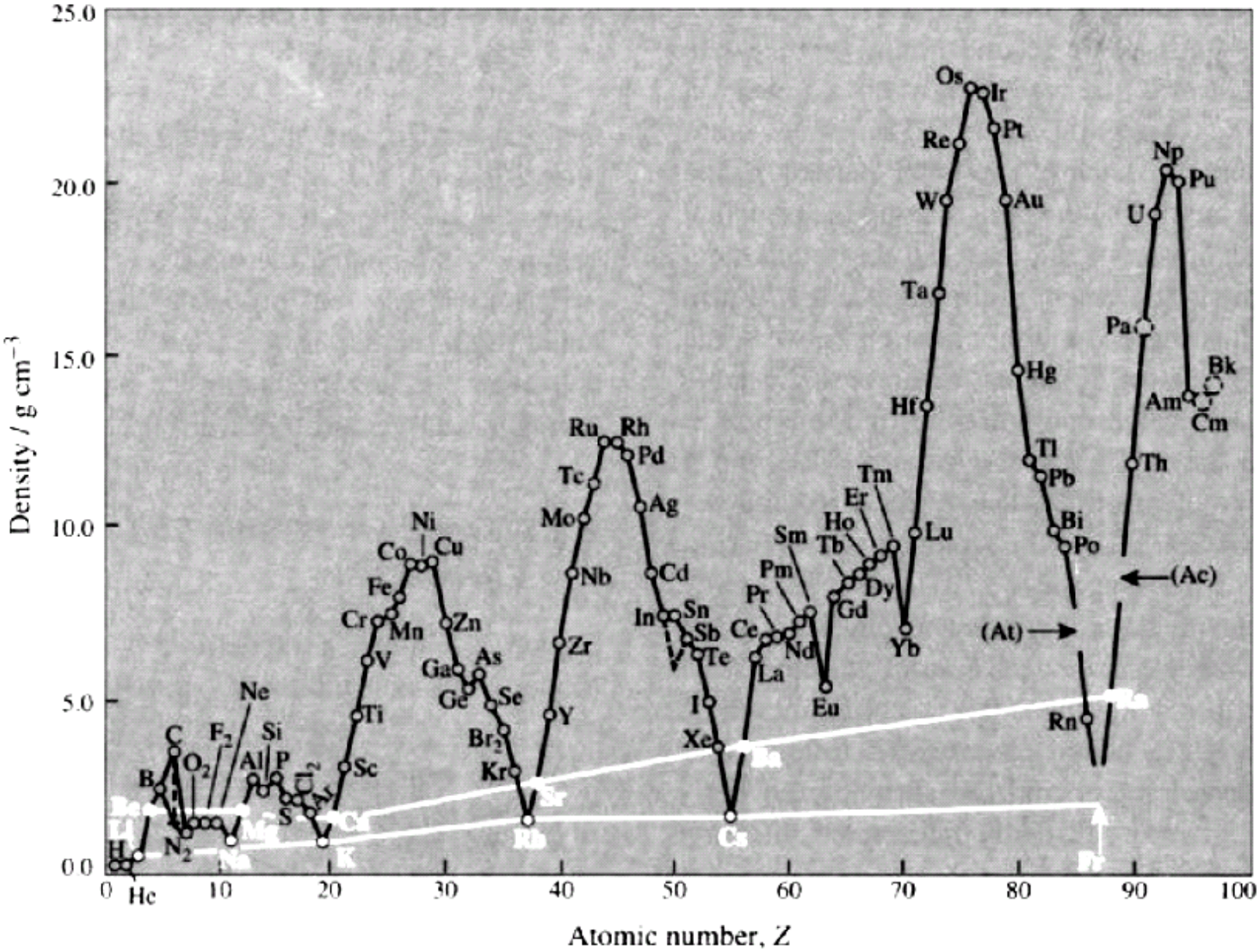


# Periodicity of physical properties



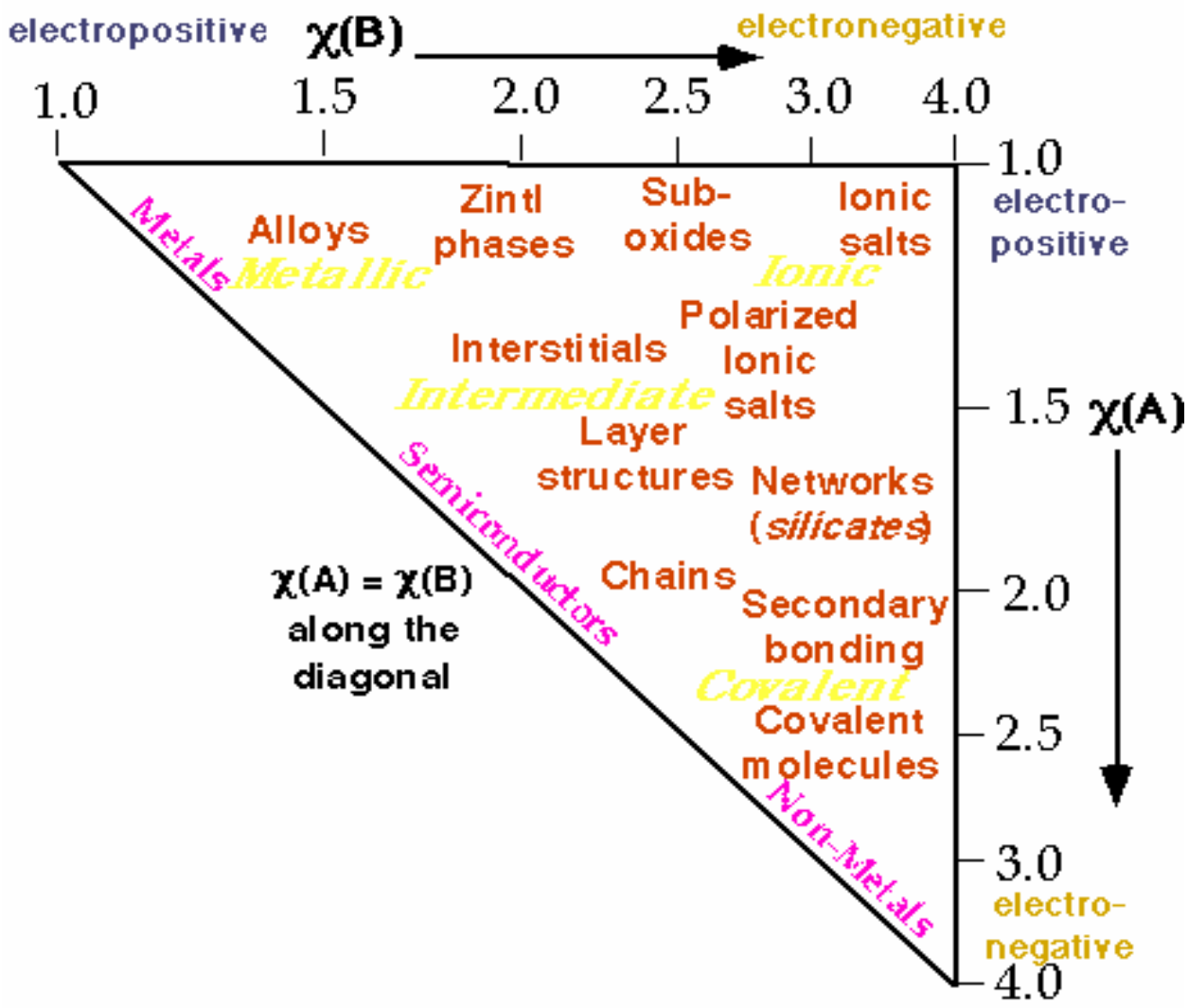

**Atomic volumes (molar volumes) of the elements in the solid state.**




**Densities of the elements in the solid state**

# Ketelaar's Triangle

Ketelaar's Triangle finds different structure types in different regions *i.e.* according to the electronegativities of A and B.



# The basic premise of the course

One can predict the properties of UNKNOWN inorganic compounds using analogy with KNOWN compound

Pro: the properties change continuously within the groups and periods

Contra: In contrast to organic chemistry, there are NO FUNCTIONAL units that help to predict the properties.

# Concept of an oxidation state

Oxidation state is a fictitious number assigned to an element to symbolize the number of given or received electrons.

Oxidation states do not reflect real charges in solids and molecules.

Oxidation states are close to real charges for dissociated ions in solutions.

# Basic definitions (reminder)

**Exchange reaction** is a reaction in which formal oxidation states of all reactants do not change

**Redox reaction** is reaction in which formal oxidation states of at least one reactant changes

**Disproportionation reaction** is a redox reaction in which some atoms of a single element in a reactant are oxidized and others are reduced.

## *Bonding theories*

- There are two currently used bonding theories, valence bond theory and molecular orbital theory.
- Valence bond theory envisions bonding as resulting from the overlap of atomic orbitals;
- Molecular orbital theory moves past atomic orbitals and derives orbitals that belong to the molecule as a whole.

## *Valence bond theory: Lewis Structures*

***Reminder: Lewis structures are useful for indicating the bonding in molecules only.***

•Rules:

–All valence electrons must appear

–The electrons are usually paired

–The valence shells are usually filled (2 electrons for H, 8 for systems with *s* and *p* orbitals)

–Multiple bonds are needed (C,N,O, S etc).

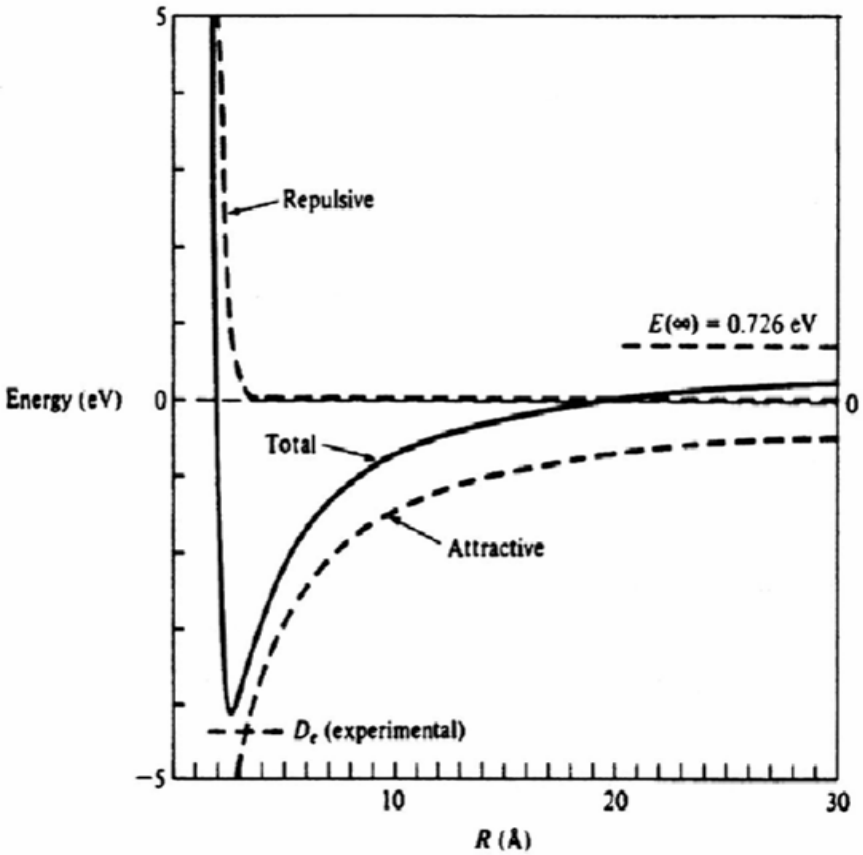
Example: N≡C–C ≡ N

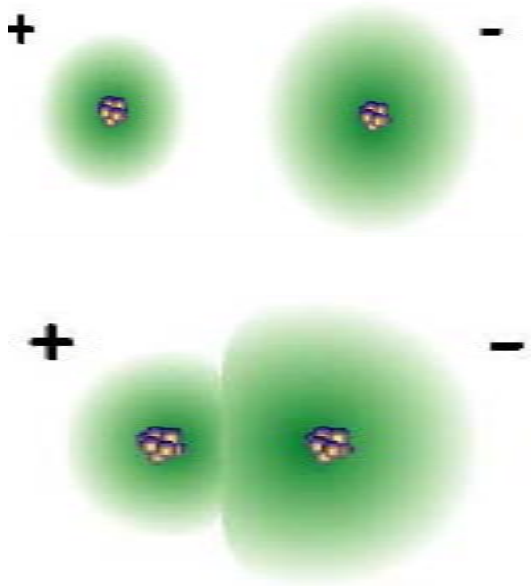
**Lewis structures are correct for most molecules but not applicable to crystalline solids**

**<u>Lewis structures are of marginal importance in inorganic chemistry</u>**

# *Simple case of a chemical Ionic bonding.*

***The Ionic (electrovalent) bond is the result of electrostatic (Coulomb) attraction between ions of opposite charge that are viewed as charged spheres.***




$$E_{att} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 R}$$

Energy of attraction

$$E_{rep} = \frac{C}{R^n}$$

n=10→12

Energy of repulsion

$z_1$ and $z_2$ are the electrical charges of the ions in units of elementary charge *e*. $\varepsilon_0$ is a dielectric permittivity of vacuum. ***R*** is the distance between the nuclei.

# **Ionic bonding**: size dependence

Ions with the same charge but different size would have the same attractive energy but different repulsive energy. For big ions, the repulsive energy kicks in at larger values of R when attractive energy is weaker. Hence big ions result in larger bond distance and weaker ionic bond energy. Bond strength decrease with ionic size.

# **Ionic bonding**: stoichiometry

The overall solid must be neutral, hence the charge of the charge of the anions must compensate the charge of the cations. Therefore, all ionic solids are highly stoichiometric = exist within a very narrow concentration range.

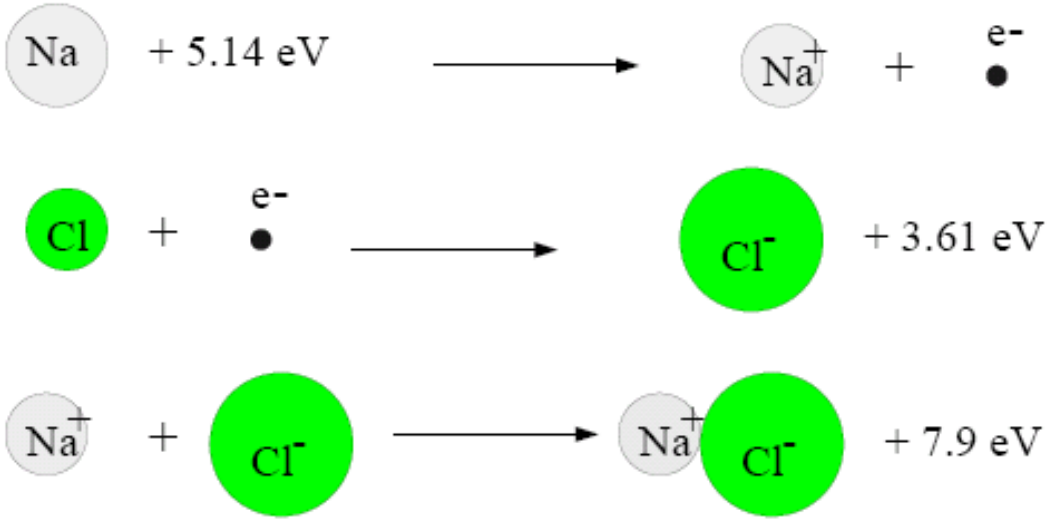
**Percent Ionic Character of a Single Chemical Bond**

| Difference in electronegativity | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 | 2.0 | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | 2.6 | 2.7 | 2.8 | 2.9 | 3.0 | 3.1 | 3.2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Percent ionic character % | 0.5 | 1 | 2 | 4 | 6 | 9 | 12 | 15 | 19 | 22 | 26 | 30 | 34 | 39 | 43 | 47 | 51 | 55 | 59 | 63 | 67 | 70 | 74 | 76 | 79 | 82 | 84 | 86 | 88 | 89 | 91 | 92 |

# *Haber-Born cycle*

***Bonding energies for ionic solids may be calculated on the basis of purely electrostatic interactions***

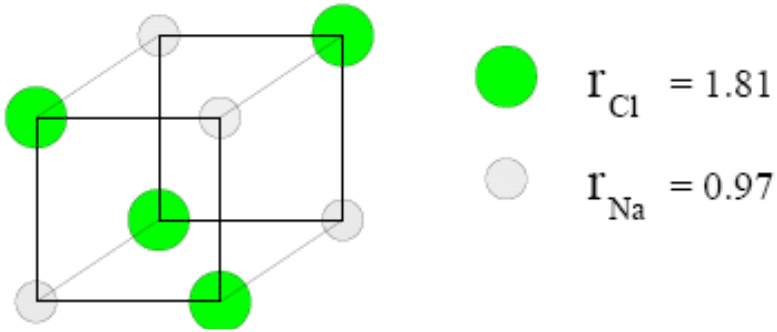
***For a pair of ions:***




***Ionic bonding is not directional.***

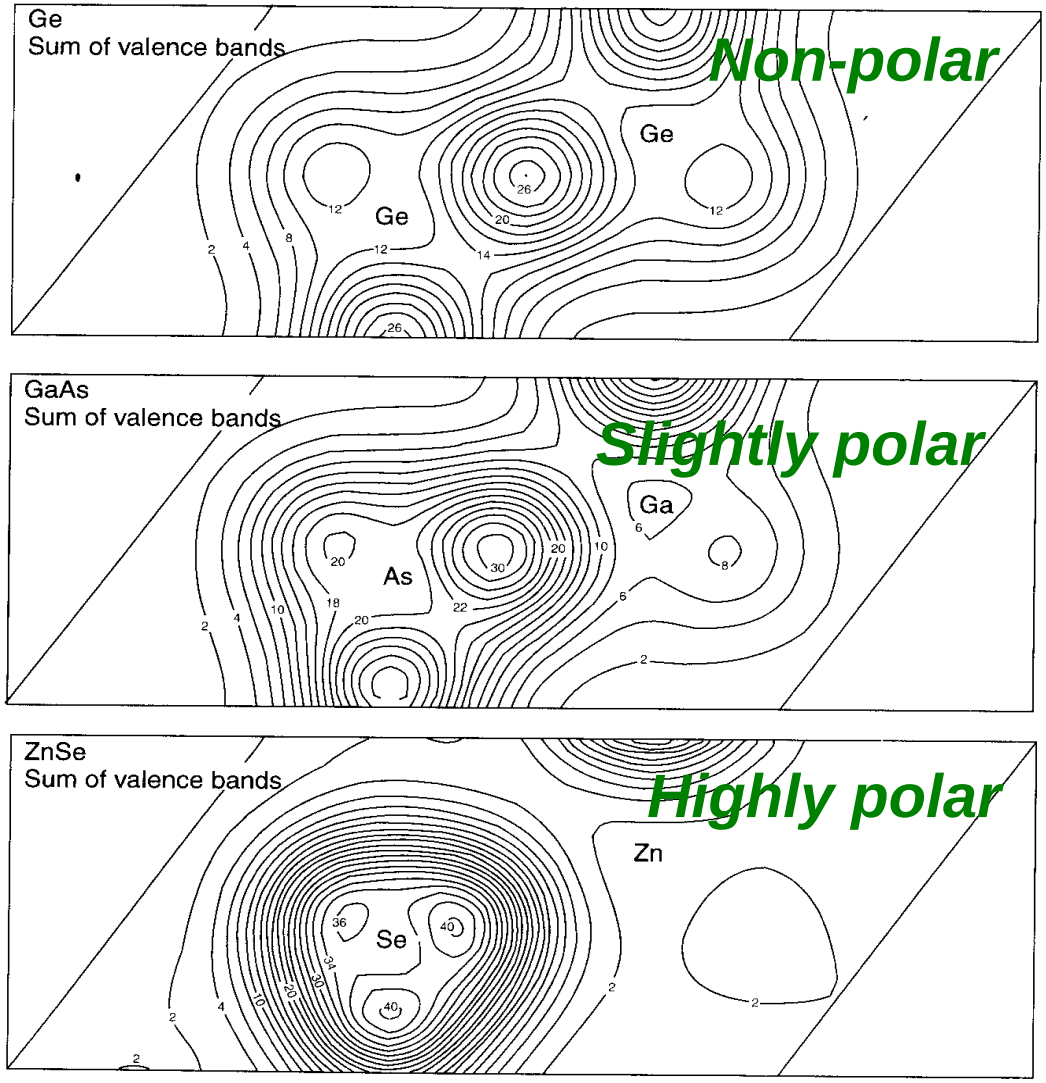
Atomic arrangement in solids with ionic bonding provides

**maximum coordination number CN.**



# *Covalent bonding*

Valence electron charge density




***Covalent bonding is a result of orbital sharing.***
***Covalent bonding dominates in atomic crystals when the number of valence electrons per atom is equal or greater than the number of bonding orbitals.***

***Number of bonding orbitals is linked to a number of nearest neighbors (NN) = coordination number (CN) .***
***Type of bonding and CN depend on external conditions.***

# *Covalent bonding. Tendencies and exceptions.*

**Structures of the Covalently Bonded Elemental Solids**

| Elements | Group Number[a] | Coordination Number CN | Local Atomic Bonding Unit | Resulting Local Structures |
|---|---|---|---|---|
| B | III | 5 | $B-B_5$ | Icosahedra |
| C (diamond), Si, Ge, gray Sn | IV | 4 | $A-A_4$ | Tetrahedra (three-dimensional) |
| C (graphite) | IV | 3 | $A-A_3$ | Planar hexagons |
| P (black), As, Sb, Bi | V | 3 | $A-A_3$ | Nonplanar hexagons |
| S, Se, Te | VI | 2 | $A-A_2$ | $A_8$ rings, spiral chains |
| F, Cl, Br, I | VII | 1 | A–A | $A_2$, diatomic molecules |

***In most of the covalent solids CN=(8 – number of valence electrons per atom)***

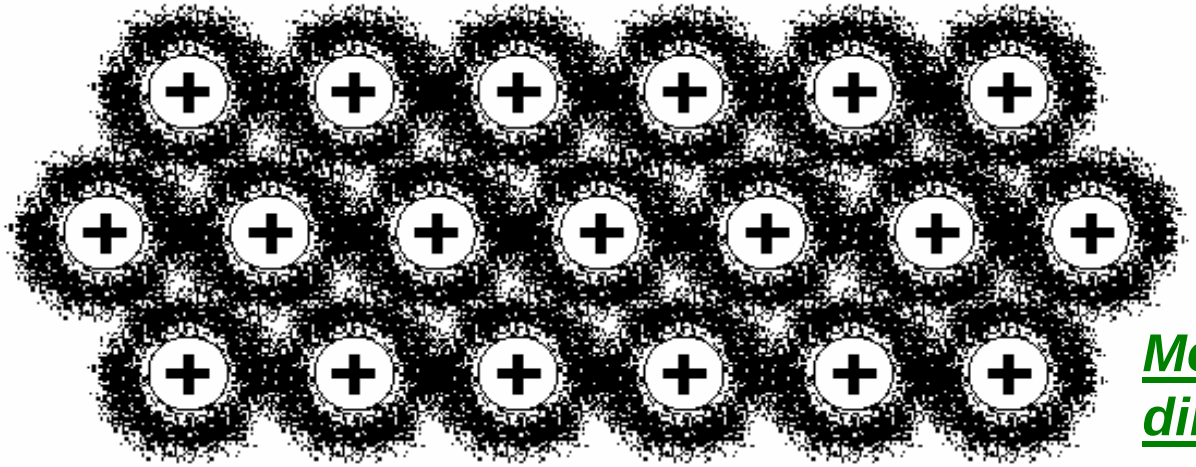
Interesting to know:
Ge (covalent semiconductor crystal at normal conditions)-> metal under 30 GPa.
$\alpha$-Sn (gray tin, covalent, semimetal) -> $\beta$ -Sn (white tin, metal) at –5 $^{o}$C

***Valences in atomic solids may be very different from that in molecular solids***

***Examples of "strange" valences in atomic solids: InTe , $VO_2$, SbSI, $Fe_3C$, $NClO_5$.***

***Crystal structure of atomic solids with covalent bonds is defined by CN***

# Metallic Sea of Electrons



Electrons are not bonded to any particular atom and are free to move about in the solid.

- High electrical conductivity
- High thermal conductivity
- High reflectivity of visible light

***Metallic bonding appears when the number of valence electrons per atom is smaller than CN***

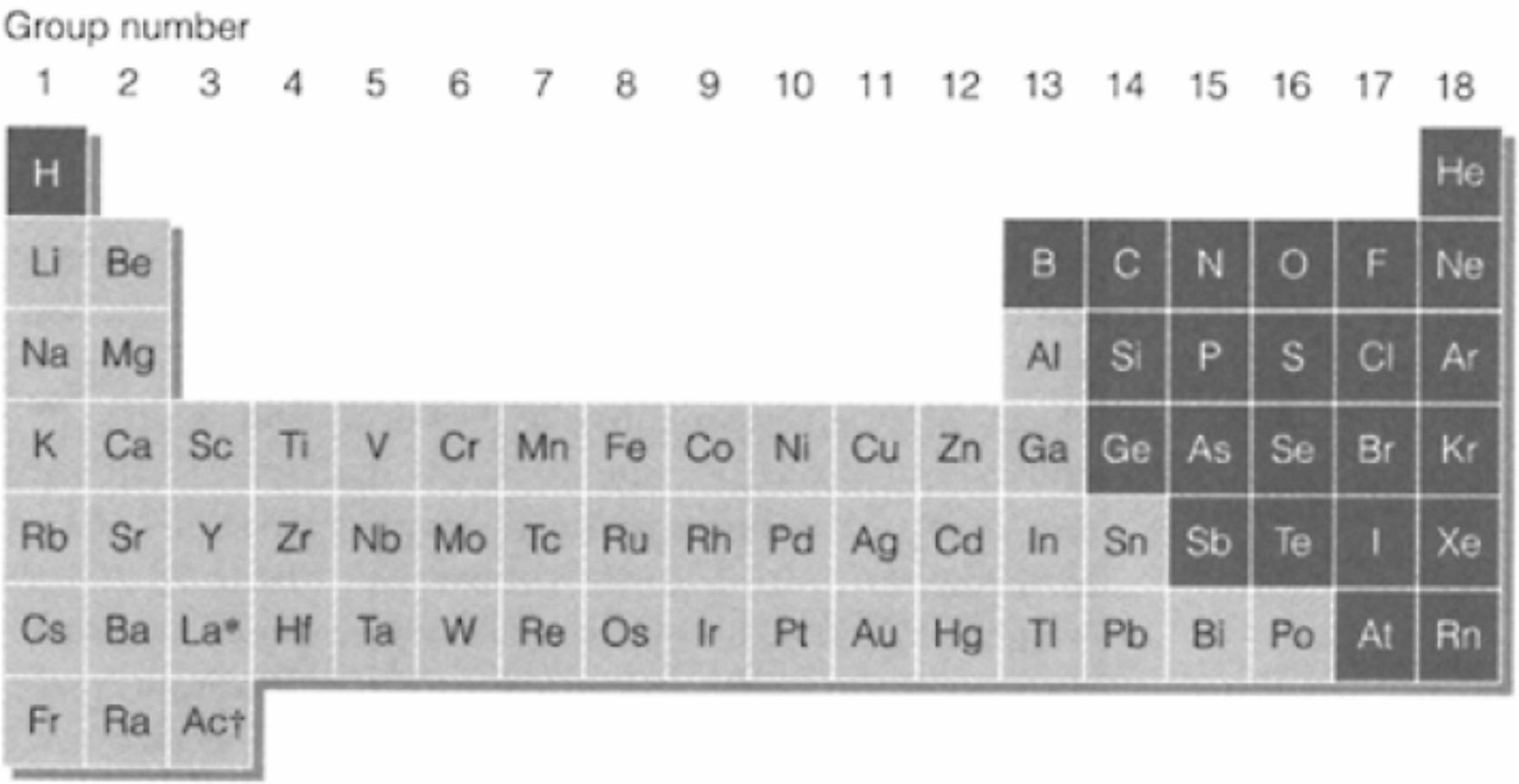
***Metallic bonding is not directional. Therefore, the resulting structures are always close packed (maximum CN). CN=8(cube), 12 (cube, hexagonal)***

Metals with ***s*** and ***p*** valence electrons are ***simple metals.***

Transition metals and rare earth metals may use ***d*** and ***f*** electrons for bonding.

# Metals vs non-metals

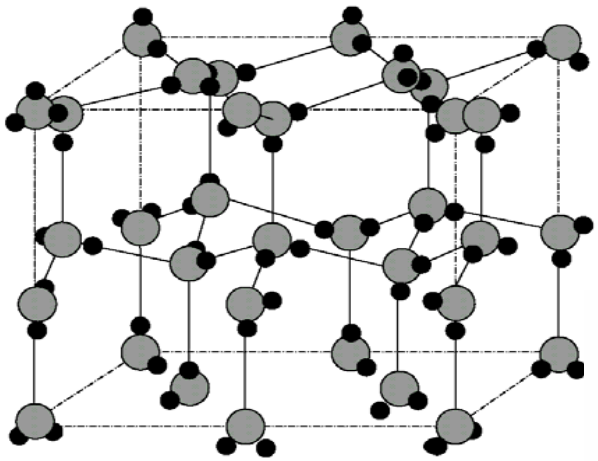
*There are very few very typical metals and non-metals*



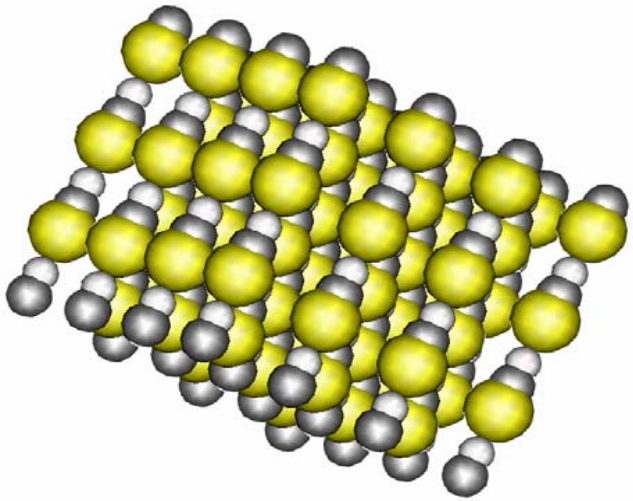
# *Hydrogen bonding*

***Each oxygen atom in ice is bonded by strong O–H $\sigma$ bonds with the two H atoms in the $H_2O$ molecule and by weaker H···O hydrogen bonds to two H atoms in neighboring $H_2O$ molecules.***

***The strengths of the two bonds in O–H···O bonding units are quite different,with the much stronger O–H bond having an energy E (O–H) ≈4.8 eV,while the much weaker H···O hydrogen bond has an energy E(H···O) of only about 0.4 eV.***



***Crystalline HCN***



***Crystal structure of ice (solid $H_2O$) illustrating hydrogen bonding and showing the disorder in the positions of the protons (H atoms).***

# *van der Waals bonding*

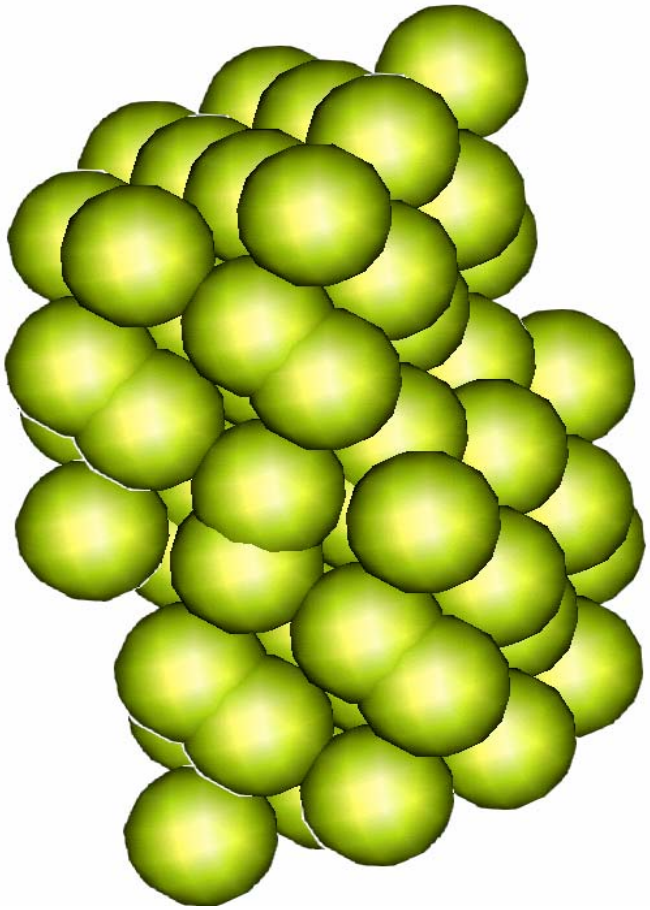
1. ***Decays as $1/r^6$***
2. ***Important in non-polar molecular solids and in noble gases.***

**van der Waals Radii**

**$r_{vdW}$ for Selected Atoms**

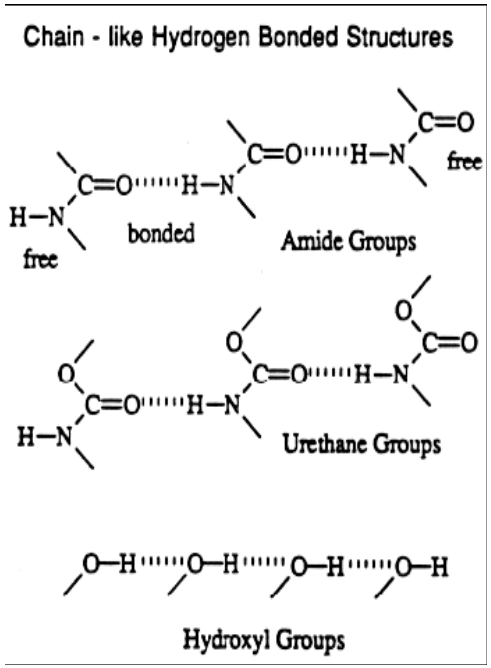
| Atom | $r_{vdW}$ (nm) |
|---|---|
| H | 0.12 |
| N | 0.15 |
| O | 0.14 |
| F | 0.135 |
| Ne | 0.158 |
| P | 0.19 |
| S | 0.185 |
| Cl | 0.18 |
| Ar | 0.188 |
| As | 0.20 |
| Se | 0.20 |
| Br | 0.195 |
| Kr | 0.205 |
| Sb | 0.22 |
| Te | 0.22 |
| I | 0.215 |
| Xe | 0.225 |

***Crystalline $Cl_2$***

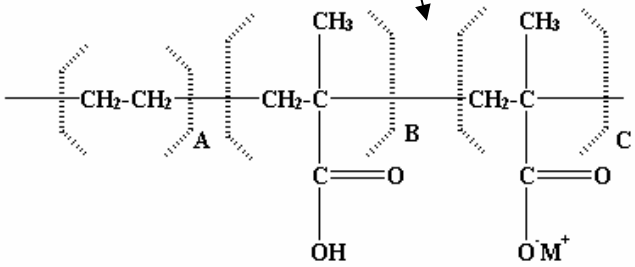


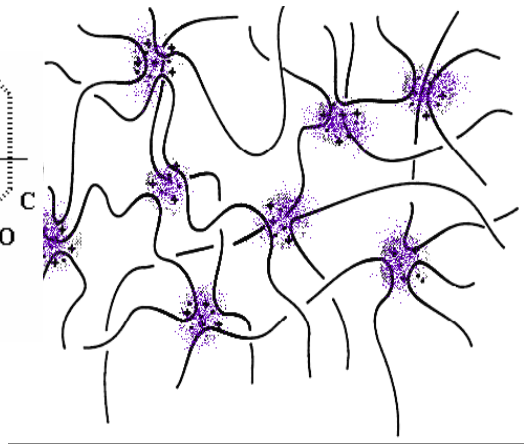
# *Supramolecular (polymer) bonding*

1. • Hydrocarbons (PE, IPP, PS, etc.) weak Dispersion Forces (Van-der-Vaals)
2. • Polar Polymers -- PVC, PAN, etc. ( Those Containing Heteroatoms (O, N, Cl, F) Dipole/dipole Interactions (Hydrogen Bonding Polymers: Nylons,–
3. Ionomers (polymers with fully ionized groups, Surlyn)




| Type of Interaction | Characteristics | Approximate Strength |
|---|---|---|
| Dispersion Forces | Short Range Varies as $1/r^6$ | ~0.2 to 2 kcal./mole |
| Dipole / dipole (Freely Rotating) | | |
| Strong Polar Forces & Hydrogen Bonds | Complex Form, but Short Range | ~ 1 to 10 kcal. / mole |
| Coulombic, as Found in Ionomers | Long Range, Varies 1/r | ~ 10 to 20 kcal/ mole (?) |



***Clusters in an Ionomer.***

# *Conclusions*

| Bond | Strength | Directionality | Localization |
|---|---|---|---|
| Ionic | + | - | + |
| Covalent | + | + | + |
| Metallic | + | - | - |
| Van der Waals | - | no | N/A |
| Hydrogen | - | yes | N/A |

1. ***In molecules bonding is predominantly covalent.***
2. ***The final structure of solid is affected by strength, localization and directionality of bonds.***
3. ***Bonds in extended atomic solids form bands=molecular orbitals that belong to the solid as a whole.***
4. ***In extended atomic solids atoms may exhibit valences that do not appear in molecules.***

# Hydrogen: $H1s^1$

***Abundance:*** Third most abundant in the earth crust 15.4% (after O and Si).
Primary natural compound: water.

**Average atomic weight: H: 1.0078**

**Stable isotopes H:1.0078** ; **D:2.0141** ;

**Unstable isotope T:3.0160 (half decay time 12.33 years).**

**Physical properties:** colorless odorless gas, almost 15 times lighter than air

Temperatures

Melting point: 14.01 K

Boiling point: 20.28 K

Critical temperature: 33 K

**Electronegativity: Pauling:2.20**

**Sanderson: 2.59**

**Allred Rochow: 2.20**

1. **Electron affinity** of hydrogen 0.754 eV, similar to alkali metals:

Li:0.618 eV or Na:0.548 eV ( for comparison F:3.4eV, Br:3.36eV)

2. Hydrogen atom has a **high ionization** energy (1312 kJ/mol, 13.6 eV)

**(resembles the halogens: Cl-12.97 eV, Br-11.8 eV)**

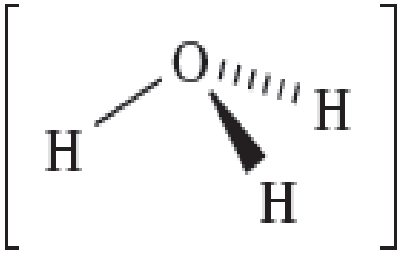
**hydrogen combines high ionization energy and low electron affinity.**

2. After ionization, the remaining radius of the proton is 0.0015 pm. Because of the high electric field **NO free proton can exist with any thermal energy**.

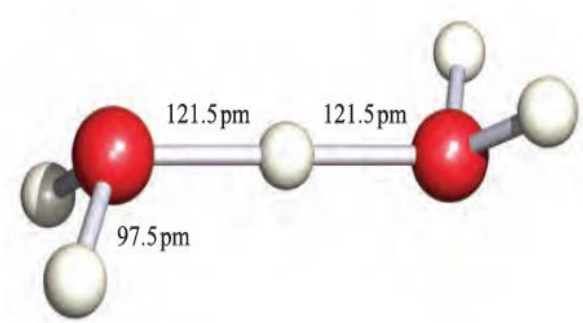
3. Once ionized hydrogen atom **always** forms bound species: $H_3O^+$ or $NH_4^+$.

The hydrated proton (oxonium) ion $H_3O^+$ is a well-defined specie which has been crystallographically characterized in various hydrated salts.

There is a whole family of hydrated protons $[H(H_2O)_n]^+$ (n = 1 to 20)



For instance in mineral alunite
$KAl_3(SO_4)_2(OH)_6$
(or) $KAl(SO_4)_2 \bullet Al_2O_3 \bullet 3H_2O$=
(or) $KAl(SO_4)_2 \bullet Al_2(H_3O)_2O_4$




In many cases the crystal-hydrates water is present as $H_3O^+$ and $O^{2-}$

The structure of $H_5O_2^+$ ion in $[V(H_2O)_6]\ H_5O_2^+\ (CF_3SO_3)_4$

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Oxonium is a relatively strong oxidizer. Therefore, all metals except the noble and semi-noble metals (remember the definition!?) react with acids.

$$Zn + 2H_3O^+ \leftrightarrow H_2 \uparrow + Zn^{2+} + H_2O$$

Laboratory way to make $H_2$

1. The rate of reaction between metals and oxonium may be **VERY** low and thermodynamically unstable metals, may be practically stable
2. The dissolution rate of metals in acids strongly depends on anions

## ✡Practical notes

**Examples of the non-noble metals that are stable in air but rapidly reacting with oxonium ( for isntance oxidized by $H^+$ of diluted HCl):**

**Mg, Al, Y, Fe, Mn, Co, Cd (Ga, In …)**

**Metals are expected to react rapidly with oxonium but the reaction is extremely slow or requires concentrated hot acid:**
**Be, Cr, V, Mo, W (Bi, Hf, Pb…)**

**[Elements in brackets are called “metals” but they are not “truly” chemically metals. We will consider the definition later]**

# Reactivity

## Main tendencies:

## $1s^1 \rightarrow 1s^2$ (oxidizer) $1s^1 \rightarrow 1s^0$(reducer)

Pure substance forms: molecule $H_2$; free radical: $H^{\bullet}$

ionized species: $H^+$; $H^-$; $H_2^+$; $H_3^+$;…….

## H–H is a high energy bond (435.88 kJ/mol)

**1. At ambient conditions $H_2$ is a very stable molecule.**
**THERMAL DISSOCIATION OF $H_2$ is VERY SMALL**
**(0.09% at 2000 K; 1.3% at 2500 K);**

**2. All reaction with $H_2$ <u>require initiation</u>**

**application: atomic hydrogen torch ( how does it work?)**

Issues for self-education: ortho- and para-hydrogen.

# Hydrides of the elements

**(incomplete)**

$CoH_x$, $x = 0.19, 0.26, 0.337$

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LiH | $BeH_2$ | | | | | | | | | | | ~40 boranes $B_mH_n$ | Innumerable hydrocarbons $C_nH_n$ | $NH_3$ $N_2H_4$ $N_3H$ | $OH_2$ $O_2H_2$ | FH | Ne |
| NaH | $MgH_2$ | | | | | | | | | | | $AlH_3$ | $Si_mH_{2m+2}$ $m = 1-8(+)$ etc. | $P_mH_{m+2}$ $m = 1-9$ etc. | $S_nH_2$ $n = 1-8(+)$ | ClH | Ar |
| KH | $CaH_2$ | $ScH_2$ | $TiH_2$ | VH $VH_2$ | CrH | $MnH_{0.07}$ Mn MnH | Fe FeH | Co | (NiH) | CuH | $ZnH_2$ | $GaH_3$ | $Ge_mH_{2m+2}$ $m = 1-5(+)$ | $AsH_3$ | $SeH_2$ | BrH | Kr |
| RbH | $SrH_2$ | $YH_2$ $YH_3$ | $ZrH_2$ | NbH $NbH_2$ | Mo MoH | Tc | Ru | Rh RhH | $PdH_{<1}$ | Ag | $(CdH_2)$ ? | $(InH_3)$ ? | $SnH_4$ $Sn_2H_6$ | $SbH_3$ | $TeH_2$ | IH | Xe |
| CsH | $BaH_2$ | $LaH_2$ $LaH_3$ | $HfH_2$ | TaH | W | Re | Os | Ir | Pt | Au | $(HgH_2)$ ? | $(TlH_3)$ ? | $PbH_4$ | $BiH_3$ | $(PoH_2)$ ? | AtH | Rn |
| Fr | Ra | $AcH_2$ | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CeH_2$ $CeH_3$ | $PrH_2$ $PrH_3$ | $NdH_2$ $NdH_3$ | Pm | $SmH_2$ $SmH_3$ | $EuH_2$ | $GdH_2$ $GdH_3$ | $TbH_2$ $TbH_3$ | $DyH_2$ $DyH_3$ | $HoH_2$ $HoH_3$ | $ErH_2$ $ErH_3$ | $TmH_2$ $TmH_3$ | $YbH_2$ $YbH_{2.5}$ | $LuH_2$ $LuH_3$ |
| $ThH_2$ $TH_4H_{15}$ | $PaH_3$ | $UH_3$ | $NpH_2$ $NpH_3$ | $PuH_2$ $PuH_3$ | $AmH_2$ $AmH_3$ | $CmH_2$ | Bk | Cf | Es | Fm | Md | No | Lr |

# Hydrogen +non-metals=molecular solids

| | Hydride formulae and names | Normal boiling point (° C) | E-H bond enthalpy (kJ $mol^{-1}$) | $\Delta G_f^{\ominus}$ (kJ $mol^{-1}$ at 298 K) |
|---|---|---|---|---|
| B | $B_2H_6$ diborane | −93 | – | +87 |
| C | $CH_4$ methane | −162 | 413 | −51 |
| | $C_2H_6$ ethane | −89 | – | −33 |
| | $C_2H_4$ ethene | −104 | – | +68 |
| Si | $SiH_4$ silane | −112 | 318 | +57 |
| | $Si_2H_6$ disilane | −14 | – | +127 |
| Ge | $GeH_4$ germane | −88 | 285 | +113 |
| N | $NH_3$ ammonia *(azane)*[a] | −33 | 391 | −17 |
| | $N_2H_4$ hydrazine *(diazane)*[a] | 113 | – | +149 |
| | $HN_3$ hydrogen azide | *36*[b] | – | +327 |
| P | $PH_3$ phosphine *(phosphane)*[a] | −88 | 321 | +13 |
| | $P_2H_4$ diphosphane | *64*[b] | – | – |
| As | $AsH_3$ arsine *(arsane)*[a] | −55 | 296 | 69 |
| O | $H_2O$ water *(oxidane)*[a] | 100 | 464 | −237 |
| | $H_2O_2$ hydrogen peroxide *(dioxidane)*[a] | 152 | – | −120 |
| S | $H_2S$ hydrogen sulfide *(sulfane)*[a] | −60 | 364 | −34 |
| | $H_2S_2$ disulfane | *70*[b] | – | – |
| Se | $H_2Se$ hydrogen selenide *(selane)*[a] | −42 | 313 | +16 |
| F | HF hydrogen fluoride | 19 | 568 | −297 |

| | | | | |
|---|---|---|---|---|
| Cl | HCl hydrogen chloride | −85 | 432 | −95 |
| Br | HBr hydrogen bromine | −68 | 366 | −53 |
| I | HI hydrogen iodide | −35 | 289 | +2 |

**1. With the exception of the boranes hydrogen always forms a single covalent bond.**

**2. Formation of hydrogen compounds with B, Si, Ge, As, Se and I is thermodynamically unfavorable.**

# Hydrogen reacts with $O_2$, $F_2$ and $Cl_2$ with explosion by a free radical mechanism

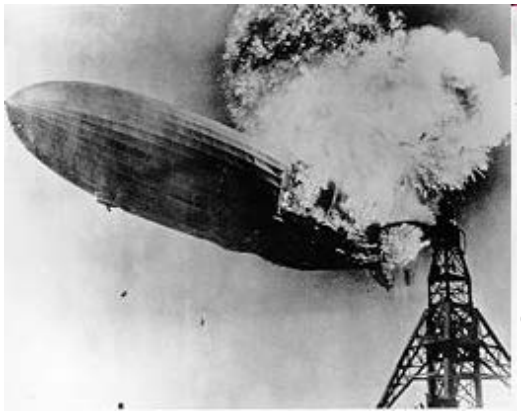
$H_2 \rightarrow 2H^{\bullet}$ *initiation*

$H_2 + O_2 \rightarrow 2OH^{\bullet}$ *initiation*

$H^{\bullet} + O_2 \rightarrow OH^{\bullet} + {}^{\bullet}O^{\bullet}$ *branching*

${}^{\bullet}O^{\bullet} + H_2 \rightarrow OH^{\bullet} + H^{\bullet}$ *branching*

$OH^{\bullet} + H_2 \rightarrow H_2O + H^{\bullet}$ *propagation*



$H_2 + X_2 \rightarrow 2HX \qquad X = F, Cl, Br, I$

$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$

Reaction with $Br_2$ or $I_2$ occur only at higher temperatures >300 °C

**Reaction with nitrogen is very slow requires high pressure (>100 at) and temperature (>300 °C)**

$$3H_2 + N_2 \leftrightarrow 2NH_3$$

**Haber-Bosh cycle (reaction)**

**If the formation of a non-metal – hydrogen compound is thermodynamically unfavorable, one can prepare it from binary compounds**

$$P_2Zn_3 + 6H_2O \rightarrow 2PH_3\uparrow + 3Zn(OH)_2$$

**Same for As**

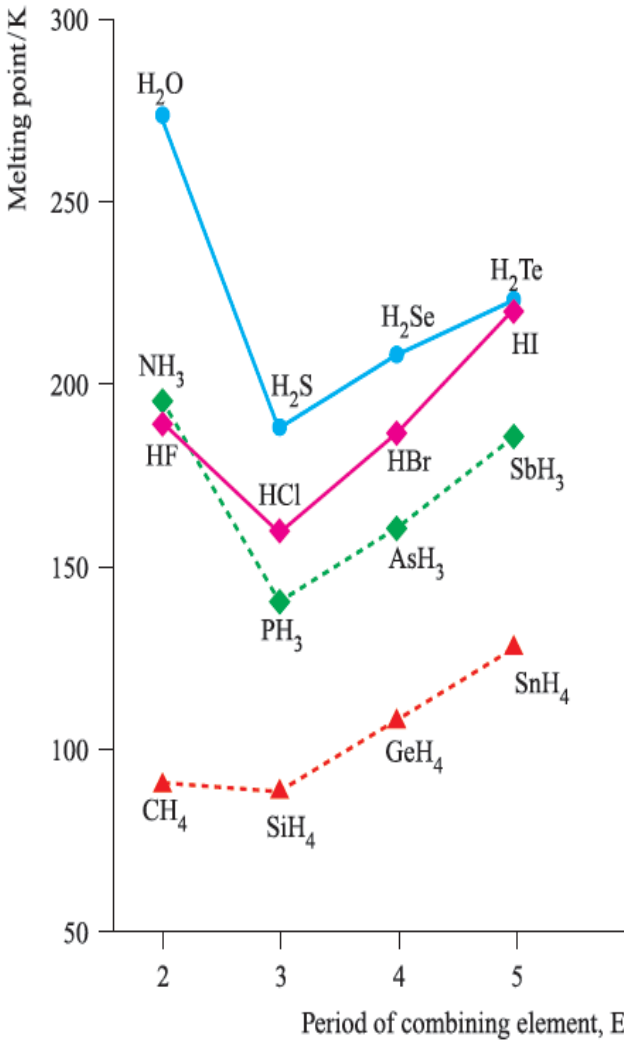
$$SiMg_2 + 4H_2O \rightarrow SiH_4\uparrow + 2Mg(OH)_2$$

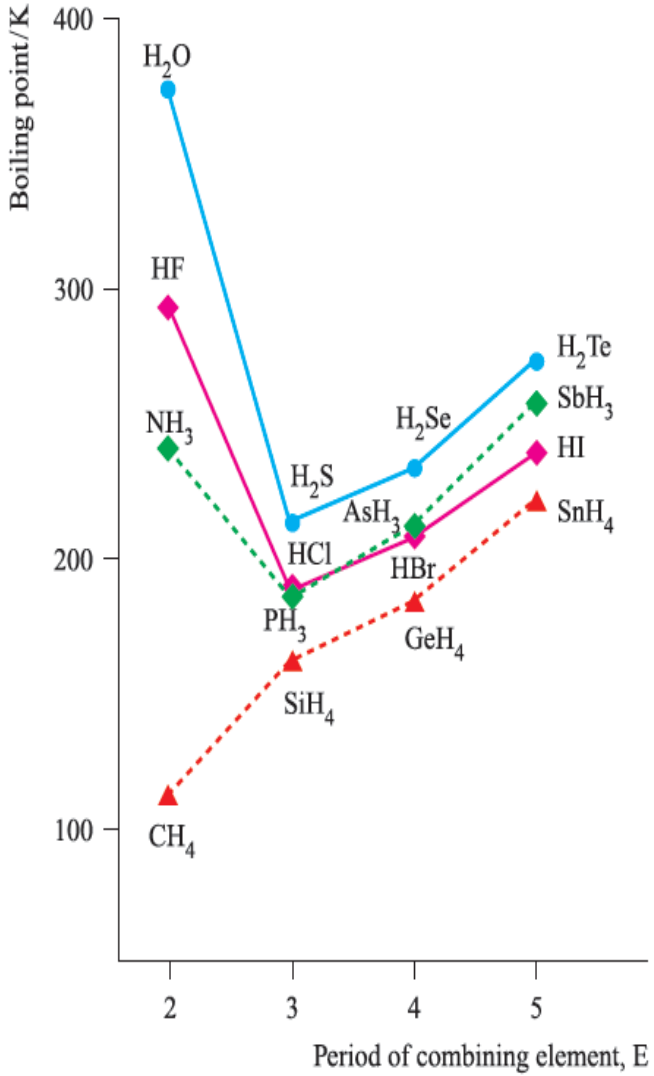
**Same for Ge**

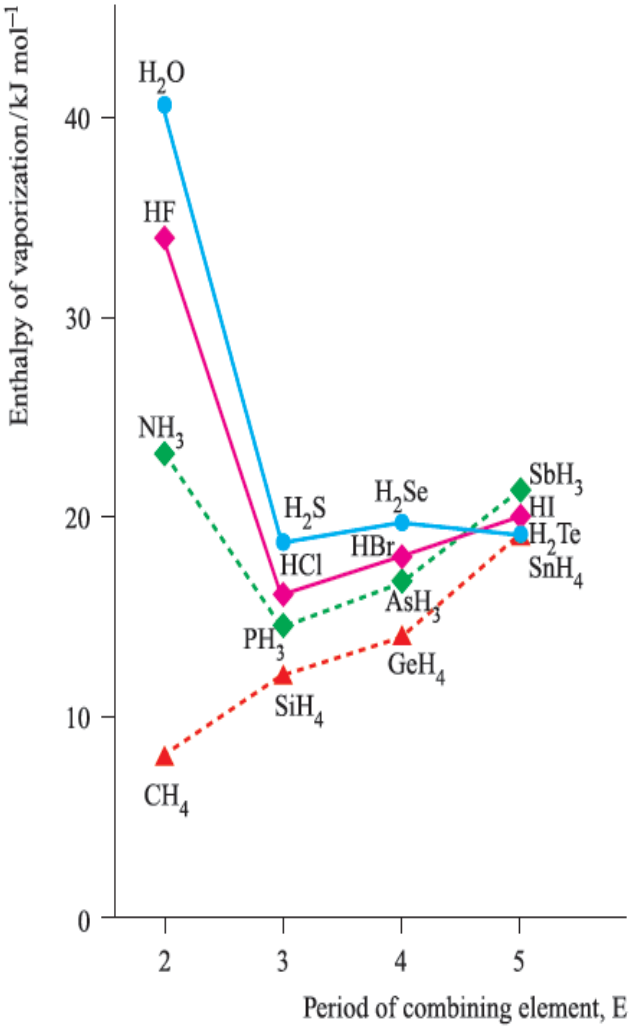
**$PH_3$ and $AsH_3$ are highly toxic and flammable.**

**$SiH_4$ and $GeH_4$ ignites spontaneously if mixed with air or oxygen.**

## All non-metal – hydrogen molecules have a tendency to form hydrogen bonds



# Enthalpies of dissociation of different types of hydrogen bonds

| Category of hydrogen bond | Hydrogen bond (····) | Dissociation enthalpy / kJ mol$^{-1}$ |
|---|---|---|
| Symmetrical | F····H····F in $[HF_2]^-$ | 163 |
| Symmetrical | O····H····O in $[H_5O_2]^+$ | 138 |
| Symmetrical | N····H····N in $[N_2H_7]^+$ | 100 |
| Symmetrical | O····H····O in $[H_3O_2]^-$ | 96 |
| Asymmetrical | N–H····O in $[NH_4]^+$····$OH_2$ | 80 |
| Asymmetrical | O–H····Cl in $OH_2$····$Cl^-$ | 56 |
| Asymmetrical | O–H····O in $OH_2$····$OH_2$ | 20 |
| Asymmetrical | S–H····S in $SH_2$····$SH_2$ | 5 |
| Asymmetrical | C–H····O in HC≡CH····$OH_2$ | 9 |
| Asymmetrical | C–H····O in $CH_4$····$OH_2$ | 1 to 3 |

# Acidity of hydrogen-metal bonds: protic acids and bases

**Group 7: Strongly acidic; Acidity increases with increasing Z; HI>HBr>HCl>HF**

**Group 6: Weak acids; Acidity increases with increasing Z;**

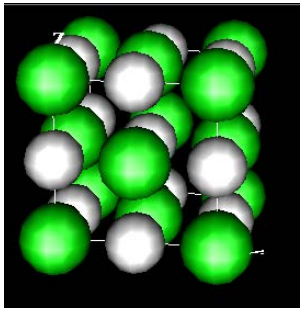
**Group 5: $NH_3$ is basic, the rest are neutral;**

| | p$K_1$ | p$K_2$ | $\Delta$p$K$ |
|---|---|---|---|
| $H_2S$ | 7 | 14 | 7 |
| $H_2Se$ | 4 | 12 | 8 |
| $H_2Te$ | 3 | 11 | 8 |

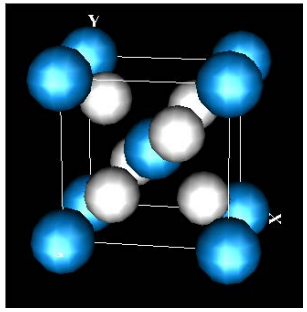
# Hydrogen +metals

**1. Highly electropositive metals (Alkali, alkali earth) react directly and form solid hydrides: LiH, $CaH_2$, $MgH_2$, including mixed hydrides. These are salt-like compounds in which hydrogen has a formal oxidation state -1.**

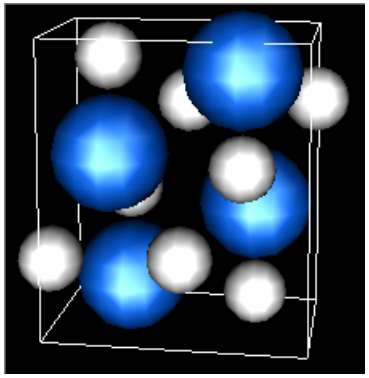
**Formal ionic radius is VERY large $H^-$ 208 pm ( oxygen $O^{2-}$ 140 pm, $S^{2-}$ 184 pm)**



**LiH rock salt structure (same NaH, KH, RbH, CsH,)**



**$MgH_2$ rutile ($TiO_2$) structure**



**$CaH_2$, $SrH_2$, $BaH_2$**

**Formation enthalpy**

| Metal | $\Delta_f H^\circ(MH)$ / kJ mol$^{-1}$ |
|---|---|
| Li | −90.5 |
| Na | −56.3 |
| K | −57.7 |
| Rb | −52.3 |
| Cs | −54.2 |

**Molten salt-like hydrides are IONIC liquids. Famous example: *electrolysis of molten LiH***

$$2H^- \rightarrow H_2 + 2e^- \qquad \textit{at the anode}$$

$$Li^+ + e^- \rightarrow Li \qquad \textit{at the cathode}$$

# All hydrides of alkali and alkali earth metals disproportionate in contact with protic solvent

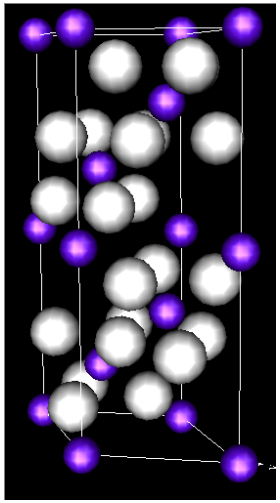
$$CaH_2 + H_2O \rightarrow Ca(OH)_2 + H_2 \uparrow$$

$$NaH + NH_3 \rightarrow NaNH_2 + H_2 \uparrow$$

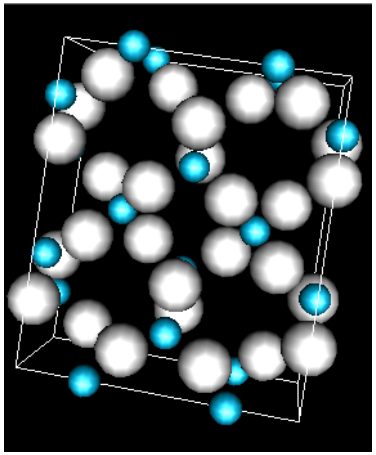
$$NaH + EtOH \rightarrow EtONa + H_2 \uparrow$$

**Many metals form more than one hydride and lose hydrogen upon heating. Thermal stability of salt-like hydrides decreases with increasing radius (Li to Cs). 10 mm of Hg pressures are: LiH 550 $^oC$, NaH and KH 210 $^oC$, RbH and CsH 170 $^oC$, $CaH_2$ 885 $^oC$, $SrH_2$ 585 $^oC$, $BaH_2$ 230 $^oC$. However, $MgH_2$ only 85 $^oC$ ( WHY????)**

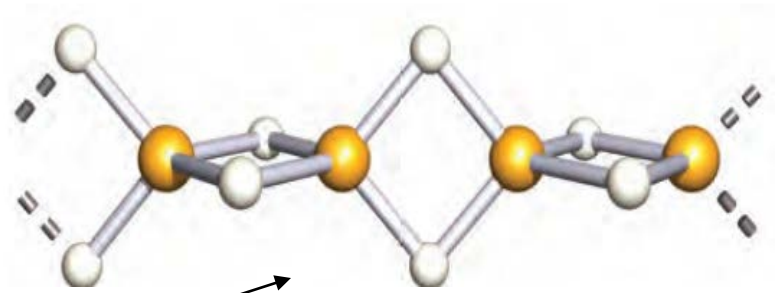
# $AlH_3$ and $BeH_2$ are polymeric hydrides



$AlH_3$



$BeH_2$

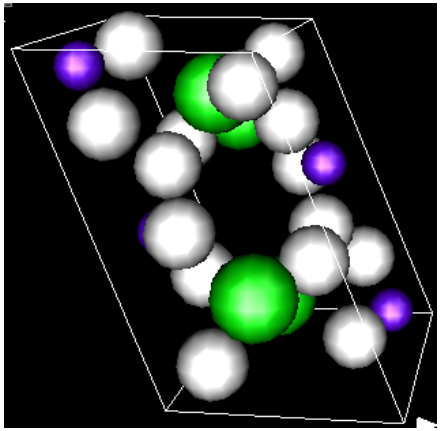


# Complex ionic hydrides formed by $s^2p^1$ –Al and B

$$4NaH + B(OMe)_3 \xrightarrow{520\ K} Na[BH_4] + 3NaOMe$$

$$4NaH + BCl_3 \longrightarrow Na[BH_4] + 3NaCl$$

Used as reducing agents

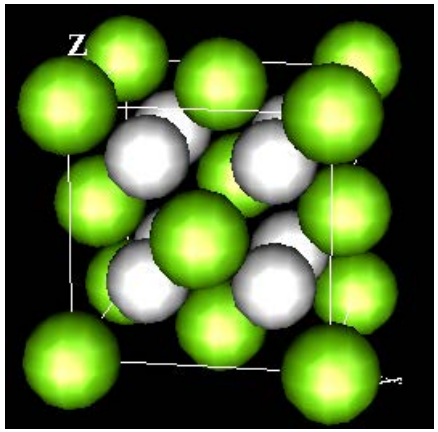


$LiAlH_4$

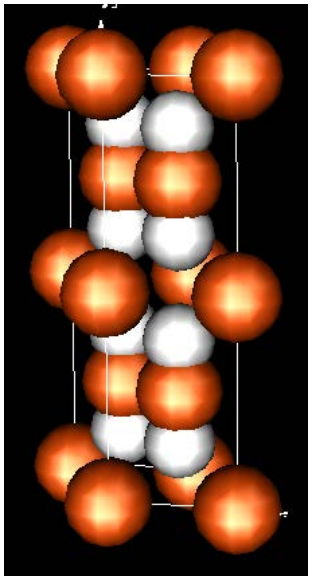
# Hydrogen +metals

**2. Most (but not all) *d*- and *f*- metals form metallic-like hydrides with variable composition (like $TaH_{0.5-2}$) . Hydrogen dissolves in them occupying the interstitial in the lattice**

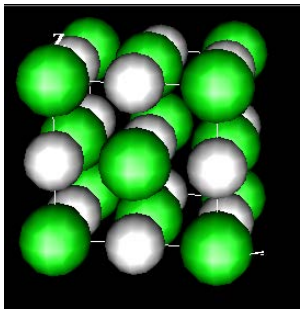
**$TiH_2$ (fluorite structure)**



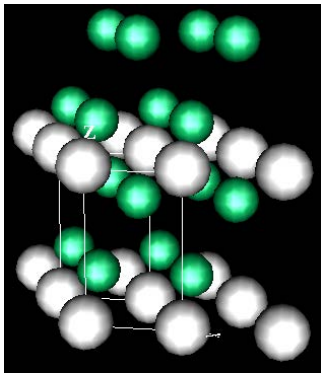
**FeH**



**NiH ($NiH_{0.6}$)**



**$Ni_2H$**



**NiH is used in NiMH batteries**

**MOST practically important metals are unstable with respect to elementary hydrogen**

**Au and Ag DO not form hydrides ( there are only unconfirmed reports)**

**Most metals of main groups form unstable covalent hydrides like $SnH_4$**

**Note: $Ga_2H_6$ does not exist, though mentioned in some sources.**

# Hydrogen +metals special cases 1.

**There are a number of noble metals (Pt, Pd) and $d^{8\text{-}10}$ elements (Ni, Fe) react with hydrogen at room temperature with elementary hydrogen at room temperature very fast. They form high-hydrogen content hydrides that have metallic character. Dissolved hydrogen causes metals to swell and become VERY brittle (hydrogen embrittlement)**

Application Nickel–metal hydride batteries

$$\textit{Anode}: \quad Ni(OH)_2 + [OH]^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} NiO(OH) + H_2O + e^-$$

$$\textit{Cathode}: \quad M + H_2O + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} MH + [OH]^-$$

$$\textit{Overall}: \quad Ni(OH)_2 + M \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} NiO(OH) + MH$$

# Hydrogen +metals special cases 2.

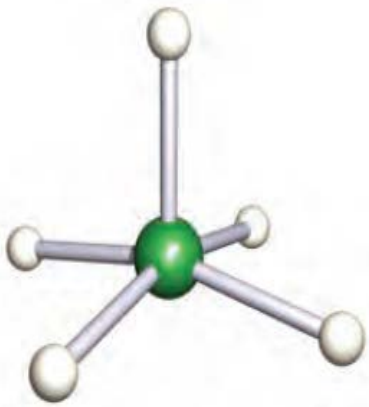
**Hydrogen reduces many metal oxides (even those that dissolves in acids!)**

$$CuO + H_2 \xrightarrow{200\ ^oC} Cu + H_2O \uparrow$$

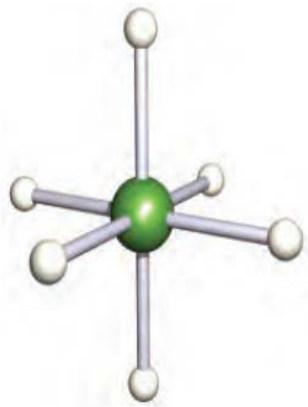
$$PbO + H_2 \xrightarrow{200\ ^oC} Pb + H_2O \uparrow$$

# Special cases: molecular complexes of d-metals

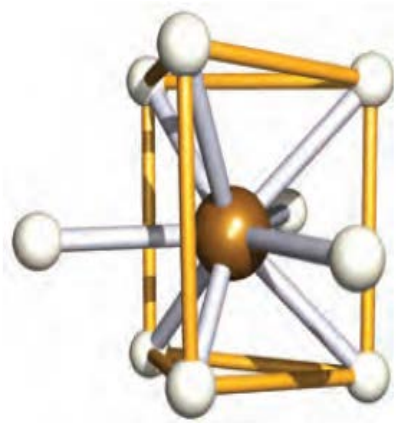
**Hydrogen may form MOLECULAR complexes with many d-metals. In this complexes, often, there is a bond H-H. Such structures can be viewed as "molecular hydrogen complexes":** $K_2ReH_9$, $Li_4RuH_6$, $Na_3RhH_6$, $Mg_2RuH_4$, $Na_3OsH_7$ and $Ba_2PtH_6$.



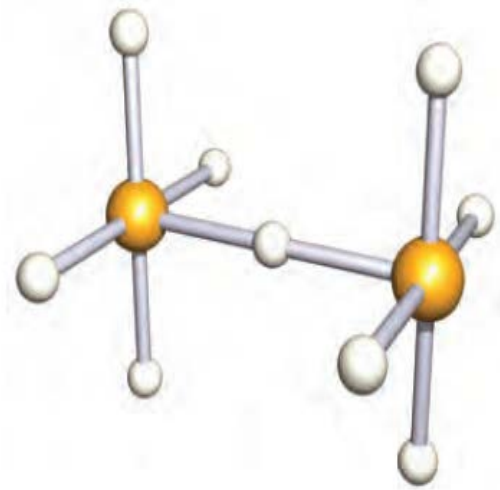
$[CoH_5]^{4-}$



$[FeH_6]^{4-}$



$[ReH_9]^{2-}$



$[PtH_9]^{5-}$

# Important chemical reactions

**Laboratory methods: Metal+acid OR Amphoteric methal+base**

$$Zn(s) + H_2SO_4(aq) \leftrightarrow H_2(g) + ZnSO_4(aq)$$

$$Al(s) + NaOH(aq) + 6H2O \rightarrow 3H_2(g) + 2Na[Al(OH)_4](aq)$$

$$Ca(s) + 2H_2O \rightarrow Ca(OH)_2 + H_2(g)$$

**Industrial production:**

**1. Water-shift reaction**

$$C(s) + 2H_2O \xrightarrow{>400\ ^oC} CO + 2H_2$$

**Syngas**

**2. Methane reforming**

$$CH_4 + H_2O \xrightarrow{1200\ K,\ Ni\ catalyst} CO + 3H_2$$

**3. Syngas shift**

$$CO + H_2O \xrightarrow{700\ K,\ iron\ oxide\ catalyst} CO_2 + H_2$$

## Main industrial use: methanol production

$$CO + 2H_2 \xrightarrow[\approx 550\ K,\ 50\ bar]{Cu/ZnO\ catalyst} CH_3OH$$

**Hydrogen can reduce many metals oxides at elevated temperatures, even those that can be oxidized by oxonium in aqueous solutions.**

$$CuO + H_2 \rightarrow Cu + H_2O$$

## ✡Interesting notes

Liquid hydrogen has a density of 0.07 gm/cm$^3$ , solid hydrogen 0.08 gm/cm$^3$

Equilibrium distance between H atoms in a molecule is 0.741 A, however, the average distance is 0.751 A. ( THINK WHY?????)

Hydrogen passes easily though almost all metals upon moderate heating (>200 C)

Some molten metals may dissolve considerable amounts of hydrogen in MOLTEN state

Orientation of hydrogen bonds in many organic and inorganic crystals ( for instance $KH_2PO_4$, $KH_2AsO_4$ , , $RbH_2PO_4$ results in dielectric anomalies (called spontaneous polarization or ferroelectricity).

# Summary

1. Hydrogen forms molecular products with non-metals. This products can be acidic, basic or neutral

2. Molecular hydrogen reacts with most metals forming hydrides

3. Molecular hydrogen is a moderately strong reducer, except with respect to alkali and alkali earth metals

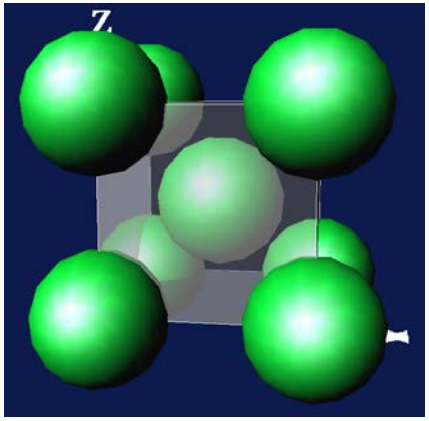
# Alkali metals [noble gas]($s^1$):Li, Na, K, Rb, Cs

***Abundance:*** **Na-2.0%; K-1.1%; Rb(0.004%)>Li (0.02%)>Cs(0.00009%);**

**Minerals:** rock salt NaCl; sylvite KCl; sylvinite KCl/NaCl; carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$;
Spodumene: $LiAlSi_2O_6$; petalite $LiAlSi_4O_{10}$; amblygonite $LiAl(F,OH)PO)_4$;
Rb no minerals; impurity in K-containing minerals; pollucite $2Cs_2O.2Al_2O_3.9SiO_2.H_2O$

| Property | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Atomic number, $Z$ | 3 | 11 | 19 | 37 | 55 |
| Ground state electronic configuration | [He]$2s^1$ | [Ne]$3s^1$ | [Ar]$4s^1$ | [Kr]$5s^1$ | [Xe]$6s^1$ |
| Enthalpy of atomization, $\Delta_a H^o(298\,K)/kJ\,mol^{-1}$ | 161 | 108 | 90 | 82 | 78 |
| Dissociation enthalpy of M–M bond in $M_2$ (298 K) / kJ mol$^{-1}$ | 110 | 74 | 55 | 49 | 44 |
| Melting point, mp / K | 453.5 | 371 | 336 | 312 | 301.5 |
| Boiling point, bp / K | 1615 | 1156 | 1032 | 959 | 942 |
| Standard enthalpy of fusion, $\Delta_{fus} H^o(mp)/kJ\,mol^{-1}$ | 3.0 | 2.6 | 2.3 | 2.2 | 2.1 |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 520.2 | 495.8 | 418.8 | 403.0 | 375.7 |
| Second ionization energy, $IE_2$ / kJ mol$^{-1}$ | 7298 | 4562 | 3052 | 2633 | 2234 |
| Metallic radius, $r_{metal}$ / pm‡ | 152 | 186 | 227 | 248 | 265 |
| Ionic radius, $r_{ion}$ / pm* | 76 | 102 | 138 | 149 | 170 |
| Standard enthalpy of hydration of $M^+$, $\Delta_{hyd} H^o(298\,K)/kJ\,mol^{-1}$ | −519 | −404 | −321 | −296 | −271 |
| Standard entropy of hydration of $M^+$, $\Delta_{hyd} S^o(298\,K)/J\,K^{-1}\,mol^{-1}$ | −140 | −110 | −70 | −70 | −60 |
| Standard Gibbs energy of hydration of $M^+$, $\Delta_{hyd} G^o(298\,K)/kJ\,mol^{-1}$ | −477 | −371 | −300 | −275 | −253 |
| Standard reduction potential, $E^o_{M^+/M}$ / V | −3.04 | −2.71 | −2.93 | −2.98 | −3.03 |
| NMR active nuclei (% abundance, nuclear spin) | $^6$Li (7.5, $I=1$); $^7$Li (92.5, $I=\frac{3}{2}$) | $^{23}$Na (100, $I=\frac{3}{2}$) | $^{39}$K (93.3, $I=\frac{3}{2}$); $^{41}$K (6.7, $I=\frac{3}{2}$) | $^{85}$Rb (72.2, $I=\frac{5}{2}$); $^{87}$Rb (27.8, $I=\frac{3}{2}$) | $^{133}$Cs (100, $I=\frac{7}{2}$) |

All pure alkali metals
Have BCC structure




**Li, Na, K Rb silvery-white**

**Cs is golden -yellow**

**➔Li, Na, K float in water**

# The factors defining the chemical properties

1. Low ionization energy => electron can be easily donated even to those species that do not usually accept electrons
2. Size effect: all alkali metals (except Li) form LARGE positive ions. Na is a intermediate case => stabilization of electrons at normally anti-bonding orbitals and unusual valence states of the elements

**Consequences:**

I. All alkali metals are very strong bases. They can force the species that do not usually behave as “acids” to behave as such.

II. Therefore, a specific property of alkali metals is ability to stabilize “unusual” valency states ( peroxides, ozonides etc).

III. Li, because of the small size, is less “basic”, but it is still as very strong base. Solubility and stability of Li salts is different from other alkali metals.

IV. Alkali metals do not form complexes and most of their salts are highly soluble

# Interesting facts about alkali metals

➔Li is the least "typical" both chemically and physically due to the small radius.
Li makes alloys only with Na above 380 $^{o}$C (molten) and completely immiscible with molten K, Rb and Cs

➔ All pairs (except Li and Na) of alkali metals are miscible with each other in all proportions

➔ The ternary alloy containing 12% Na, 47% K and 41% Cs has the lowest known m.p. -78 °C of any metallic system

➔ Li shows many similarities to Mg. This so-called "diagonal relationship" stems from the similarity in ionic size of the two elements: r(Li+) 76 pm, r(Mg2+) 72 pm, compared with r(Na+) 102 pm;

➔ Most Li compounds are far less soluble than the corresponding compounds of other alkali metals.

➔ Li salts of large, non-polarizable anions such as $ClO_4^-$ are much more soluble than those of the other alkali metals

➔ Most alkali metals are highly compressible;

relative volume at $10^5$ at

| Li | Na | K | Rb | Cs |
|---|---|---|---|---|
| 0,672 | 0,606 | 0,500 | 0,473 | 0,368 |

Cs under pressure transforms into FCC

➔ flame test colors: Li-crimson; Na-yellow; K-lilac; Rb-red-violet; Cs-blue)

➔Vapors of alkali metals are MONOATOMIC ($Me_2$ molecule exist but comprise only few %)

➔ All alkali metals form amalgams (soluble in mercury)

# Alkali metals are strong reducers

**1. Alkali metals burn in halogens (in F, Cl-spontaneously):**

**$2Me+X_2 \rightarrow 2MeX$; X=F,Cl,Br,I; the salts are ionic (>85%)**

| M | $\Delta_f H^o(MX)$ / kJ mol$^{-1}$ | | | | $\Delta_{lattice} H^o(MX)$ / kJ mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Halide ion size increases → | | | | Halide ion size increases → | | | |
| | F | Cl | Br | I | F | Cl | Br | I |
| Li | −616 | −409 | −351 | −270 | −1030 | −834 | −788 | −730 |
| Na | −577 | −411 | −361 | −288 | −910 | −769 | −732 | −682 |
| K | −567 | −436 | −394 | −328 | −808 | −701 | −671 | −632 |
| Rb | −558 | −435 | −395 | −334 | −774 | −680 | −651 | −617 |
| Cs | −553 | −443 | −406 | −347 | −744 | −657 | −632 | −600 |

Metal ion size increases ↓

→ **MOST salts of alkali metals are soluble, with few exceptions (like LiF or $Na[Sb(OH)_6]$).**

→ **K, Rb and Cs salts with large anions $ClO_4^-$, $ReO_4^-$, $BF_4^{2-}$, $SiF_6^{2-}$, $ZrF_6^{2-}$, $TiF_6^{2-}$ are poorly soluble (<1g/l); Solubility quickly increases with temperature.**

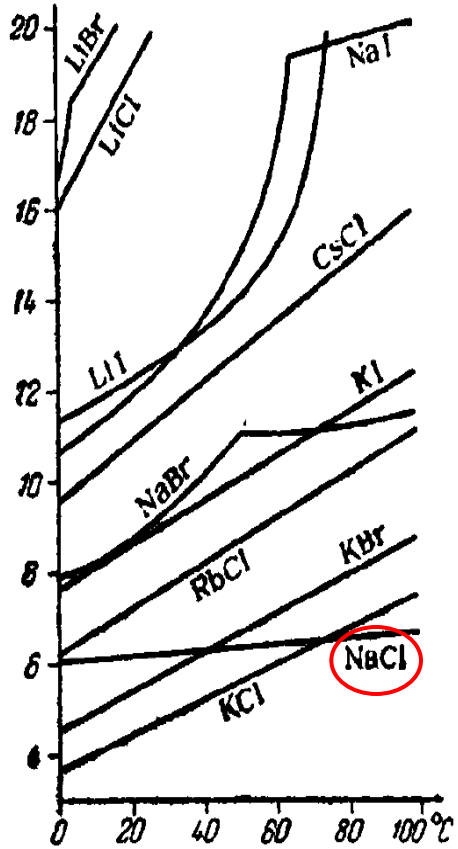
→ **Li salts of these anions are relatively well soluble.**

## In dilute solutions, alkali metal ions rarely form complexes

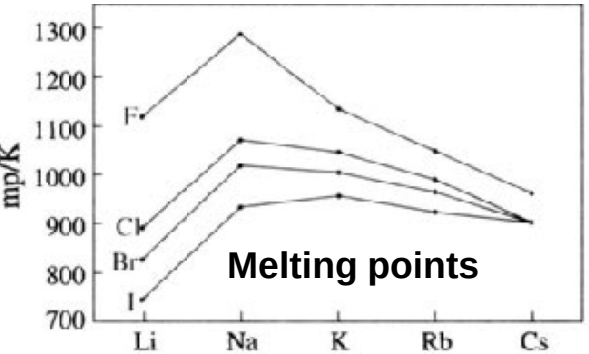
**Some complexes are formed with $[P_2O_7]^{4-}$ and $[EDTA]^{4-}$ and some other organic ligands, mostly with polyvalent**

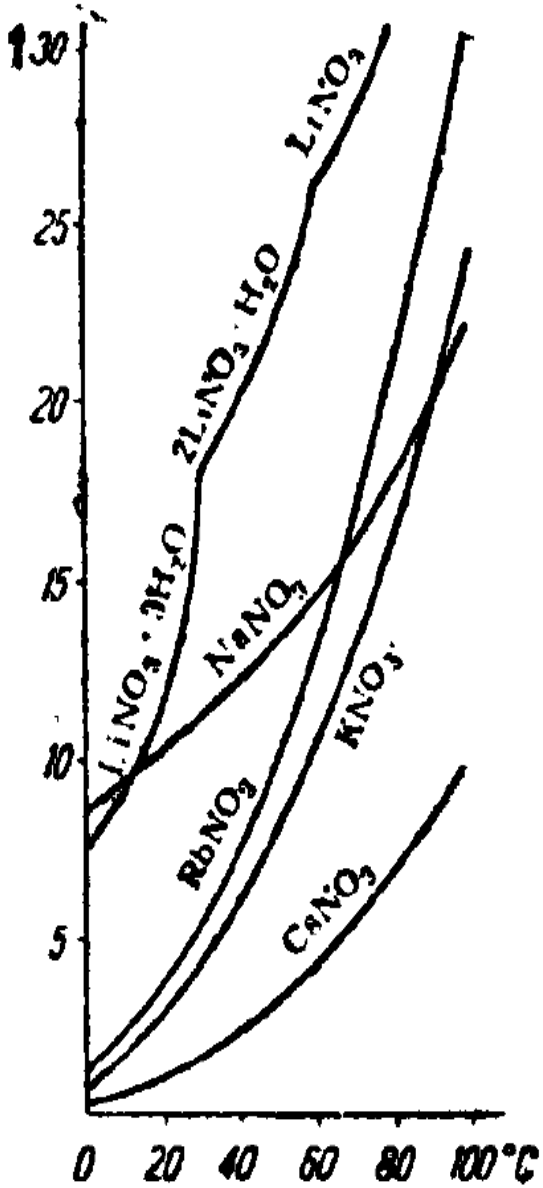
**Complex stability always DECREASES from $Li^+$ to $Cs^+$.**

# Solubility of the alkali halides, nitrates and sulfates

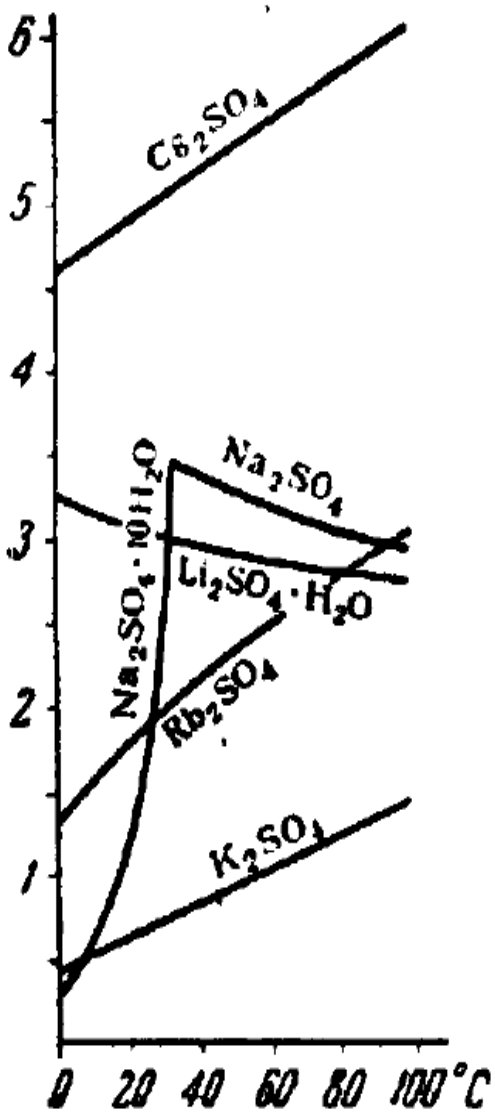



Solubility in mol/l




Solubility in mol/l




Solubility in mol/l

# Alkali metals + water and other protic solvents

**1. All alkali metals react with water producing hydroxide and hydrogen**

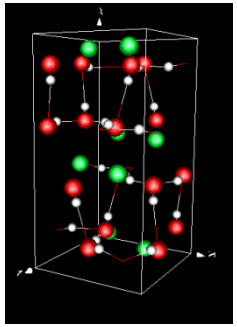
$$2Me+2H_2O \rightarrow H_2(g)+2MeOH;\ Me=Li, Na, K, Rb, Cs;$$

**2. The activity with respect to water quickly increases from Li to Cs ( the larger Z the more metallic the element is). Cs explodes on contact with water.**

**3. Solubility and alkalinity of the hydroxides increases from Li to Cs;**

**All the hydroxides are ionic crystals and fully dissociate in aqueous solutions**

**3. All alkali metals react with other protic solvents and species: $NH_3$, R-OH**



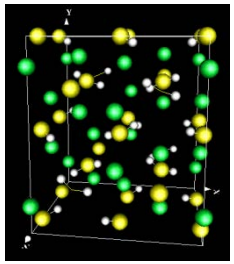
**NaOH**

$$2Na(s)+2NH_3 \rightarrow 2NaNH_2+H_2(g)$$

$$2K(s)+2CH_3CH_2OH \rightarrow 2CH_3CH_2OK+H_2(g)$$

$$CH\equiv CH(g)+2K(s) \xrightarrow{Liquid\ NH_3} K_2C_2(s)+H_2(g)$$

**$NaNH_2$ is an ionic compound with a fairly complicated structure with $NH_2^-$ anions**



**Li forms "neutral" salt $Li(NH_3)_4$ in which $NH_3$ formally accepts electron (see later IIa group). Another example: $Na(C_5H_5N)_2$**

# Interesting facts:

✡ At high temperatures (>500 ˚C) equilibrium reactions of the type

$$KCl + Na \leftrightarrow NaCl + K$$

Strongly depend on the VAPOR pressure. Since, K has higher vapor pressure than Na (WHY???), K is obtained from KCl by reducing it with Na and evaporating an alloy containing 45-95% of K ( the rest is Na).

✡Alkali metals may donate electrons to CO forming $(Me^{+})_2[OC{\equiv}CO]^{2-}$. The reaction takes place in liquid ammonia. However, potassium ( and ???) forms it according to the reaction: $K_2CO_3 + 2C \xrightarrow{300-500\ ^{o}C} K_2[C_2O_2] + CO(\text{or } CO_2)$ Note: in these compounds CO acts as an ELECTRON ACCEPTOR. All $(Me^{+})_2[OC{\equiv}CO]^{2-}$ have a tendency to explode

✡Cs is far stronger reducer than other alkali metals. It can

a) directly interact with $CO_2$ (if made into a thin film or powder in vacuum) producing Cs-COO-Cs;

b) attach to ethylene giving $Cs\text{-}CH_2\text{-}CH_2\text{-}Cs$;

c) Cs ( and upon heating Rb) DIRECTLY reacts with benzene giving $C_6H_5Cs$ (and what other product?).

# Alkali metals + oxygen

→ **There is a strong difference in the behavior of the alkali metals if combined with elementary oxygen. All react, but Li, Na and K react slowly with dry $O_2$. Rb and Cs must be stored in an inert atmosphere.**

→ $4Li + O_2 \longrightarrow 2Li_2O$ *oxide formation*

$2Na + O_2 \longrightarrow Na_2O_2$ *peroxide formation*

$K + O_2 \longrightarrow KO_2$ **(Cs & Rb)** *superoxide formation*

**(excess of oxygen)**

**In peroxide and <u>especially</u> super-oxide ions, some electrons are at the anti-bonding orbital stabilized by the presence of a large cation (K, Rb, Cs, Sr, Ba)**

$[\ddot{O}\cdots\ddot{O}]^{-}$ $O_2 + e \leftrightarrow [O \cong O]^{-} + 93 kJ/mole$

→**Upon heating, oxides uptake oxygen and transform to peroxides (not superoxides).**

→**Upon further heater, peroxides and superoxides decompose** $K_2O + O_2 \leftrightarrow K_2O_2$

→**Oxide, peroxide and superoxide can be prepared for all metals**

$Na_2O_2 + 2Na \longrightarrow 2Na_2O$

$NaOH + Na \longrightarrow Na_2O + \frac{1}{2}H_2$

$NaNO_2 + 3Na \longrightarrow 2Na_2O + \frac{1}{2}N_2$

$LiOH.H_2O + H_2O_2 \longrightarrow LiOOH.H_2O + H_2O$

$2LiOOH.H_2O \xrightarrow{heat} Li_2O_2 + H_2O_2 + 2H_2O$

✡**$LiO_2$ and $NaO_2$ exist, but difficult to prepare. They are far less stable than other super-oxides**

→ **The product of the interaction between alkali metals and oxygen is defined by the amount of available oxygen**

$$2Na + \frac{1}{2}O_2 \xrightarrow{heat} Na_2O \xrightarrow{\frac{1}{2}O_2} Na_2O_2$$

$$Na_2O_2 + O_2 \underset{spontaneous}{\overset{150\,atm\,O_2,\,400\,^oC}{\rightleftharpoons}} NaO_2$$

→ **Peroxides of alkali metals react with acids releasing $H_2O_2$.**

$$M_2O_2 + H_2SO_4 \longrightarrow M_2SO_4 + H_2O_2;$$

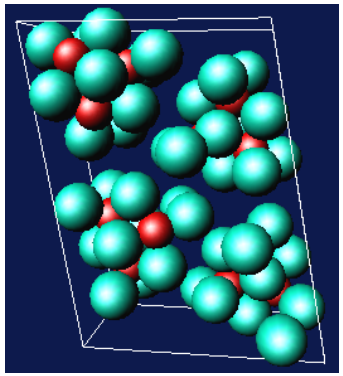
→ **$H_2O_2$ is less acidic than water; therefore, ALL peroxides undergo hydrolysis**

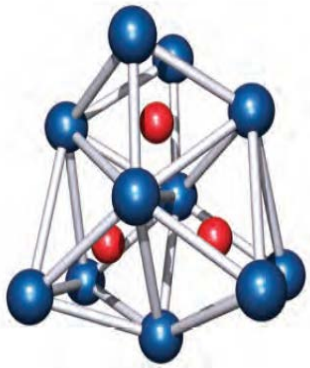
$$M_2O_2 + H_2O \longrightarrow 2MOH + H_2O_2$$

→ **ALL peroxides are strong oxidizers, components of many explosive mixtures**

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

→ **Cs and Rb form sub-oxides upon partial oxidation at low temperatures: $Rb_6O$, $Rb_9O_2$, $Cs_7O$, $Cs_{11}O_3$. Structures face-sharing octahedra of metal ions with the oxygen in the center**





$Cs_{11}O_3$

→ **All peroxides and superoxides react with $CO_2$ and release oxygen**

$$2KO_2 + CO_2 \leftrightarrow K_2CO_3 + 1\frac{1}{2}O_2$$

$$Na_2O_2 + CO_2 \leftrightarrow Na_2CO_3 + \frac{1}{2}O_2$$

→ **Equal molar mixture of $Na_2O_2$ and $KO_2$ replaces $CO_2$ mole per mole. This is the mixture used in $CO_2$ scrubbers and re-breathers.**

→**K, Rb and Cs form ozonides form peroxides and superoxides. More general way is MeOH+ozone and extraction by liquid $NH_3$. All ozonides are highly explosive.**

$$Cs_2O_2 + 2O_3 \leftrightarrow 2CsO_3 + 2O_2$$

$$3KOH\,(dry!) + 2O_3 \leftrightarrow 2KO_3 + KOH \cdot H_2O + \frac{1}{2}O_2$$

→**Ozonides contain linearly conjugated ion $O_3^-$ (to be considered later).**

**ALL ozonides decompose slowly:** $MO_3 \longrightarrow MO_2 + \frac{1}{2}O_2$

$$4MO_3 + 2H_2O \longrightarrow 4MOH + 5O_2$$

**Note about peroxides, super-oxides and ozonides:**

**<u>Large cations with small charge (1 or 2 ) STABILIZE anti-bonding orbital</u>**

➔Reaction of dry alkali peroxides with water releases A LOT OF HEAT (tens of kJ/mol). Solid peroxi-hydrates are formed $Na_2O_2 \bullet 8H_2O$;

✡In presence of $H_2O_2$ mixed peroxides-hydrates may form $Na_2O_2 \bullet 2H_2O_2 \bullet 4H_2O$;

✡ $NaO_2H$ (hydro-peroxides) can be prepared. They are less stable than peroxides(WHY?)

# Oxides and hydroxides

➔All oxides $Me_2O$ of alkali metals except Li react with water producing a lot o heat (>50 kJ/mol)

$$Me_2O + H_2O \rightarrow 2MeOH$$

➔$Li_2O$ reacts with water slowly and its solubility is water is much less than that of other alkali metals. Alkali metal hydroxides are the STRONGEST KNOWN bases.

➔ All hydroxides except LiOH can be melted without decomposition (compare with IIa group hydroxides). LiOH decomposes upon heating to $Li_2O$ and $H_2O$.

➔<u>ALL alkali hydroxide form hydrates with variable water content</u>

Examples: $LiOH \cdot H_2O,\ NaOH \cdot nH_2O\,(n = 1,\ 2, 2.5,\ 3.5, 5.25, 7)$

All these solids contain hydrogen bonded chains, in which the distinction between -OH form water and –OH from the hydroxide is difficult to make.

✡The rate of dissolution of hydrates in water may be much lower than the rate of dissolution of anhydrous hydroxides

✡The rate of reaction of hydrates with acidic anhydrides is faster that anhydrous hydroxides (especially with $CO_2$ and $H_2S$)

➔Most used compounds NaOH and KOH

➔Concentrated solutions and melts of alkali hydroxides cause many amphoteric oxides (Al, Zn, Ga, Sn, Pb etc) to behave as acids.

➔ NOTE: concentrated solutions of ALL alkali hydroxide dissolve $SiO_2$ and MOST Si-based glasses

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

➔Molten hydroxides of alkali metals are one of the most aggressive substances known

They react with most other metallic and non-metallic oxides

$$2KOH + Al_2O_3 \rightarrow 2KAlO_2 + H_2O$$

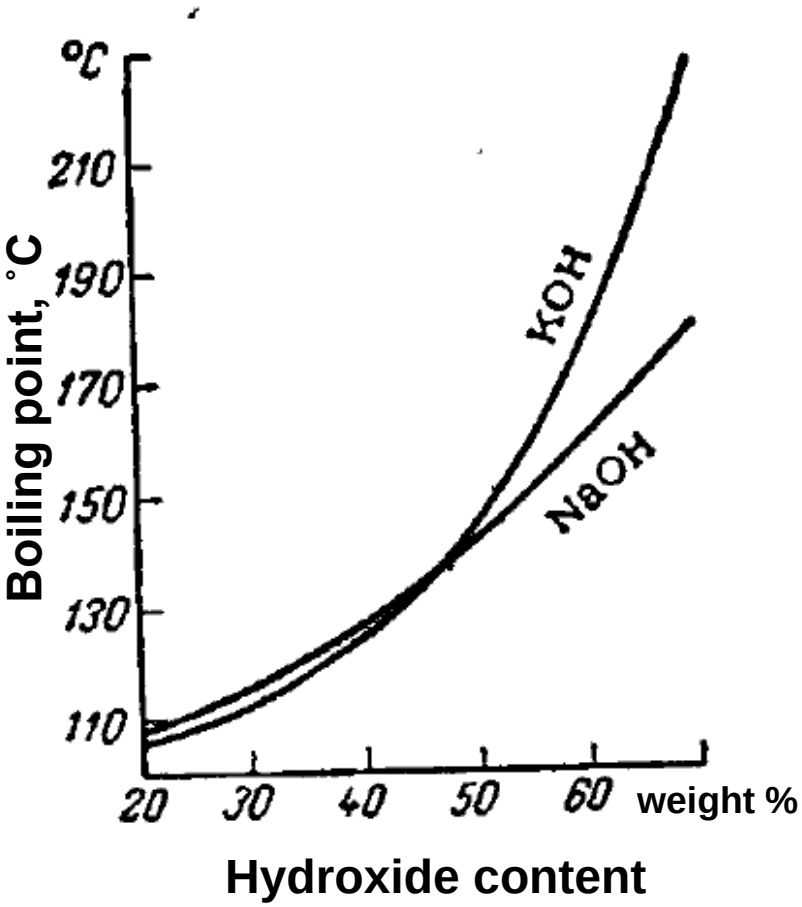
In their presence noble metals ( Au, Pt, etc) react with oxygen forming mixed oxides

$$2NaOH + Pt + \tfrac{1}{2}O_2 \rightarrow Na_2PtO_2 + H_2O \ \ (\text{or } Na_2PtO_3)$$

depending on temperature and amount of oxygen

➔with other metal molten alkali hydroxides give $2NaOH + Zn \rightarrow ZnO + Na_2O + H_2$

✡Boiling points ( at 1 atm) of alkali hydroxide water solutions. (What is unusual in the graph?)



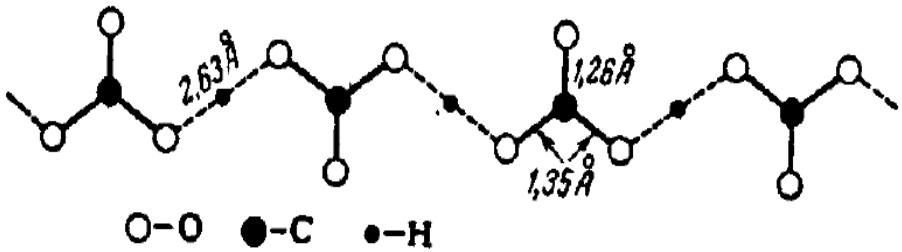
# Carbonates and Sulfates

➔ Carbonates have high solubility and form hydrates ( <u>crystalline soda</u> $Na_2CO_3 \cdot 10\ H_2O$).

$Li_2CO_3$ is poorly soluble and non-hygroscopic.

➔ All carbonates and <u>sulfates</u> form with alkali metals normal and bi-salts ( most known examples <u>baking soda</u> $NaHCO_3$ =mineral nahkolite).

➔ All bicarbonates contain $HCO_3^-$ ion and decompose upon heating, usually below 50 °C

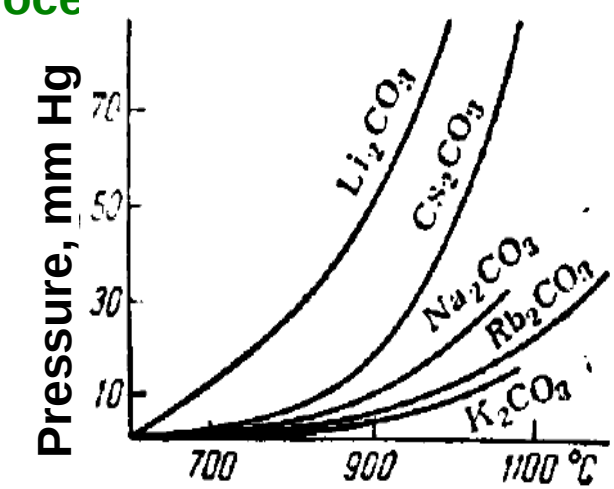


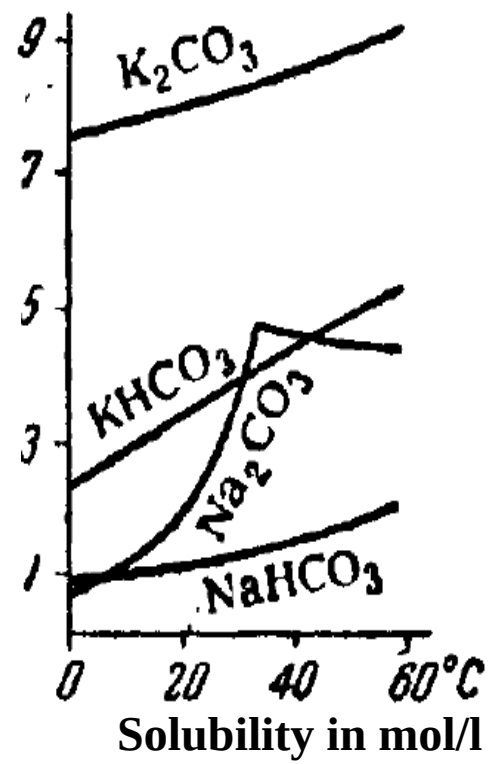

➔ Carbonates can be obtained directly from oxides or hydroxides. However, other proce[illegible] is used (see later)

$$NaCl(aq) + NH_4HCO_3(aq) \rightarrow NaHCO_3(s) + NH_4Cl$$

➔ Important names potash $K_2CO_3$ ;

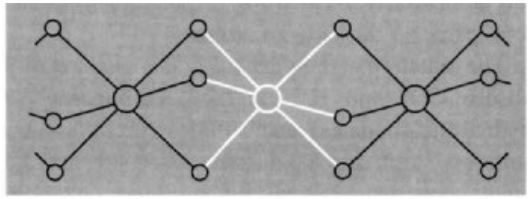
mirabilite $Na_2SO_4 \cdot 10\ H_2O$;



# General properties of alkali metal salts

➔ Salts of alkali metals have a tendency to form hydrates, however, direct precipitation of some halides produces anhydrous salts. Lithium salts are typically $LiX \cdot 3H_2O$, x = Cl, Br, I, $ClO_3$, $ClO_4$, $NO_3$, $MnO_4$. In all salts Li is coordinated with 6 molecules of water.



➔ Na, K, Cs and Rb salts of oxo-acids form a large number of hydrates including mixed-metal hydrates.

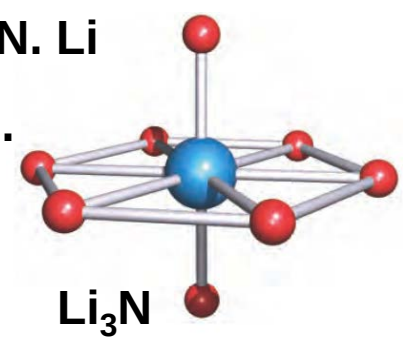
✡ Similar to peroxides, Na, K, Rb and Cs may stabilize poly-halide salts in solutions $MeX_n$, Me= Na, K, Rb and Cs, X= Br, I ( but not F and rarely for Cl), n=2 or 3,5. Stability increases from Na to Cs (Why??) and from Cl to I ( Why??). Some of these salts may be prepared anhydrous: $RbICl_2$, $CsICl_2$, $RbIBr_2$, $CsIBr_2$….. All poly-halides decompose releasing halogens ( think what will be the product of decomposition of $CsICl_2$)

# Alkali metals + other non-metals

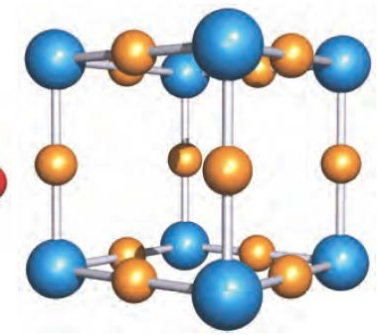
→ **Alkali metals react with most non-metals forming corresponding salts. All these salts undergo hydrolysis ( exceptions halogens and sulfur). Hydrides (see previous lecture)**

$$S(s) + K(s) \rightarrow K_2S \text{ (with explosion) also polysulfides } K_2S_{1+n} \ (n = 1-5)$$

→ **Nitrides of the alkali metals are unstable except for $Li_3N$. Li is the only nitride that can be obtained by reaction with N.**



**$Li_3N$**



**$Na_3N$**

→ **$Na_3N$ decomposes slowly, other nitrides decompose with explosion (Why?)**

→ **Phosphides are stable but hydrolyze by water. ALL binary compounds of alkali metals with non metals except halides, oxides and nitrides undergo hydrolysis (why???).**

$$P(s) + K(s) \rightarrow K_3P \qquad K_3P(s) + 3H_2O \rightarrow PH_3 + 3KOH$$

→ **Li and Na may react with carbon forming <u>acetylenides</u>** $Li-C\equiv C-Li$

→ **Reaction of Li and Na with acetylene at room temperature and above DOES NOT result in acetylenides. However, reaction in liquid $N_2$ does produce acetylenides.**

→ **K, Rb or Cs react with carbon producing intercalation compounds, $C_nM$ (n = 8, 24, 36, 48, 60) and DO NOT produce carbides or acetylenides.**

→ **Alkali metals react with Si forming** $Me_2Si,\ Me_4Si,\ MeSi\,(Me = Na, K, Rb, Cs)$

→ **Reaction with many non-metals produces compounds of variable composition**

# Stabilization of unusual valance states

→ **Alkali metals are may reduce transition metal complexes to unusually low oxidation states either with or without bond cleavage**

$$K_2[Ni(CN)_4] + 2K \xrightarrow{NH_3/-33^\circ} K_4[Ni(CN)_4];$$

i.e. Ni(0)

$$[Pt(NH_3)_4]Br_2 + 2K \xrightarrow{NH_3/-33^\circ} [Pt(NH_3)_4] + 2KBr;$$

i.e. Pt(0)

$$Mn_2(CO)_{10} + 2K \xrightarrow{NH_3/-33^\circ} 2K[Mn(CO)_5];$$

i.e. Mn(−1)

$$Fe(CO)_5 + 2Na \xrightarrow{NH_3/-33^\circ} Na_2[Fe(CO)_4] + CO;$$

i.e. Fe(−2)

→ **Solution of alkali metals in liquid $NH_3$ (amids) react with CO and form**

$$Me^+[OC \equiv CO]^{2-} Me^+$$

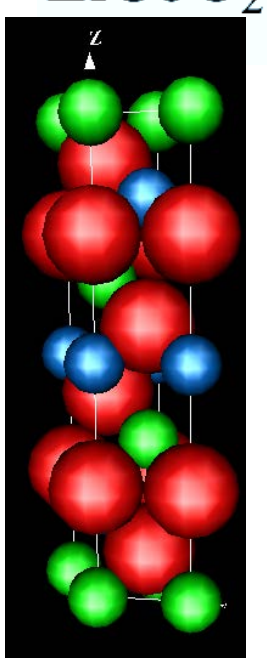
# Interstitial solution of Li and Na. Intercalation.

→BECAUSE OF THE SMALL SIZE $Li^+$ and $Na^+$ may diffuse in and incorporate into many solids with <u>layered</u> structures ( for instance graphite and $CoO_2$, $WO_3$, β-alumina etc) forming a continuous composition range like $Li_xCoO_2$ x=0-1 and $Li_yC_6$ y=0-1

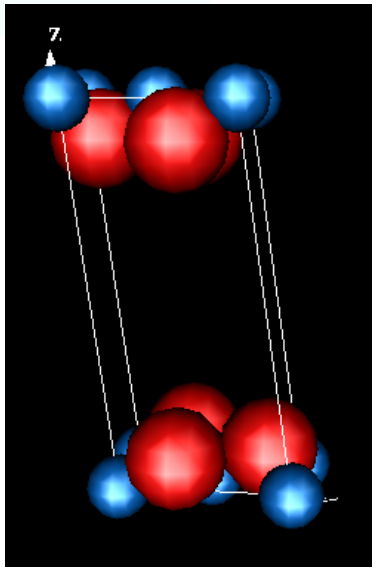
→Application of the intercalation: Li ion batteries

Li-Co battery

$$LiCoO_2 + 6C(\text{graphite}) \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} LiC_6 + CoO_2$$



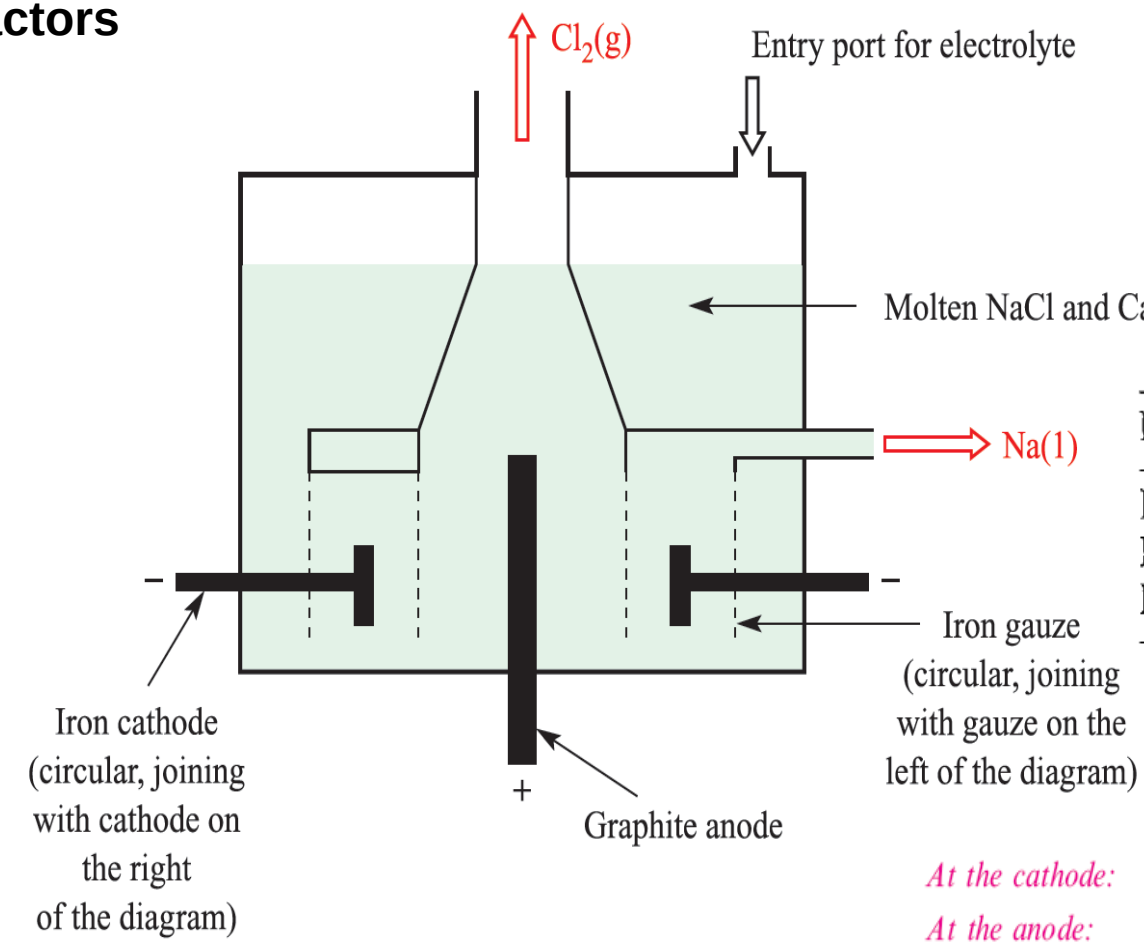
→$TiS_2$-C battery operates similarly



# Use and production of alkali metals

**→Only Na and Li are used as pure metals at large scale.**

**Na is used as a coolant in exhaust valves of internal combustion engines and nuclear reactors**




| Metal | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Price/\$ $kg^{-1}$ | 36.3 | 1.50 | 34.4 | 827 | 716 |
| Relative cost (per kg) | 24 | 1 | 23 | 550 | 477 |
| Relative cost (per mol) | 7.3 | 1 | 39 | 2050 | 2760 |

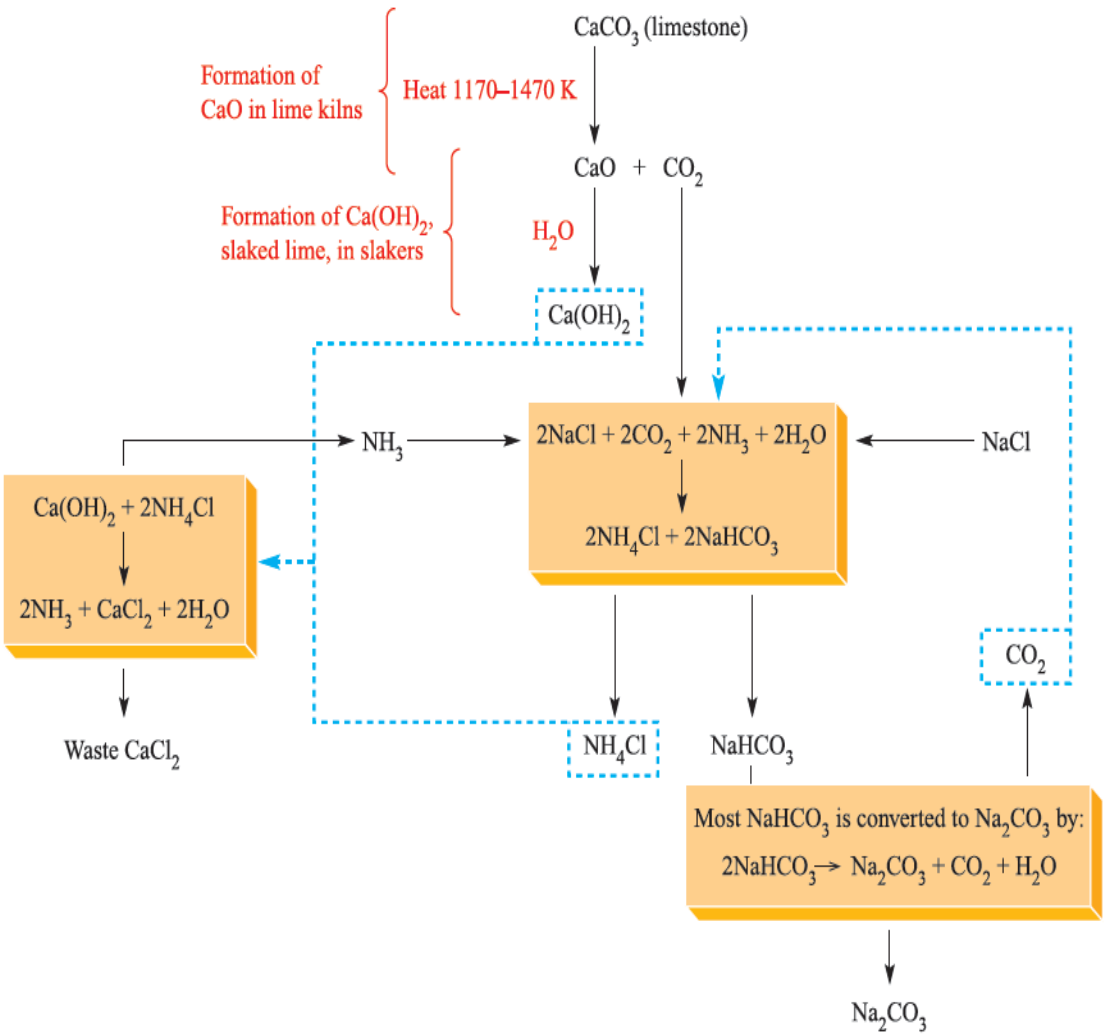
*At the cathode:* $Na^+(l) + e^- \rightarrow Na(l)$

*At the anode:* $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

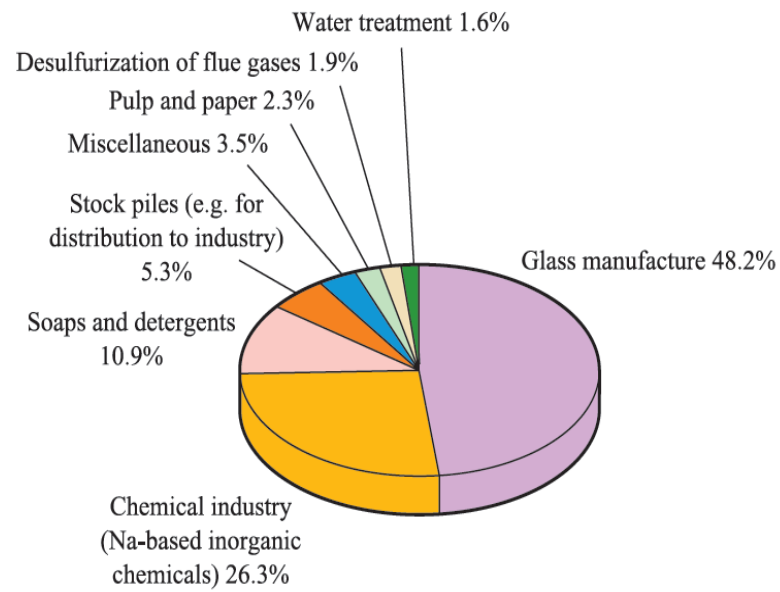
*Overall reaction:* $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$

the Downs process to produce sodium

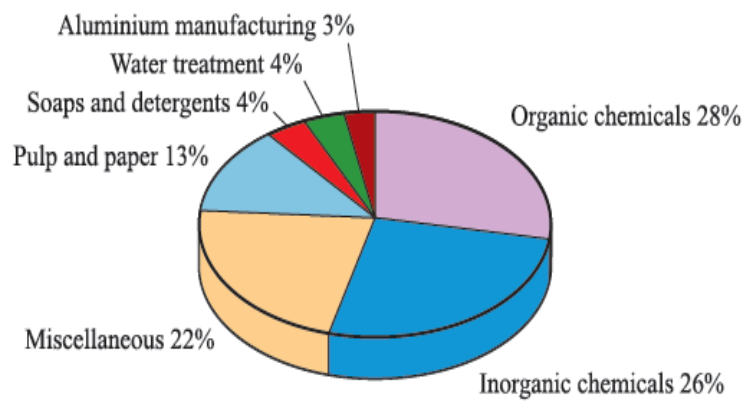
# Soda production and use




The Solvay process for the manufacture of $Na_2CO_3$ and $NaHCO_3$ from $CaCO_3$, $NH_3$ and NaCl

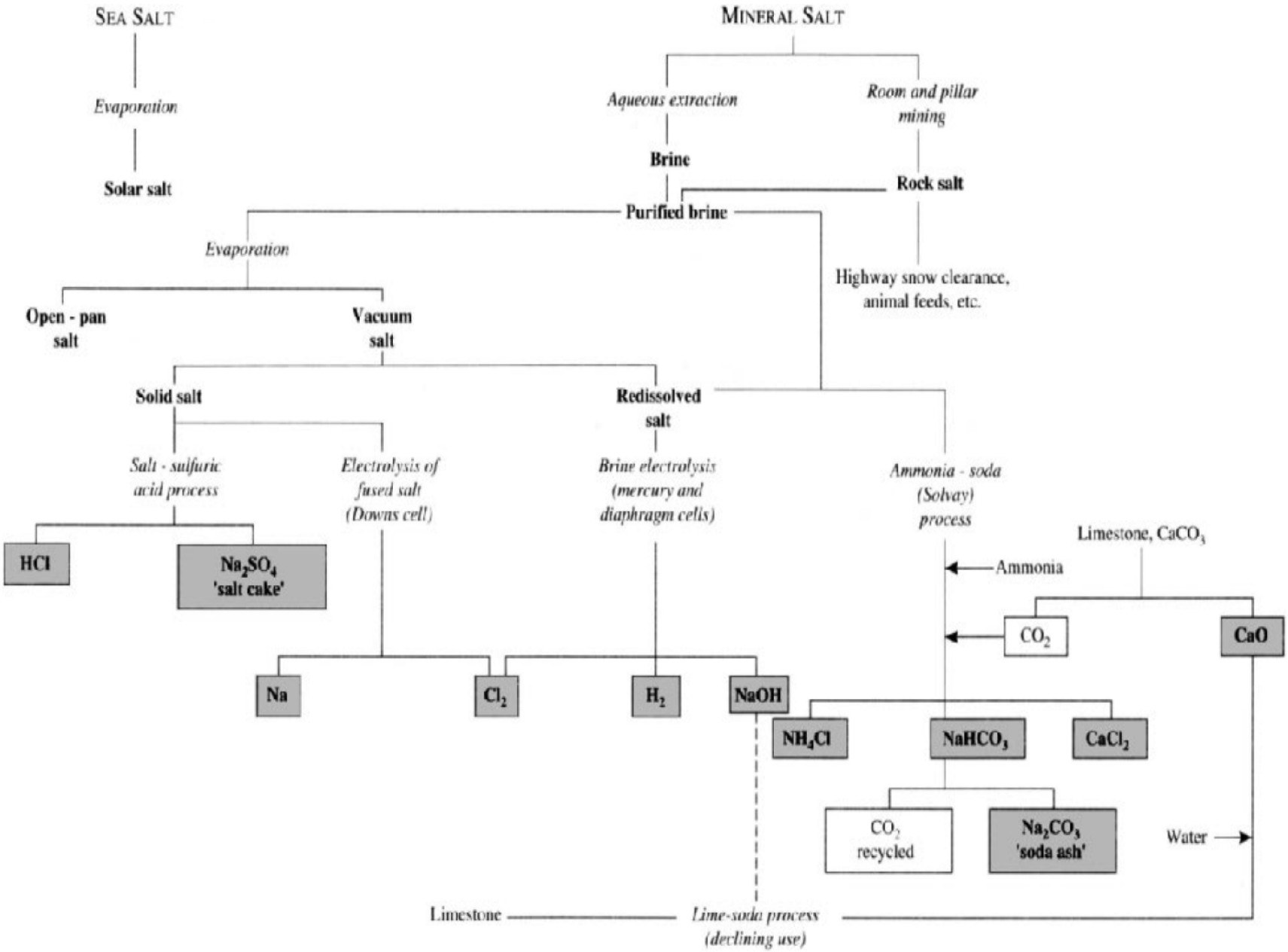



Uses of $Na_2CO_3$ in the US in 2001




industrial uses of NaOH

# Large scale production and use of NaCl



# Alkaline earth metals [noble gas]($s^2$):Be, Mg, Ca, Sr, Ba

**Minerals:** Beryl (emerald) $Be_3Al_2(SiO_3)_6$; forsterite $Mg_2SiO_4$; dolomite $MgCO_3 \bullet CaCO_3$; magnesite $MgCO_3$; periclase MgO; lime stone $CaCO_3$ (various types: chalk, marble, corals, calcite, aragonite, dolomite); olivine $(Mg,Fe)_2SiO_4$; gypsum ($CaSO_4 \cdot 2H_2O$), fluorspar (flourite) $CaF_2$ ; apatite $[Ca_5(PO_4)_3]F$; Barite $BaSO_4$;

**Structures: HCP: Be, Mg; FCC: Ca, Sr; BCC: Ba (like Alk-metals)**

## Comparison of Ionic radii

| Be | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| 27 | 72 | 100 | 126 | 142 |
| Li | Na | K | Rb | Cs |
| 76 | 102 | 138 | 149 | 170 |

| Property | Be | Mg | Ca | Sr | Ba | Ra |
|---|---|---|---|---|---|---|
| Atomic number, $Z$ | 4 | 12 | 20 | 38 | 56 | 88 |
| Ground state electronic configuration | $[He]2s^2$ | $[Ne]3s^2$ | $[Ar]4s^2$ | $[Kr]5s^2$ | $[Xe]6s^2$ | $[Rn]7s^2$ |
| Enthalpy of atomization, $\Delta_a H^\circ(298\,K)/kJ\,mol^{-1}$ | 324 | 146 | 178 | 164 | 178 | 130 |
| Melting point, mp / K | 1560 | 923 | 1115 | 1040 | 1000 | 973 |
| Boiling point, bp / K | ≈3040 | 1380 | 1757 | 1657 | 1913 | 1413 |
| Standard enthalpy of fusion, $\Delta_{fus}H^\circ(mp)/kJ\,mol^{-1}$ | 7.9 | 8.5 | 8.5 | 7.4 | 7.1 | – |
| First ionization energy, $IE_1/kJ\,mol^{-1}$ | 899.5 | 737.7 | 589.8 | 549.5 | 502.8 | 509.3 |
| Second ionization energy, $IE_2/kJ\,mol^{-1}$ | 1757 | 1451 | 1145 | 1064 | 965.2 | 979.0 |
| Third ionization energy, $IE_3/kJ\,mol^{-1}$ | 14850 | 7733 | 4912 | 4138 | 3619 | 3300 |
| Metallic radius, $r_{metal}$ / pm‡ | 112 | 160 | 197 | 215 | 224 | – |
| Ionic radius, $r_{ion}$ / pm* | 27 | 72 | 100 | 126 | 142 | 148 |
| Standard enthalpy of hydration of $M^{2+}$, $\Delta_{hyd}H^\circ(298\,K)/kJ\,mol^{-1}$ | −2500 | −1931 | −1586 | −1456 | −1316 | – |
| Standard entropy of hydration of $M^{2+}$, $\Delta_{hyd}S^\circ(298\,K)/J\,K^{-1}\,mol^{-1}$ | −300 | −320 | −230 | −220 | −200 | – |
| Standard Gibbs energy of hydration of $M^{2+}$, $\Delta_{hyd}G^\circ(298\,K)/kJ\,mol^{-1}$ | −2410 | −1836 | −1517 | −1390 | −1256 | – |
| Standard reduction potential, $E^\circ_{M^{2+}/M}$ / V | −1.85 | −2.37 | −2.87 | −2.89 | −2.90 | −2.92 |

**Electronegativity**

| | |
|---|---|
| 3 Li 1.0 | 4 Be 1.5 |
| 11 Na 0.9 | 12 Mg 1.2 |
| 19 K 0.8 | 20 Ca 1.0 |
| 37 Rb 0.8 | 38 Sr 1.0 |
| 55 Cs 0.7 | 56 Ba 0.9 |

# Factors defining the chemical properties

**General note: difference in chemical properties between the top-row and the bottom-row members of a group is the largest for group IVa and decreases towards the edges of the table (Ia and VIIa)**

1. **A-E metals have much higher electronegativity than corresponding Alk-metal.**
2. **Ionic radii of A-E metals vary strongly, with $Be^{2+}$ being one of the SMALLEST ions, and $R(Mg^{2+})=R(Li^{+})$**
3. **Ionic radii increase and electronegativity decreases quickly with increasing atomic number**

**Consequences:** **<u>Chemical reactivity quickly increases from Be to Ba</u>**

I. **A-E metals are much weaker bases than Alk-metals.**

II. **Chemical properties of Be are very different from Mg Ca, Sr, Ba and Be is strongly amphoteric.**

III. **Chemical properties of Mg are intermediate between Be and Ca, Sr, Ba**

IV. **Ca, Sr Ba are strong bases, whith alkalinity increasing quickly from Ca to Ba**

V. **Be and Mg may have a tendency for complex-formation with strong ligands.**

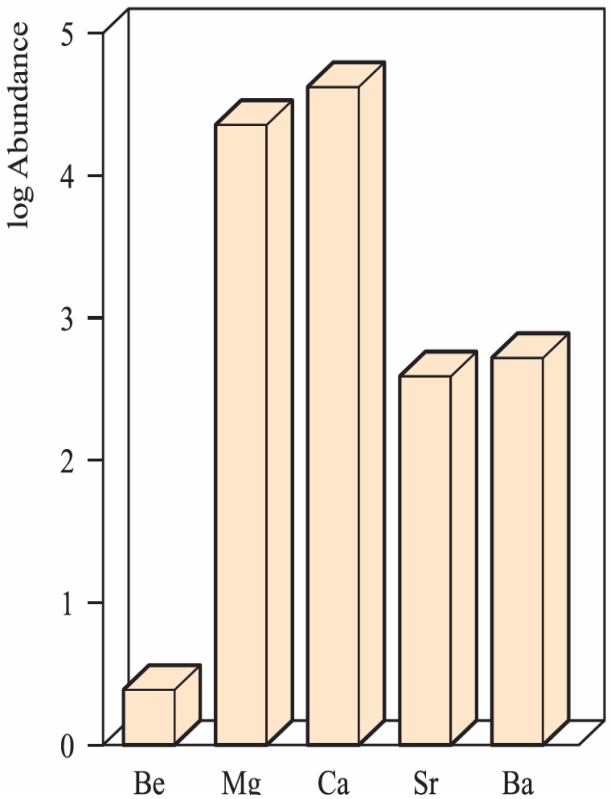
VI. **Charge +2, makes the salts of A-E metals far less soluble than Akl-metals**

# Interesting facts about alkaline earth metals

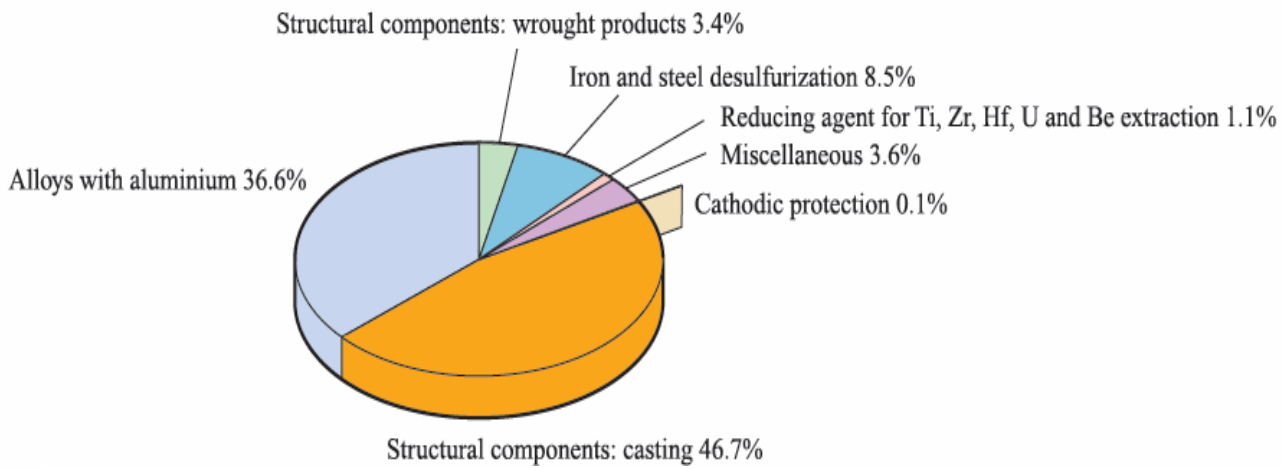
➔ Be is one of the lightest metals known, nonmagnetic and has a high thermal conductivity and melting point (1560 K). Be is used for high-speed aircraft, missiles and satellites

➔ Be has very small X-Rays absorption coefficient and used for X-Ray windows.

➔ Mg is usually used as an alloy with Al, which makes it harder and decreases corrosion.




Abundances in ppm




**Only Mg is used a pure metal. It is produced by electrolysi of molten $MgCl_2$. Mg is moderately hard; the rest are fairly soft. Mg alloys are of strategic importance.**

**<u>Be and Mg are stable in air; The rest react with $O_2$ and water at ambient conditions.</u>**

# Chemical properties of the pure metals

➔ Upon heating ALL alkaline earth metals react with $O_2$ and $N_2$ , sulfur and halogens showing the oxidation state of +2

$$2M + O_2 \xrightarrow{\Delta} 2MO$$

**Mg and Be powders burn with flash**

$$3M + N_2 \xrightarrow{\Delta} M_3N_2$$

$$8M + S_8 \xrightarrow{\Delta} 8MS$$

$$M + X_2 \xrightarrow{\Delta} MX_2 \qquad X = F, Cl, Br, I$$

➔ Pyrotechnique lesson: simple illumination charge (w/w): 45% Mg powder; 48% $NaNO_3$; 7% starch (binder);

➔ Be does not react with water at all, even upon heating; Mg reacts with boiling water (steam); Ca, Sr and Ba react with water and form hydroxides

$$Ca(s) + 2H_2O \rightarrow 2Ca(OH)_2 + H_2(g)$$

**Mg+$H_2O$**

➔ Be and Mg are stable in air; Ca, Sr and Ba react with air, especially with wet air

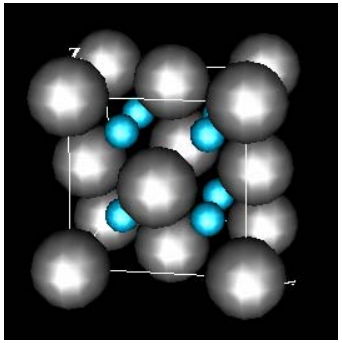
➔ ALL alkaline earth metals react with hydrogen. However, $BeH_2$ is polymeric, the rest are salt-like. Ba and Sr absorb hydrogen till $SrH_4$.

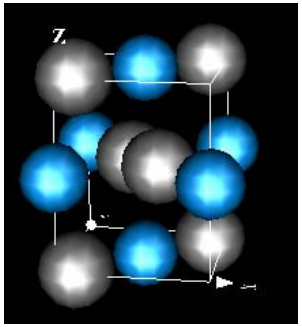
# Chemical properties of the pure (cont)

➔ Be reaction with carbon leads to a carbide $Be_2C$. Mg, Ca, Sr and Ba form acetylenides $MgC_2$ (compare with alkali metals)

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

$$MC_2 + 2H_2O \rightarrow M(OH)_2 + C_2H_2 \quad M = Mg, Ca, Sr, Ba \quad -Me-C \equiv C-Me-$$





➔ All alkaline earth metals react with ammonia, Ca,Sr and Ba with protic solvents

$$3Be(s) + 2NH_3(g) \rightarrow Be_3N_2(s) + 3H_2(g)$$

➔ **All alkaline earth metals dissolve in weak mineral acids.** Exception is: Mg is stable with respect to HF because $MgF_2$ is completely insoluble (a rare case!); Be does not react with cold $HNO_3$.

➔ Be dissolves in strong basis (NaOH, KOH) forming <u>salt</u> of "beryllium acid"

$$Be(s) + NaOH(aq) + H_2O \rightarrow NaBeO_2(aq) + H_2(g)$$

# Chemical properties of compounds

**Be halides** are completely different from other alkaline earth halides. Be has a strong tendency to *sp*-hybridization and coordination number 4

➔ Be halides and are completely covalent: $BeF_2$ and $BeCl_2$ have relatively low melting points (797 °C and 540 °C) but the melts are not conductive;

➔ Although Be dissolves in HF and HCl. $BeF_2$ and $BeCl_2$ cannot be prepared from the water solutions because beryllium forms $[Be(H_2O)_4]^{2+}$.

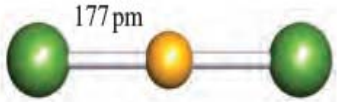
➔ All Be halides are water soluble ( guess why?)

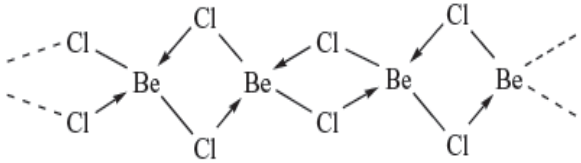
$$Be(s) + 2HF(aq) + 2NH_3(aq) \xrightarrow{Aq} [NH_4]_2[BeF_4](aq) + H_2(g)$$

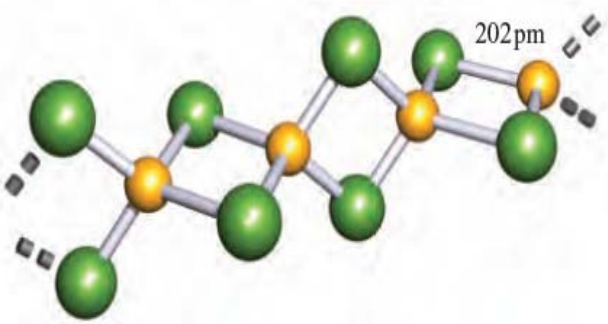
$$[NH_4]_2[BeF_4](s) \xrightarrow{Sublimation} BeF_2(s) + 2NH_4F(g)$$

$$2BeO + CCl_4 \xrightarrow{1070\,K} 2BeCl_2 + CO_2$$

$$[Be(H_2O)_4]Cl_2 \xrightarrow{\Delta} Be(OH)_2 + 2H_2O + 2HCl$$




polymeric structure of $BeCl_2$ (compare with $BeH_2$!)

**Molecule of $BeCl_2$ (vapor)**
**Also forms dimers with a plane trigonal configuration**

**Halides** of Mg, Ca, Sr and Ba are ionic. The degree of ionicity increases from Mg to Ba. Mg halides are slightly reminiscent of Be.

→ $MgF_2$, $CaF_2$ , $SrF_2$ and $BaF_2$ are poorly soluble in water; Mg dissolves in fluorides $MgF_2(s) + 2KF(aq) \leftrightarrow K_2[MgF_4](aq)$ (same for $BeF_2$):

→ Upon heating in vacuum all halides form molecules (for self-education)

→ All halides of Mg, Ca, Sr and Ba except fluorides are highly soluble and very hygroscopic.

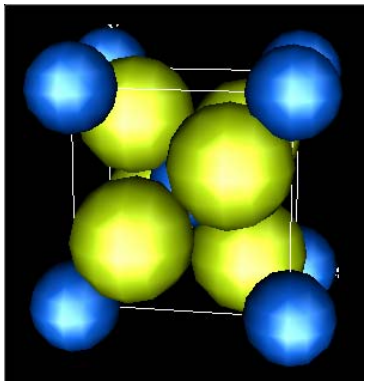
They can be prepared by crystallizing from aqueous solutions.

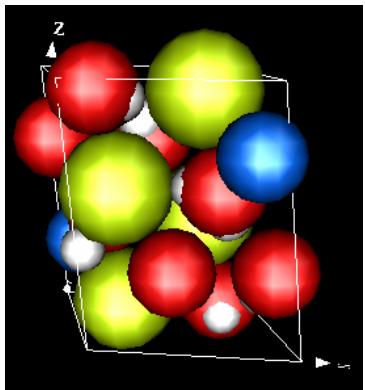
→ $CaCl_2$ is one of the most used drying agent ( may go to $CaCl_2 \cdot 6H_2O$)

→ Drying ability is related to hydration of $Me^{2+}$, which forms a stable cation rigidly coordinated with water molecules $[Mg(H_2O)_6]^{2+}$, $[Ca(H_2O)_6]^{2+}$

→ All Alkaline Earths have a tendency to form crystalline stoichiometric hydrates

$$CaCl_2 + 2H_2O \leftrightarrow CaCl_2 \cdot 2H_2O$$





***** look at the structure at http://icsd.fiz-karlsruhe.de/icsd/StartActionPath.do**

Crystal structures of alkaline earth halides[a]

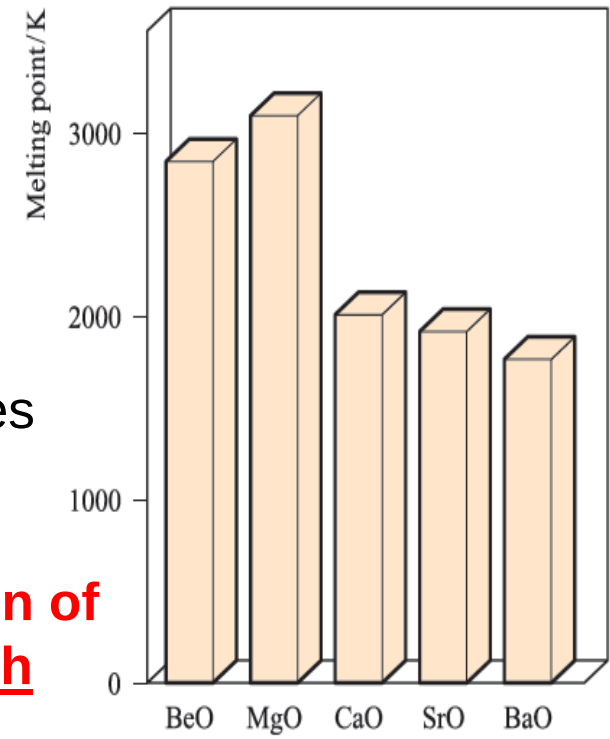
| | Be | Mg | Ca | Sr | Ba |
|---|---|---|---|---|---|
| F | Quartz | Rutile($TiO_2$) | Fluorite | Fluorite | Fluorite |
| Cl | Chain | $CdCl_2$ | Deformed $TiO_2$ | Deformed $TiO_2$ | $PbCl_2$ |
| Br | Chain | $CdI_2$ | Deformed $TiO_2$ | Deformed $PbCl_2$ | $PbCl_2$ |
| I | — | $CdI_2$ | $CdI_2$ | $SrI_2$ | $PbCl_2$ |

**CN=4** **CN=6** **CN=8** **CN=7**

# Oxides

**➔ Oxides are prepared from carbonates (think why?). Stability of carbonates increases with increasing Z (similar to alkali metals)**

$$MCO_3 \xrightarrow{T\,K} MO + CO_2 \qquad \begin{cases} M = Mg & T = 813\,K \\ \quad\;\; Ca & \quad\;\; 1173\,K \\ \quad\;\; Sr & \quad\;\; 1563\,K \\ \quad\;\; Ba & \quad\;\; 1633\,K \end{cases}$$




➔ **With the exception of Be, all oxides of alkaline earth metals are strong bases.** The strength of the bases increases from Be to Ba.

➔ BeO is insoluble in water.

➔ **BeO is amphoteric and dissolves in bases (see reaction of Be with NaOH) <u>because electric feld near $Be^{2+}$ is very high</u>**

➔ MgO react with water very slow

➔ Ca, Sr and Ba oxides react with water rapidly and exothermally

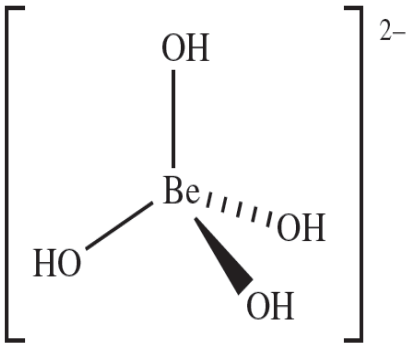
CaO mixed with oil and wax is an incendiary mixture used by Romans (probably to burn Jerusalem)

# Hydroxides

➔ $Be(OH)_2$ may form an anion $[Be(OH)_4]^{2-}$

$$Be(OH)_2 + 2[OH]^- \longrightarrow [Be(OH)_4]^{2-}$$

$$Be(OH)_2 + H_2SO_4 \longrightarrow BeSO_4 + 2H_2O$$




➔ $Be(OH)_2$ precipitates at 12>pH>5.7; $Mg(OH)_2$ precipitates at pH>10.5

➔MgO is a very weak base; but does not exhibit any acidity

$$Mg(OH)_2(s) + H_2O + 2NaOH\ (65\%) \underset{\text{complete hydrolysis (room temperature)}}{\overset{100\ ^oC}{\rightleftarrows}} Na_2[Mg(OH)_4]$$

➔Solubility of hydroxides quickly increases from $Be(OH)_2$ to $Ba(OH)_2$

➔$Sr(OH)_2$ to $Ba(OH)_2$ are very strong bases (complete dissociation)

➔ Solutions of Ca, Sr and Ba hydroxides quickly absorb $CO_2$ form air.

$$CaO(s) + H_2O \xrightarrow{Aq} Ca(OH)_2 \xrightarrow{CO_2} CaCO_3$$

# Peroxides

➔ BaO and SrO uptake oxygen upon moderate heating and pressure of $O_2$ of a few hundred atm.

$$2BaO(s) + O_2 \leftrightarrow 2BaO_2$$

➔ peroxides of Mg and Ca can be prepared from $H_2O_2$ and hydroxide

$$Ca(OH)_2 + H_2O_2 + 6H_2O \longrightarrow CaO_2 \cdot 8H_2O$$

➔ All peroxides decompose upon heating and used ($BaO_2$) as strong oxidizing agents
➔ All peroxides react with acids and produce $H_2O_2$

$$SrO_2 + 2HCl \longrightarrow SrCl_2 + H_2O_2$$

# Alkaline earth salts with oxo-acids

1. Be salts are quite different in their behavior

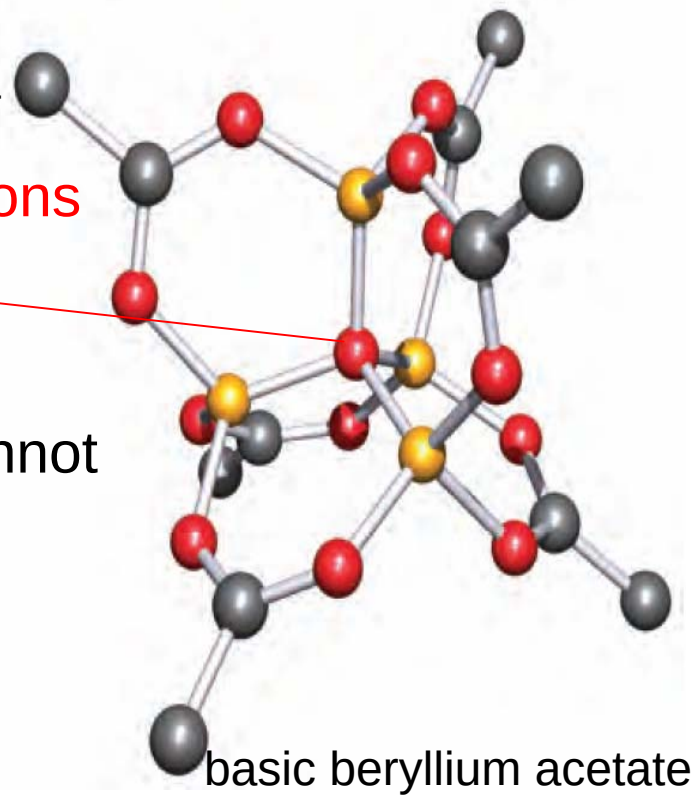
➔Most Be salts of STRONG oxo-acids are soluble and Be-ion is present as tetra-hydrate $[Be(H_2O)_4]^{2+}$;

➔Be salts of weak oxo-acids hydrolyze (why?). One of the most known examples is Be acetate and nitrate. Acetate has a structure $[Be_4O]^{6+}(O_2C\text{-}Me)_6^-$

➔Be nitrate has a similar structure $[Be_4O]^{6+}(O_2NO)_6^-$

Tendency to form "central" oxygen ion with four cations is common to weak bases

➔In many cases anhydrous salts of weak acids cannot be isolated. For instance $Be(O_2C\text{-}Me)_2$ is not known



basic beryllium acetate

# Alkaline earth salts with oxo-acids

2. Mg and Ca carbonates undergo only partial hydrolysis. Only bicarbonates are noticeably soluble

$$Ca(HCO_3)_2(aq) \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O(l)$$

$$Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \longrightarrow 2CaCO_3(s) + 2H_2O$$

3. Sr and Ba carbonates are stable and soluble ( think why?)

4. Alkaline earth oxo-salts have a VERY STRONG tendency to hydrate (like halides). **EVEN INSOLUBLE SALTS MAY FORM HYDRATES**!

Example: Plaster-Gypsum. Gypsum is a very important decorative material

$$CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O \underset{200\ ^oC}{\overset{\text{room temperature}}{\rightleftharpoons}} CaSO_4 \cdot 2H_2O$$

$$CaSO_4.2H_2O \xrightarrow{\sim 150^\circ} CaSO_4.\tfrac{1}{2}H_2O \xrightarrow{\sim 200^\circ}$$

$$\gamma\text{-}CaSO_4 \xrightarrow{\sim 600^\circ} \beta\text{-}CaSO_4 \xrightarrow{\sim 1100^\circ} CaO + SO_3$$

5. Alkaline earth sulfates are insoluble. $BaSO_4$ is used to detect sulfates

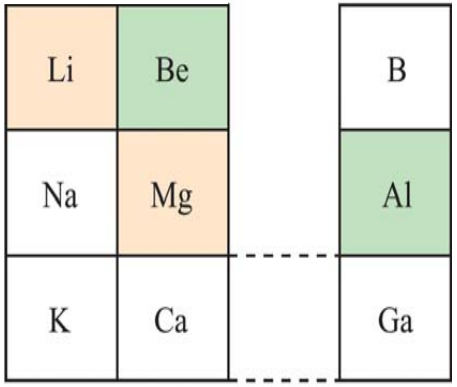
6. Most salts of alkaline earths with poly-based oxo-acids are insoluble. The bi-salts and salts of uni-based acids are moderately soluble.

7. Be and Mg form complex sulfates (why not Ca, Sr and Ba?): $K_6[Mg(SO_4)_4]\cdot 6H_2O$ (example)

# Diagonal relationships between Li and Mg, and between Be and Al

$$\text{Charge density on ion} = \frac{\text{charge on ion}}{\text{surface area of ion } (4\pi r_{ion}^2)}$$

| Property | Group 1 | | | Group 2 | | | Group 13 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Li | Na | K | Be | Mg | Ca | B | Al | Ga |
| Metallic radius, $r_{metal}$ / pm‡ | 157 | 191 | 235 | 112 | 160 | 197 | – | 143 | 153 |
| Ionic radius, $r_{ion}$ / pm* | 76 | 102 | 138 | 27 | 72 | 100 | – | 54 | 62 |
| Pauling electronegativity, $\chi^P$ | 1.0 | 0.9 | 0.8 | 1.6 | 1.3 | 1.0 | 2.0 | 1.6 | 1.8 |
| $\Delta_{atom}H^o(298\text{ K})$ / kJ mol$^{-1}$ | 161 | 108 | 90 | 324 | 146 | 178 | 582 | 330 | 277 |




**Small cations with large charge (charge/radius ratio) DISTORT surrounding anions and have a strong tendency to COVALENT bonding**

**1. Li and Mg:**

→Nitrides are easily formed and stable $3Mg + N_2 \rightarrow Mg_3N_2$ | $Li + N_2 \rightarrow Li_3N$

→Reaction with oxygen yields oxides, not peroxides

$$2Mg + O_2 \rightarrow 2MgO$$
$$2Li + O_2 \rightarrow Li_2O$$

$$2LiOH + H_2O_2 \rightarrow Li_2O_2 + 2H_2O$$
$$Mg(OH)_2 + H_2O_2 \rightarrow MgO_2 + 2H_2O$$

→Carbonates decompose easily upon heating to $CO_2$ and the oxides

→Nitrates decompose to oxides not to nitrites

$$LiNO_3 \rightarrow Li_2O + N_2O_4 + O_2$$ compare $$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$
$$Mg(NO_3)_2 \rightarrow MgO + N_2O_4 + O_2$$

→LiF and $MgF_2$ are insoluble, the rest Na, K, Rb and Cs fluorides are soluble

**2. Be and Al:**

→Be and Al dissolve in bases (NaOH) liberating $H_2$. (Mg does not)

→$Be(OH)_2$ and $Al(OH)_3$ are amphoteric, reacting with both acids and bases

→$BeCl_2$ and $AlCl_3$ easily decompose to oxides and HCl

# Practically important compounds

➔ Soda lime is a mixture of NaOH and $Ca(OH)_2$ and is manufactured from CaO and aqueous NaOH

➔ Industrial production of HF

$$CaF_2 + 2H_2SO_4 \xrightarrow{\text{conc}} 2HF + Ca(HSO_4)_2$$

➔ Industrial $SO_2$ scrubbers: gases containing $SO_2$ are passed through absorbers containing slaked lime or limestone

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

$$H_2SO_4 + CaCO_3 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

➔CaO is used for production of sugar (1t of sugar requires up to 0.25 t of CaO);

➔ CaO is used to remove P, S and Si from still

$$CaO + Si(\text{molten Fe}) + O_2 \longrightarrow Ca_2SiO_4(\text{floating in molten Fe})$$

# ****Other interesting information

➔Mg may form $C=C=C^{4-}$ carbides; $Mg_4C_3$

# Group 3A [noble gas]($s^2p$): B, Al, Ga, In and Tl

## Boron is a non-metal. Al is an amphoteric metals with only some similarities to B

**Boron: Bright crystals (pure); Black crystals (impure)**
**Al, Ga, In, Tl are silvery metals**

| Property | B | Al | Ga | In | Tl |
|---|---|---|---|---|---|
| Atomic number, $Z$ | 5 | 13 | 31 | 49 | 81 |
| Ground state electronic configuration | [He]$2s^2 2p^1$ | [Ne]$3s^2 3p^1$ | [Ar]$3d^{10} 4s^2 4p^1$ | [Kr]$4d^{10} 5s^2 5p^1$ | [Xe]$4f^{14} 5d^{10} 6s^2 6p^1$ |
| Enthalpy of atomization, $\Delta_a H^o(298\,K)$ / kJ mol$^{-1}$ | 582 | 330 | 277 | 243 | 182 |
| Melting point, mp / K | 2453‡ | 933 | 303 | 430 | 576.5 |
| Boiling point, bp / K | 4273 | 2792 | 2477 | 2355 | 1730 |
| Standard enthalpy of fusion, $\Delta_{fus} H^o$(mp) / kJ mol$^{-1}$ | 50.2 | 10.7 | 5.6 | 3.3 | 4.1 |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 800.6 | 577.5 | 578.8 | 558.3 | 589.4 |
| Second ionization energy, $IE_2$ / kJ mol$^{-1}$ | 2427 | 1817 | 1979 | 1821 | 1971 |
| Third ionization energy, $IE_3$ / kJ mol$^{-1}$ | 3660 | 2745 | 2963 | 2704 | 2878 |
| Fourth ionization energy, $IE_4$ / kJ mol$^{-1}$ | 25 030 | 11 580 | 6200 | 5200 | 4900 |
| Metallic radius, $r_{metal}$ / pm* | – | 143 | 153 | 167 | 171 |
| Covalent radius, $r_{cov}$ / pm | 88 | 130 | 122 | 150 | 155 |
| Ionic radius, $r_{ion}$ / pm** | – | 54 ($Al^{3+}$) | 62 ($Ga^{3+}$) | 80 ($In^{3+}$) | 89 ($Tl^{3+}$) 159 ($Tl^{+}$) |
| Standard reduction potential, $E^o$ ($M^{3+}$/M) / V | – | −1.66 | −0.55 | −0.34 | +0.72 |
| Standard reduction potential, $E^o$ ($M^{+}$/M) / V | – | – | −0.2 | −0.14 | −0.34 |

### Comparison of Ionic radii

| Li | Na | K | Rb | Cs |
|---|---|---|---|---|
| 76 | 102 | 138 | 149 | 170 |
| Be | Mg | Ca | Sr | Ba |
| 27 | 72 | 100 | 126 | 142 |
| | Al | Ga | In | Tl |
| | 54 | 62 | 80 | 89 |

### Electronegativity

| | | |
|---|---|---|
| 3 Li 1.0 | 4 Be 1.5 | 5 B 2.0 |
| 11 Na 0.9 | 12 Mg 1.2 | 13 Al 1.5 |
| 19 K 0.8 | 20 Ca 1.0 | 31 Ga 1.6 |
| 37 Rb 0.8 | 38 Sr 1.0 | 49 In 1.7 |
| 55 Cs 0.7 | 56 Ba 0.9 | 81 Tl 1.8 |

**oxidation states +3**
**oxidation states +1: Inert $s^2$ pair effect**

# The factors defining chemical properties

1. **Electro-negativity of B (2.0) is similar to other NON-metals (Si-1.8, P-2.1, As-2.0).**
2. **Electronegativity in the line Al-Tl <u>increases</u> (compare with Ia and IIa)**
3. **$Al^{3+}$--$Tl^{3+}$ ionic radii <u>are small</u> (Al in particular). Therefore, there is a profound tendency for covalent bonding.**
4. **$s^2$ electron pair becomes inert in the line Al-Tl.**

**Consequences:**

**I. B is a non-metal with unique properties (closer to Si or C rather than to Al-Tl). Extremely small size leads to profound tendency to B-B bonds (catenation).**

**II. Chemical reactivity DECREASES in line Al-Tl.**

**III. Al and Ga are strongly amphoteric (WHY?) In and Tl are almost pure metallic.**

**IV. Stability of $1^+$ oxidation state increases from Al to Tl. For Tl $1^+$ state is dominant.**

# ***Natural abundance and usage

**Minerals:** Borax: $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$; kernite $Na_2[B_4O_5(OH)_4]\cdot 2H_2O$;
Bauxite: $Al_2O_3$; cryolite $Na_3[AlF_6]$ part of many alumo-silicates;
Ga, In, Tl are trace elements (Ga in Al,

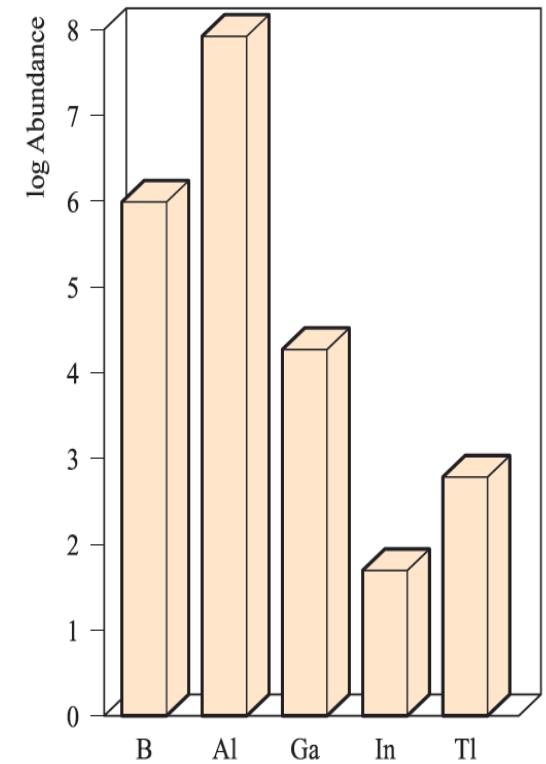
**Isolation:**

**B**

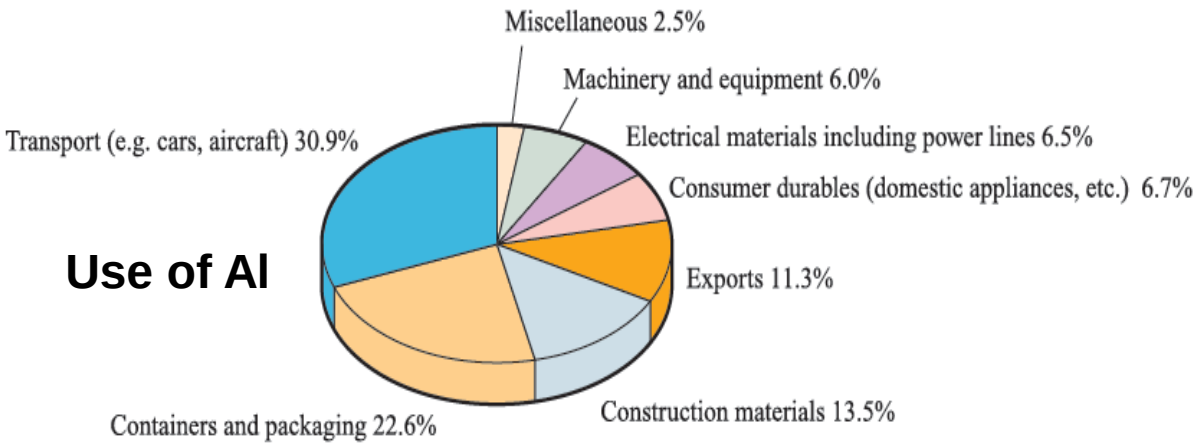
$$Na_2[B_4O_5(OH)_4]\cdot 8H_2O + H_2SO_4 \rightarrow B(OH)_3\downarrow + Na_2SO_4 + 5H_2O$$

$$2B(OH)_3 \xrightarrow{\text{heating}} B_2O_3 + 3H_2O \,|||\, B_2O_3 + 3Mg \xrightarrow{\text{heating}} 2B + 3MgO$$

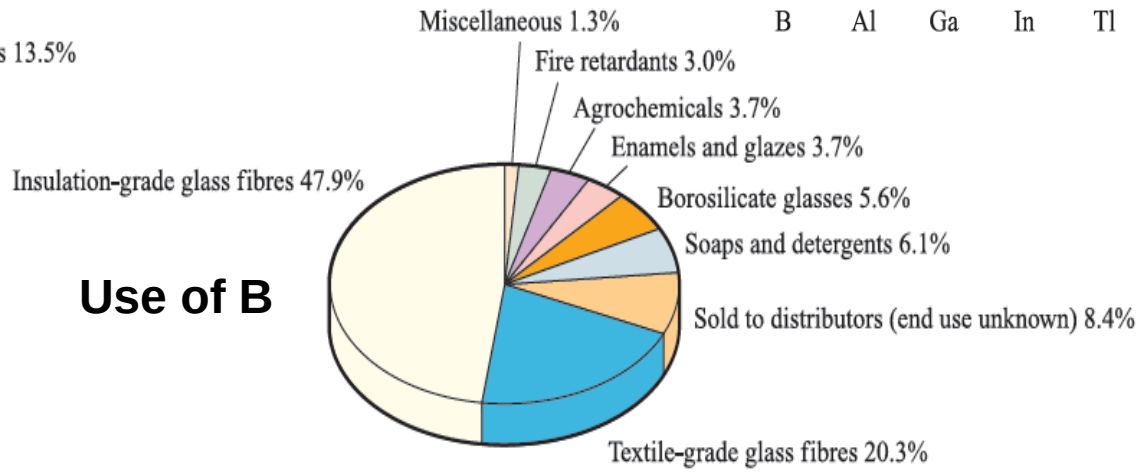
**Al is produced by electrochemical reduction of the melt of**




**Use of Al**

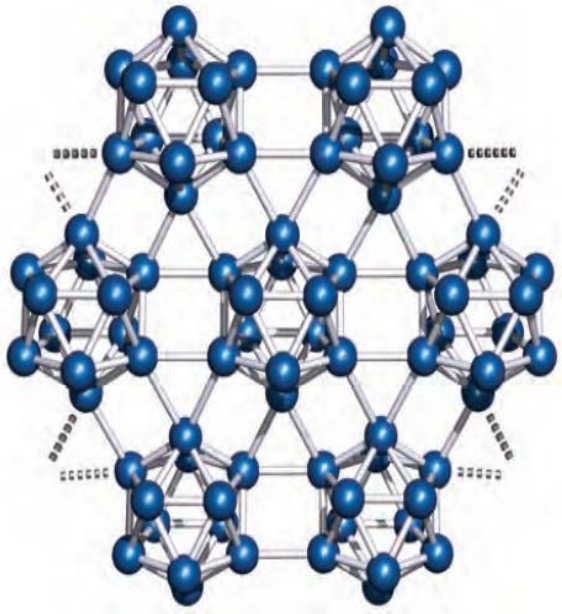



**Use of B**



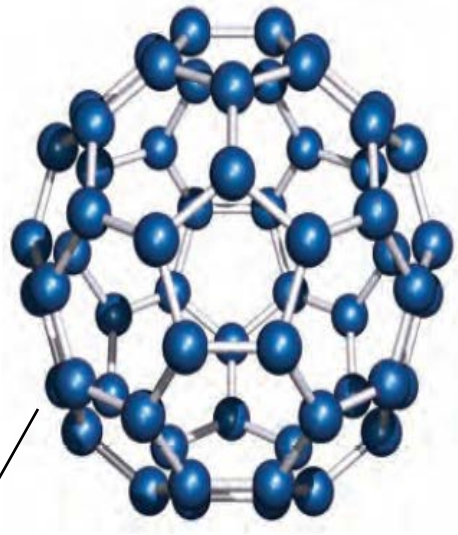
# Pure elements structure

**B has a tendency to form B-B bonds (compare with carbon);**

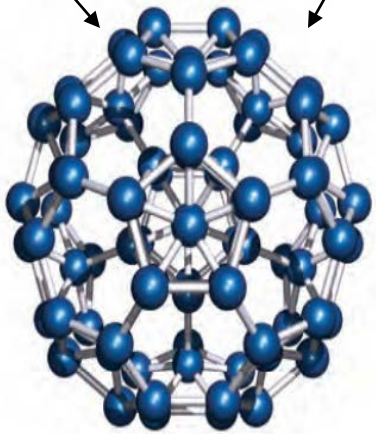


**α-Rhombohedral boron**

**$B_{12}$-icosahedra**



**$B_{60}$-shell**



**$B_{84}$-unit forming β- Rhombohedral boron**

**Lattices (all metallic):**

**Al - FCC**

**Ga and In - orthorhombic**

**Tl-HCP**

# Boron

➔ **Boron is inert under normal conditions (except $F_2$).**

➔ **At high temperatures, Boron reacts with most non-metals (exceptions include $H_2$), most metals and with $NH_3$. In this compounds it has oxidation state (+-3)**

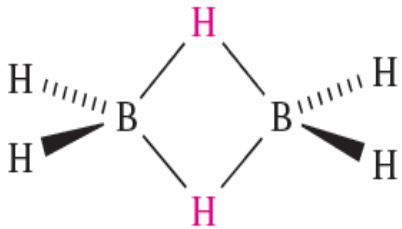
$$2B + N_2 \rightarrow BN \qquad 4B + 3O_2 \rightarrow 2B_2O_3$$

➔**BN is iso-electronic to carbon. It forms cubic phase, almost as hard as diamond;**

**Hexagonal phase, similar to graphite and nano-tubes**

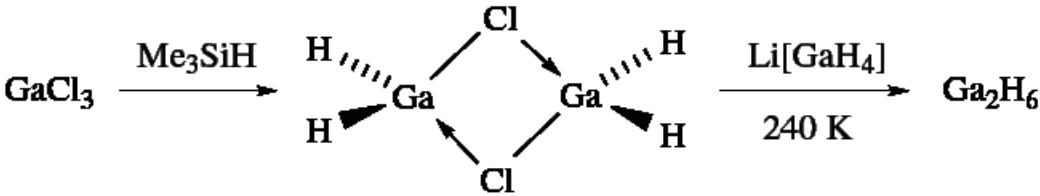
➔**Boron hydride $BH_3$ (can be obtained from borides) forms dimers and polymers (di-boranes and poly-boranes, for instance tetra-borane). They contain DELOCALIZED (three atom) electron forming a bond that some times called banana (tri-center) -bond**

$$2BF_3 + 6NaH \xrightarrow{450\,K} B_2H_6 + 6NaF$$




➔**Al does not form molecular poly-hydrides. $AlH_3$ is a crystalline solid with a larger degree of covalent bonding. There some data about $Ga_2H_6$**

$$3Li[AlH_4] + AlCl_3 \rightarrow \frac{4}{n}[AlH_3]_n + 3LiCl$$

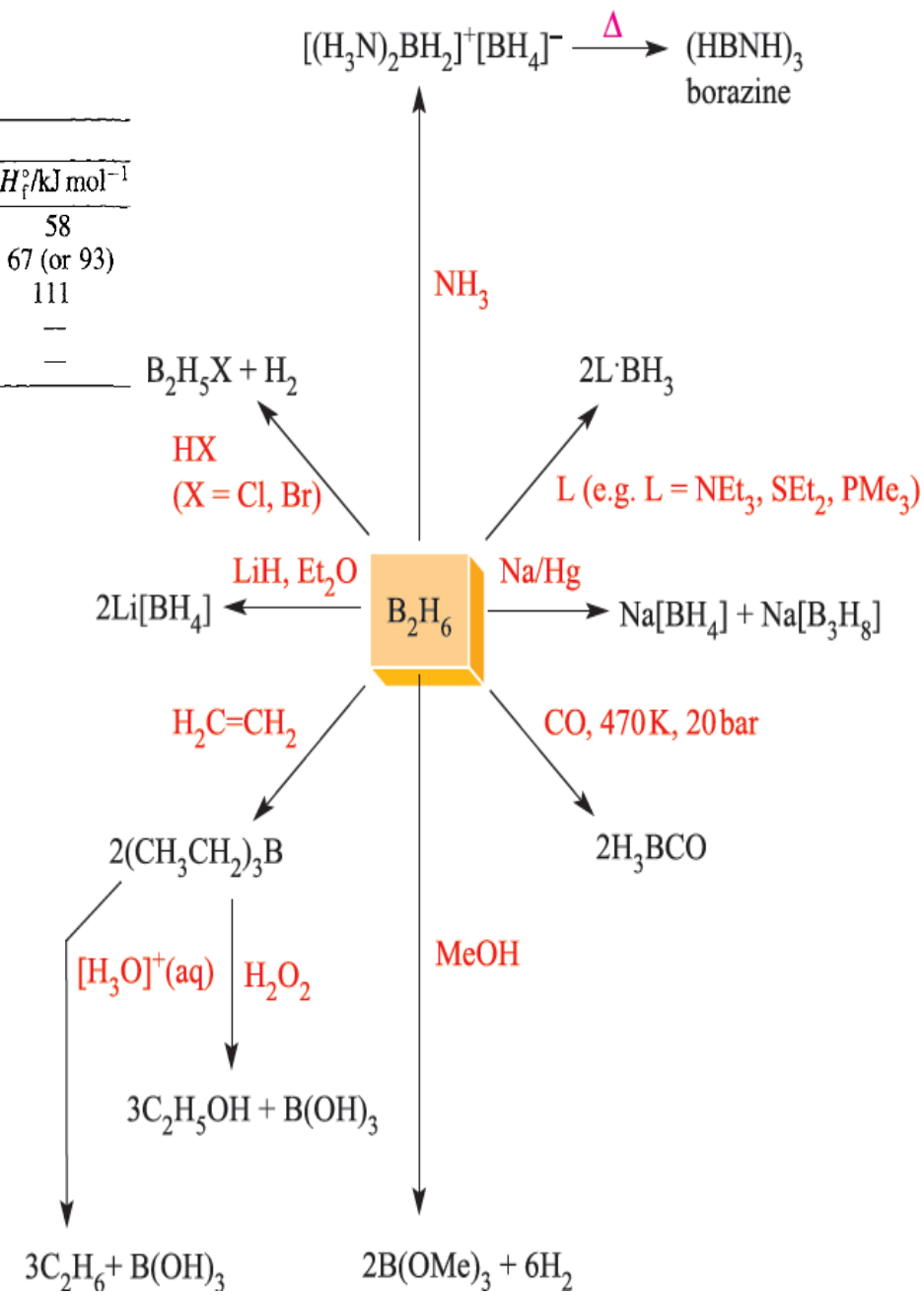


# ***Selected reactions of $B_2H_6$

Properties of some boranes

| *Nido*-boranes | | | | *Arachno*-boranes | | | |
|---|---|---|---|---|---|---|---|
| Compound | mp | bp | $\Delta H_f^\circ$/kJ mol$^{-1}$ | Compound | mp | bp | $\Delta H_f^\circ$/kJ mol$^{-1}$ |
| $B_2H_6$ | −164.9° | −92.6° | 36 | $B_4H_{10}$ | −120° | 18° | 58 |
| $B_5H_9$ | −46.8° | 60.0° | 54 | $B_5H_{11}$ | −122° | 65° | 67 (or 93) |
| $B_6H_{10}$ | −62.3° | 108° | 71 | $B_6H_{12}$ | −82.3° | ~85° (extrap) | 111 |
| $B_8H_{12}$ | Decomp | above −35° | — | $B_8H_{14}$ | Decomp | above −30° | — |
| $B_{10}H_{14}$ | 99.5° | 213° | 32 | $n$-$B_9H_{15}$ | 2.6° | 28°/0.8 mmHg | — |

**Many boranes may serve as ligands with transition metals**



➔**Boranes explode in contact with $O_2$ or water**

$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2$$ **( what is oxidizer and reducer in this reaction?)**

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

$$\Delta_r H^o = -2138 \text{ kJ per mole of } B_2H_6$$

➔**All 3A elements have a tendency to form complex hydride ions: $LiAlH_4$ and $LiBH_4$**

$$4LiH + AlCl_3 \xrightarrow{Et_2O} 3LiCl + Li[AlH_4]$$

$$Li + Al + 2H_2 \xrightarrow{250 \text{ bar}, 400 \text{ K}, \text{ether}} Li[AlH_4]$$

$$Li[AlH_4] + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

➔**Boron reacts with metals and metal oxides forming metal borides that may have a variable stoichiometry. Borides of many transition metals (W, Ti..) are very hard solids.**

$$Cr + nB \xrightarrow{1150^\circ} CrB_n \qquad V_2O_5 + B_2O_3 + 8C \xrightarrow{1500^\circ} 2VB + 8CO$$

**Borides can be both <u>boron rich and metals rich</u> (why?) and have complicated structures (chaines, zigzags, coordinated polygons)** $M_5B$, $M_4B_7$ $M_3B$, $M_5B_2$….. $M_{11}B_8$, MB, $M_{10}B_{11}$, $M_3B_4$, $M_2B_3$, $M_3B_5$, $MB_2$, $M_2B_5$, …. $MB_{18}$ and $MB_{66}$

# Boron halides: $BX_3$ and $B_2X_4$

➔ **Boron trihalides are monomeric and highly volatile under ordinary conditions ($BF_3$ is a colorless gas (bp 172 K), $BCl_3$ and $BBr_3$ are colorless liquids ($BCl_3$, mp 166 K, bp 285 K; $BBr_3$, mp 227 K, bp 364 K), while $BI_3$ is a white solid (mp 316 K). All can react directly**

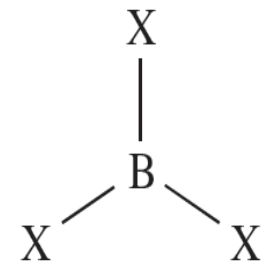
➔ **The molecules are planar and easily hydrolyze (why hydrolyze?)**

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

**(100%)**

$$4BF_3 + 6H_2O \longrightarrow 3[H_3O]^+ + 3[BF_4]^- + B(OH)_3$$

$$BX_3 + 3H_2O \longrightarrow B(OH)_3 + 3HX \quad X = Cl, Br, I$$




B–X distance:

| | |
|---|---|
| X = F | 131 pm |
| X = Cl | 174 pm |
| X = Br | 189 pm |
| X = I | 210 pm |

➔ **$HBF_4$ is a well defined compound, stable in water (why?) and it is a VERY STRONG acid (proton donor; think why?)**

$$B(OH)_3 + 4HF \longrightarrow [H_3O]^+ + [BF_4]^- + 2H_2O$$

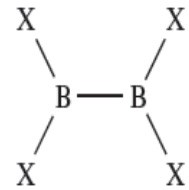
➔ **Halides react with protic compounds.**

**$BF_3$ form an adduct ; Other halides react by exchange.**

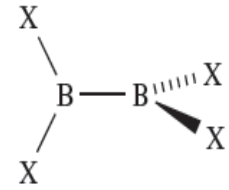
$$BF_3 + NH_3 \rightarrow BF_3 \cdot NH_3$$

$$BCl_3 + NH_3 \rightarrow B(NH_2)_3 + 3HCl$$

**Di-halides**

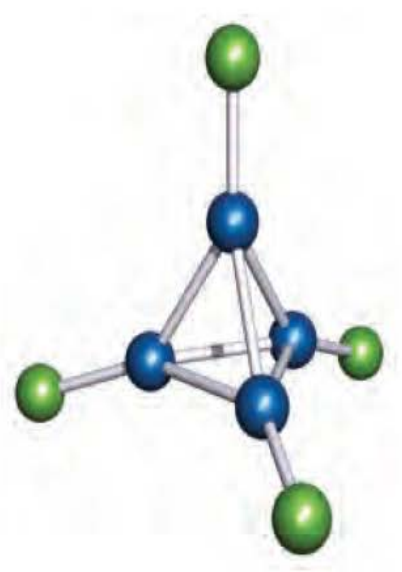



**$B_2F_4$**

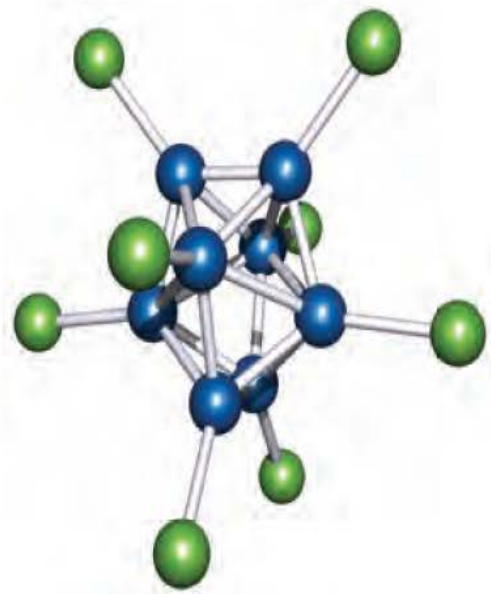



**$B_2Cl_4$**

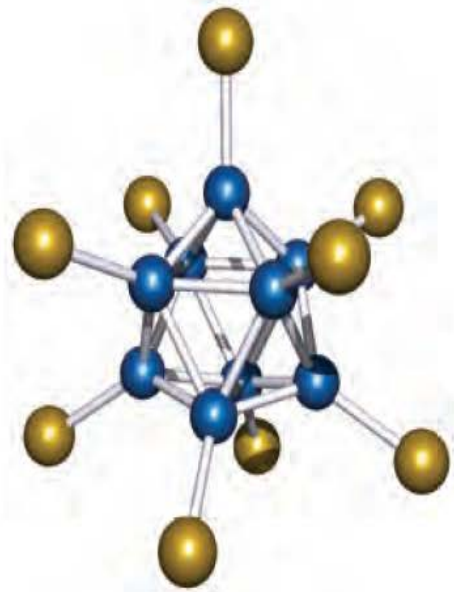
# ***The family of BnXn (X=Cl, Br, I)



$B_4Cl_4$



$B_8Cl_8$



$B_9Cl_9$

$$B_{10}H_{14} + 13X_2 \xrightarrow[470\,K,\,20\,h]{\text{In an autoclave}} B_9X_9 + BX_3 + 14HX$$

(X = Br or I)

# Pure metals

➔ **Aluminum readily oxidizes in air (as powder; bulk is protected by the oxide); in dilute mineral acids but is passivated by concentrated $HNO_3$ (and 100% $H_2SO_4$).**

$$Al + 3H_2SO_4 \longrightarrow Al(SO_4)_3 + 3H_2$$

➔ **Aluminum react with water (if its protective Al-oxide layer is removed, for instance by Hg)**

➔ **Similar to Be, aluminum dissolves in strong bases**

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2$$

➔ **In and Ga do not react with water but slowly oxidized by air and dissolve in acids**

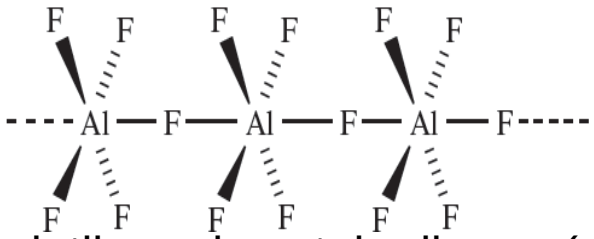
➔ **Ga slowly reacts with bases; In does not (can you guess why?)**

➔**Tl does not react with water and bases. VERY slowly reacts with HX (X=F,Cl forming Tl(I); dissolves in $HNO_3$, $HClO_4$, $H_2SO_4$**

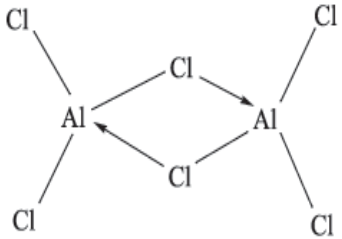
# Halides of Al-Tl

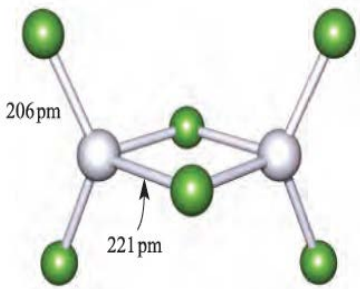
➔ The tri-fluorides of Al, Ga, In and Tl are non-volatile solids with high melting points (can be be obtained directly) or at high temperatures:

$$Al_2O_3 + 6HF \xrightarrow{970\,K} 2AlF_3 + 3H_2O$$




➔All other $MX_3$ (M=Al, Ga or In, X=Cl, Br or I) are volatile and contain dimers ( compare with diborane!) $M_2X_6$ in solid and in vapor state.




➔ solid $AlCl_3$ hydrolyze upon contact with water (compare with B). In dilute solutions $AlCl_3$ gives

$$AlCl_3 + H_2O \rightarrow [Al(H_2O)]_6^{3+} + 3Cl^-$$

➔ Excess of Cl- causes formation of $[AlCl_4)]^-$ (do you expect it with F?)

➔Halides (III) of Ga and In are stable solids but hydrolyze easily (why?)

➔ Tl tri-halides are less stable and convert into Tl(I) salts due to **$s^2$ neutrality effect**

$$TlBr_3 \longrightarrow TlBr + Br_2$$

**( what is oxidizer and reducer in this reaction?)**

➔ **The decrease in stability of the higher oxidation state on going from the binary fluoride to iodide is a general feature of all metals that exhibit more than one oxidation state.**

**Lower oxidation state Al, Ga, In and Tl halides**

➔AlX (X=F, Cl, Br or I) are unstable but can be prepared at high temperature

$$AlCl_3 + 2Al \xrightarrow{900\ ^oC} 3AlCl$$

At lower temperature reaction goes in the opposite direction

➔ In and Ga do not form MX (M=In, Ga; X=F, Cl, Br or I) but $Ga^+[GaCl_4]^-$ $In^+[InCl_4]^-$

( InCl is marginally stable)

➔ Tl mono-halides are stable and poorly soluble

**( What would happen to $AlCl_3$ upon heating to 1000 ˚C in vacuum?)**

# Oxides and hydroxides

➔ Note that in p-block:

- **boron oxides are exclusively acidic;**
- **aluminum and gallium oxides are amphoteric;**
- **indium and thallium oxides are exclusively basic;**
- **TlOH is a strong base (as strong as KOH)**

➔ $B_2O_3$ is a glassy solid containing randomly connected $BO_3$ triangular units. It also forms a crystal. $B_2O_3$ is soluble in water and forms boric acid ($H_3BO_3$) is a very weak **monobasic** acid and acts exclusively by hydroxylion acceptance rather than proton donation:

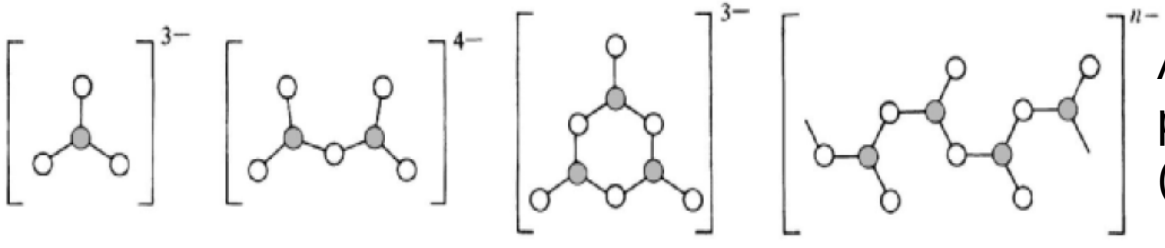
$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + B(OH)_4^-$$

➔ $H_3BO_3$ acts as a strong acid in anhydrous $H_2SO_4$

$$H_3BO_3 + 6H_2SO_4 \rightarrow H_2O^+ + H_2SO_4^- + [B(H_2SO_4^-)_4]^-$$

➔ $H_3BO_3$ decomposes upon heated already at 100 °C $H_3BO_3 \rightarrow H_2O + HBO_2$

➔ In borates Boron usually keeps link to 3 oxygen ions; some times to four oxygen ions (tetrahedral). Orthoborates (isolated $BO_3$) are rare: M $BO_3$

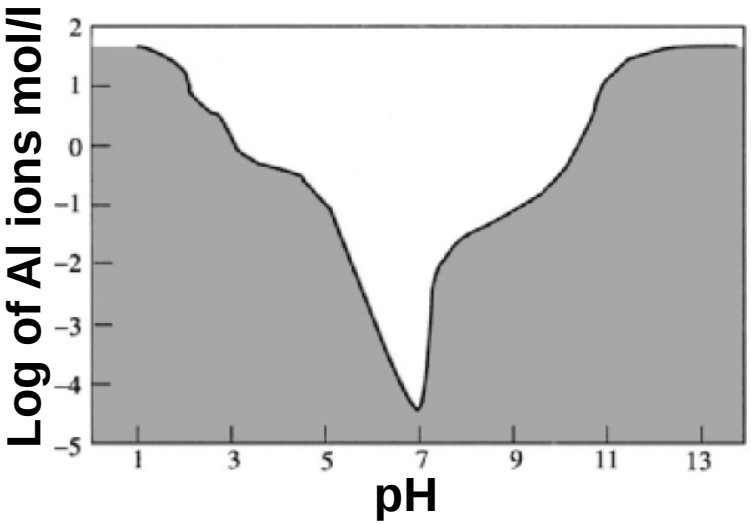


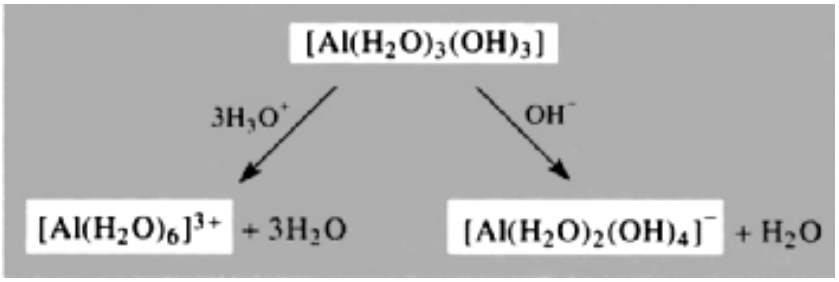
(113) $[BO_3]^{3-}$ (114) $[B_2O_5]^{4-}$ (115) $[B_3O_6]^{3-}$ (116) $[(BO_2)^-]_n$

Almost all borates are POLYNUCLEAR: pyroborates $Mg_2B_2O_5$ (Co, Fe) (also tetraborates; pentaborates etc)

# Stability of cations (salts) in aqueous solution

➔ Al (think about Ga, In and Tl) salts are stable only in very high or very low pH.



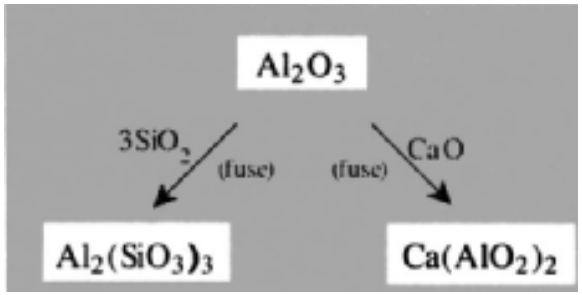




➔Al salts of weak acids (cyanides, acetates, phosphates) hydrolyze;

➔The rate of dissolution of $Al_2O_3$ and its hydrates strongly depends on microstructure. Bulk $Al_2O_3$ is almost completely inert towards mineral acids. AlO(OH) is more reactive;

$Al(OH)_3$ dissolves easily in acids and bases.

➔ Al-containing melts are also amphoteric



➔ $Al_2O_3$ bulk (crystal sapphire) is inert and dissolves noticeably only in phosphoric acid above 150 C;
➔ nanocrystalline $Al_2O_3$ is soluble in bases and acids;
➔ there are number of modifications of AlO(OH) and $Al(OH)_3$ soluble both in acids and bases;
➔ upon heating they lose water

➔ $Al_2O_3$ forms many ternary mixed oxides $M^{2+}Al_2O_4$ (spinel); β-alumina $Na_2O{\bullet}11Al_2O_4$;
$Ca_3Al_2O_6$ is the main component of Portland cement;
It hydrates forming hexa-hydrate: $Ca_3Al_2O_6{\bullet}6H_2O$

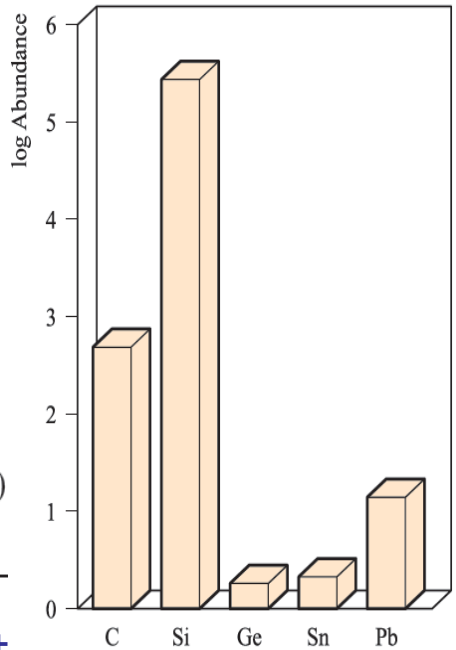
➔ In and Ga salts are similar to that of Al; They form similar compounds.
➔ Tl (III) is highly unstable. Tl(I) is similar to potassium
➔ In, Ga and Al compounds with the group 5A (nitrides, arsenide, phosphides) are important semiconductors GaAs, InP, GaN, AlP etc.

# Group 4A [noble gas]($s^2p^2$): C, Si, Ge, Sn and Pb

| Property | C | Si | Ge | Sn | Pb |
|---|---|---|---|---|---|
| Atomic number, $Z$ | 6 | 14 | 32 | 50 | 82 |
| Ground state electronic configuration | $[He]2s^22p^2$ | $[Ne]3s^23p^2$ | $[Ar]3d^{10}4s^24p^2$ | $[Kr]4d^{10}5s^25p^2$ | $[Xe]4f^{14}5d^{10}6s^26p^2$ |
| Enthalpy of atomization, $\Delta_a H^o(298\,K)/kJ\,mol^{-1}$ | 717 | 456 | 375 | 302 | 195 |
| Melting point, mp / K | >3823‡ | 1687 | 1211 | 505 | 600 |
| Boiling point, bp / K | 5100 | 2628 | 3106 | 2533 | 2022 |
| Standard enthalpy of fusion, $\Delta_{fus} H^o(mp)/kJ\,mol^{-1}$ | 104.6 | 50.2 | 36.9 | 7.0 | 4.8 |
| First ionization energy, $IE_1/kJ\,mol^{-1}$ | 1086 | 786.5 | 762.2 | 708.6 | 715.6 |
| Second ionization energy, $IE_2/kJ\,mol^{-1}$ | 2353 | 1577 | 1537 | 1412 | 1450 |
| Third ionization energy, $IE_3/kJ\,mol^{-1}$ | 4620 | 3232 | 3302 | 2943 | 3081 |
| Fourth ionization energy, $IE_4/kJ\,mol^{-1}$ | 6223 | 4356 | 4411 | 3930 | 4083 |
| Metallic radius, $r_{metal}$ / pm | – | – | – | 158 | 175 |
| Covalent radius, $r_{cov}$ / pm* | 77 | 118 | 122 | 140 | 154 |
| Ionic radius, $r_{ion}$ / pm** | – | – | 53 ($Ge^{4+}$) | 74 ($Sn^{4+}$)<br>93 ($Sn^{2+}$) | 78 ($Pb^{4+}$)<br>119 ($Pb^{2+}$) |
| Standard reduction potential, $E^o(M^{2+}/M)/V$ | – | – | – | −0.14 | −0.13 |
| Standard reduction potential, $E^o(M^{4+}/M^{2+})/V$ | – | – | – | +0.15 | +1.69*** |
| NMR active nuclei (% abundance, nuclear spin) | $^{13}C$ (1.1, $I=\frac{1}{2}$) | $^{29}Si$ (4.7, $I=\frac{1}{2}$) | $^{73}Ge$ (7.8, $I=\frac{9}{2}$) | $^{117}Sn$ (7.6, $I=\frac{1}{2}$);<br>$^{119}Sn$ (8.6, $I=\frac{1}{2}$) | $^{207}Pb$ (22.6, $I=\frac{1}{2}$) |

**Electronegativity**

| | | | |
|---|---|---|---|
| 3<br>Li<br>1.0 | 4<br>Be<br>1.5 | 5<br>B<br>2.0 | 6<br>C<br>2.5 |
| 11<br>Na<br>0.9 | 12<br>Mg<br>1.2 | 13<br>Al<br>1.5 | 14<br>Si<br>1.8 |
| 19<br>K<br>0.8 | 20<br>Ca<br>1.0 | 31<br>Ga<br>1.6 | 32<br>Ge<br>1.8 |
| 37<br>Rb<br>0.8 | 38<br>Sr<br>1.0 | 49<br>In<br>1.7 | 50<br>Sn<br>1.8 |
| 55<br>Cs<br>0.7 | 56<br>Ba<br>0.9 | 81<br>Tl<br>1.8 | 82<br>Pb<br>1.8 |




**4A elements are relatively abundant**

# The factors defining chemical properties

1. **Carbon is a very typical non-metal with high electronegativity (like S, As, P) and extremely small valence radius.**
2. **Si-Pb have similar electronegativity.**
3. **Covalent radii increase Si-Pb=> strength of the covalent bond drops;**
4. **Inert $s^2$ pair effect increases quickly from Ge to Pb**

1. **Non-metallic properties (strength of C-O bond) rapidly drop in line C-Pb.**
2. **Carbon may have CN from 3 and 4 (typical) to 8 (very rare). As <u>a non-metal with a small radius</u> it has a strong tendency to catenation (=all organic compounds) and covalent bonding to other non-metals.**
3. **Si has much weaker tendency to catenation (WHY???) and almost always has CN=4. Acidity is much weaker than that of C. No basic properties. Strong tendency to form strong Si-O-Si bonds (WHY???)**
4. **Ge, Sn and Pb are amphoteric. Ge is more acidic than basic. Pb is more basic than acidic (look at the radii!).**
5. **Sn and Pb form stable 2+ state. For Pb 2+ state is dominant.**

# *****1. Inorganic chemistry of carbon

1. Exists in at least seven modifications: 2 forms of graphite; 2 forms of diamond (cubic and hexagonal); lonsdaleite; fullerenes (family); nano-tubes; amorphous.

$$C(\text{diamond}) \rightarrow C(\text{graphite})$$

$\alpha$ graphite is the stable phase at room temperature

$$\Delta_r G^o(298\,K) = -2.9\,kJ\,mol^{-1}$$

All forms of graphite are semimetals; all diamonds are dielectrics.

2. In graphite and fullerenes, C has a planar triangular coordination. In diamonds, C has tetrahedral (4NN) coordination

3. ****Find out what is the difference between $\beta$ and $\alpha$ graphite.*

4. Carbon has a number of excited states (3 states s2p2 and two states s1p3). Experimentally observed only four of them (s1p3 is uncorrelated spins is hypothetical).

**end of *****

---

6. **Carbon may CN from 0 to 8, which is the main reason for the richness of its chemistry. Typical CN is 3 or 4.**

# Chemical properties of carbon

1. Diamond is extremely unreactive at room temperature due to KINETIC reasons.

**The chemistry of carbon is defined by its ability to change hybridization and coordination number**

2. Graphite can be oxidized at low temperatures (<100 C) by concentrated $HNO_3$, $HNO_3/H_2SO_4+KClO_4$; electrochemically in $NaNO_3/KMnO_4$+conc $H_2SO_4$. The products "graphite oxides" are of variable stoichiometry.

$$C(\text{graphite}) \xrightarrow{\text{Hot concentrated } HNO_3} C_6-(COOH)_6 \text{ [mellitic acid]}$$

3. Graphite reacts with $F_2$ above 400 C and gives non-stoichiometric $CF_x$; At high temperatures, the reaction gives $CF_4$, $C_2F_6$ and other $C_xF_{2x+2}$

***4. At room temperature gaseous mixture of $F_2$/HF reacts with graphite and gives insertion products: $C_xF$ x=3.57 – 4;

***5. At high temperature C reacts with most non-metals (O, S, Si, B and others) and metals.

***6. Graphite forms with alkali metals intercalation compounds (example $K_8C$); (see the lecture on alkali metals)

# Carbides

➔ Carbon forms binary compounds with **most elements**. Carbides are those among them, in which carbon is formally an oxidizer. Carbides can be obtained by:

a) Direct combination of the elements above 2000 C;

b) Reaction of the metal oxide with carbon at high temperature;

c) Reaction of the heated metal with gaseous hydrocarbons;

d) Reaction of acetylene with electropositive metal ion in water or liquid ammonia.

➔ Carbides can be divided in a few groups:

a) Salt like carbides containing

✱ $C^{4-}$ ion: $Be_2C$; $Al_4C_3$ formed with small cations with high charges.

✱ Acetylides contain $C_2^{2-}$ ions are formed by alkali metals, alkaline earth metals, lanthanoids, group 1b (Cu, Ag, Au), group 2b (Zn, Cd, Hg). Practically important $CaC_2$ (millions tons per year)

$$CaO + 3C \xrightarrow{2200-2250^\circ C} CaC_2 + CO; \quad CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

$$CaC_2 + N_2 \xrightarrow{1000^\circ - 1200^\circ} CaCN_2 + C$$

# Carbides

➔ Salt like carbides (continuation)

✸ Carbides containing linear $C_3^{2-}$ ions $Li_4C_3$, $Mg_2C_3$;

b) Interstitial carbides $M_3C$ are formed by all lanthanides (NaCl structures with 1/3 occupancy)

c) Carbides MC M=Ti, Zr, Hf; V, Nb, Ta; Mo, W

All interstitial carbides are VERY hard, metallic like and have extremely m.p.

➔ Cr, Mn, Fe, Co, Ni form $M_3C$ or $M_2C$ carbides with large CN

# Hard covalent carbides

➔Carbon forms very hard (like diamond) SiC (carborundum, rare mineral moissanite). Forms more than 200 phases. Most important hexagonal with CN=4 ( why?).

➔Carbon forms $B_4C$ which contains C-C-C links inside boron lattice. It is extremely hard. Used as a component of tank armor.

# Hydrides, Halides and Oxo-halides of Carbon

| Property | $CH_4$ | $CF_4$ | $CCl_4$ | $CBr_4$ | $CI_4$ |
|---|---|---|---|---|---|
| MP/°C | −182.5 | −183.5 | −22.9 | 90.1 | 171 (d) |
| BP/°C | −161.5 | −128.5 | 76.7 | 189.5 | ~130 (subl) |
| Density/g cm$^{-3}$ (at $T$°C) | 0.424 (−164°) | 1.96 (−184°) | 1.594 (20°) | 2.961 (100°) | 4.32 (20°) (s) |
| $-\Delta H_f^\circ$/kJ mol$^{-1}$ | 74.87 | 679.9 | 106.7 (g) 139.3 (l) | 160 (l) | — |
| $D(X_3C-X)$/kJ mol$^{-1}$ | 435 | 515 | 295 | 235 | — |

➔ Stability of halides quickly drops from F to I. $CF_4$ is completely inert; $CI_4$ is unstable. In all halides, carbon has CN=4

$$CO_2 + 2F_2 \rightarrow CF_4 + O_2$$

***➔ Carbon forms two main oxides: CO and $CO_2$ and a number of less stable oxides: $C_3O_2$, $C_5O_2$ and $C_{12}O_9$ (and non-stoichiometric graphite oxide). Example of the structure: $O = C = C = C = O$

***➔ Carbon forms oxo-halides $COX_2$ (X=F, Cl, Br, I)

➔ Carbon and $CO_2$ are in equilibrium: $C + CO_2 \leftrightarrow 2CO$ (Above 1000 °C)

***➔ CO is a strong reducer. At room temperature it reduces noble metals from aqueous solutions; At elevated temperature it reduces many semi-noble metals from oxides.

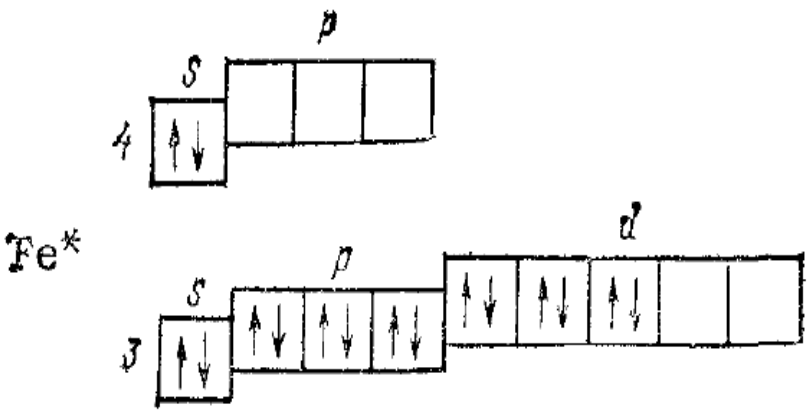
***➔Main source of CO is the water shift reaction: $C + H_2O \rightarrow CO + H_2$

➔In CO the bonding is σ+π+donated-π. Therefore, CO may participate in a variety of reaction:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (50\text{-}100\ \text{atm}, 400\ ^{o}C)$$

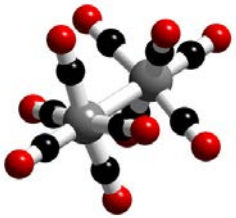
$$CO + NaOH \leftrightarrow CHO_2Na$$

➔CO forms compounds with d-elements- carbonyls by DONATING the electron pair until all orbitals are filled (what would be if Ni reacts with CO?)




$$Fe + CO \rightarrow Fe(CO)_5$$

➔If the number of available orbitals becomes odd, di-carbonyls are formed: $Mn_2CO_{10}$.
What is Co carbonyl?



➔$CO_2$ is a typical acid anhydride. In water it is partly hydrated.

$$\left.\begin{array}{l} CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (slow)} \\ H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \text{ (fast)} \end{array}\right\} pH < 8$$

$$\left.\begin{array}{l} CO_2 + OH^- \rightleftharpoons HCO_3^- \text{ (slow)} \\ HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \text{ (fast)} \end{array}\right\} pH > 10$$

➔Carbonates of alkali and alkaline earth metals are stable. Many carbonates of transition metals, noble metals or semi-noble metals decompose in contact with water.

***➔Carbon forms a number of chalcogenides: $CS_2$, CS and $C_3S_2$ and a number of compounds with S-S and C-C bonds (see below)

# Cyanides and Other Carbon – Nitrogen Compounds

➔Cyanide $CN^-$ is isoelectronic to $C_2^{2-}$, CO, $N_2$

Cyanides are SIMILAR to halogenides

➔Cyanate ion OCN- is isoelectronic with $CO_2$, $N^{3-}$

➔HCN is a very weak acid (weaker than HF and $H_2CO_3$)

| Name | Conventional formula | $r$(C–N)/pm | Remarks[a] |
|---|---|---|---|
| Cyanogen | N≡C–C≡N | 115 | Linear; $r$(C–C) 138 pm (short) |
| Paracyanogen | $(CN)_x$ | — | Involatile polymer, see text |
| diisocyanogen | CN–NC | 118 (calc.) | Linear, symmetric, unstable[140] |
| isocyanogen | CN–CN | 118&116 (calc.) | Zig-zag, unsymmetric, stable[140] |
| Hydrogen cyanide | H–C≡N | 115.6 | Linear; $r$(C–H) 106.5 pm |
| Cyanide ion | $(C{\equiv}N)^-$ | 116 | $r_{eff}$ 192 pm when "freely rotating" in MCN |
| Cyanides (nitriles) | M–C≡N (R–C≡N) | 115.8 | Linear; $r$(C–C) 146.0 pm (for MeCN) |
| Isocyanides | R–N≡C | 116.7 | Linear, $r$($H_3C$–N) 142.6 pm (for MeNC). Coordinated isocyanides are slightly bent, e.g. $[M(\leftarrow C{=}N{-}C_6H_5)_6]$ angle CNC 173°. $r$(C=N) 117.6 pm: bridging modes are also known, e.g. structure (1), p. 321 |
| Cyanogen halides (halogen cyanides) | X–C≡N | 116 | Linear |
| Cyanamide | $H_2N$–C≡N | 115 | Linear NCN; $r$(C–$NH_2$) 131 pm |
| Dicyandiamide | N≡C–N=C$(NH_2)_2$ | 122–136 | See structure (2), p. 321 |
| Cyanuric compounds | $\{-C(X){=}N-\}_3$ | 134 | Cyclic trimers; X = halogen, OH, $NH_2$ |
| Cyanate ion | $(O{-}C{\equiv}N)^-$ | ~121 | Linear |
| Isocyanates | R–N=C=O | 120 | Linear NCO; ∠RNC ~ 126° |
| Fulminate ion | $>(C{=}N{-}O)^-$ | 109 | Linear; another form of AgCNO has $r$(C–N) 112 pm |
| Thiocyanate ion | $(S{-}C{\equiv}N)^-$ | 115 | Linear |
| Thiocyanates | R–S–C≡N (M–S–C≡N) | 116 | Linear NCS; ∠RSC 100° in MeSCN; ∠MSC variable (80–107°) |
| Isothiocyanates | R–N=C=S | 122 | Linear NCS; ∠HNC 135° in HNCS; ∠MNC variable (111–180°) |

# ****Cyanides

**Andrussow process**

$$CH_4 + NH_3 + 1\tfrac{1}{2}O_2 \xrightarrow[2\ atm/1000-1200^\circ]{Pt/Rh\ or\ Pt/Ir} HCN + 3H_2O$$

Degussa process

$$CH_4 + NH_3 \xrightarrow[1200-1300^\circ]{Pt} HCN + 3H_2$$

➔Production of HCN is >800,000 tons. Used for production of nitriles.

---

➔$CN^-$ is a VERY strong ligand. In its presence many semi-noble metals are oxidized by hydrogen and noble metals by oxygen forming complex cyanides

$$H[Au(CN)_2]$$

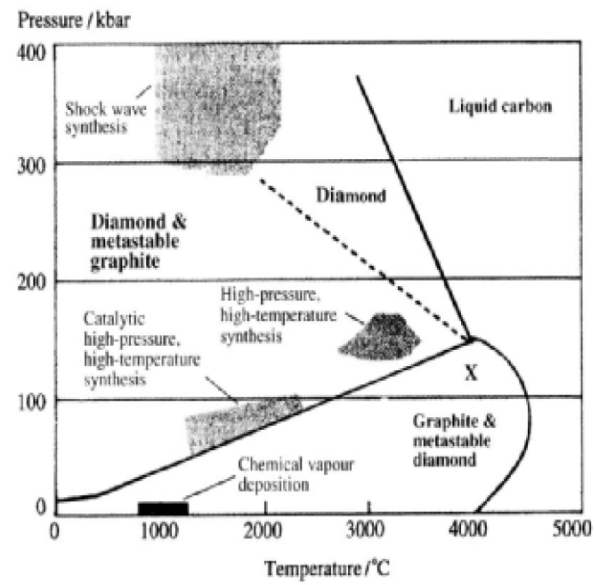
$$K[Ag(CN)_2]$$

***➔Dehydration of HCN produces CN-CN, which easily polymerizes in polycyane $(-C{=}N-)_n$

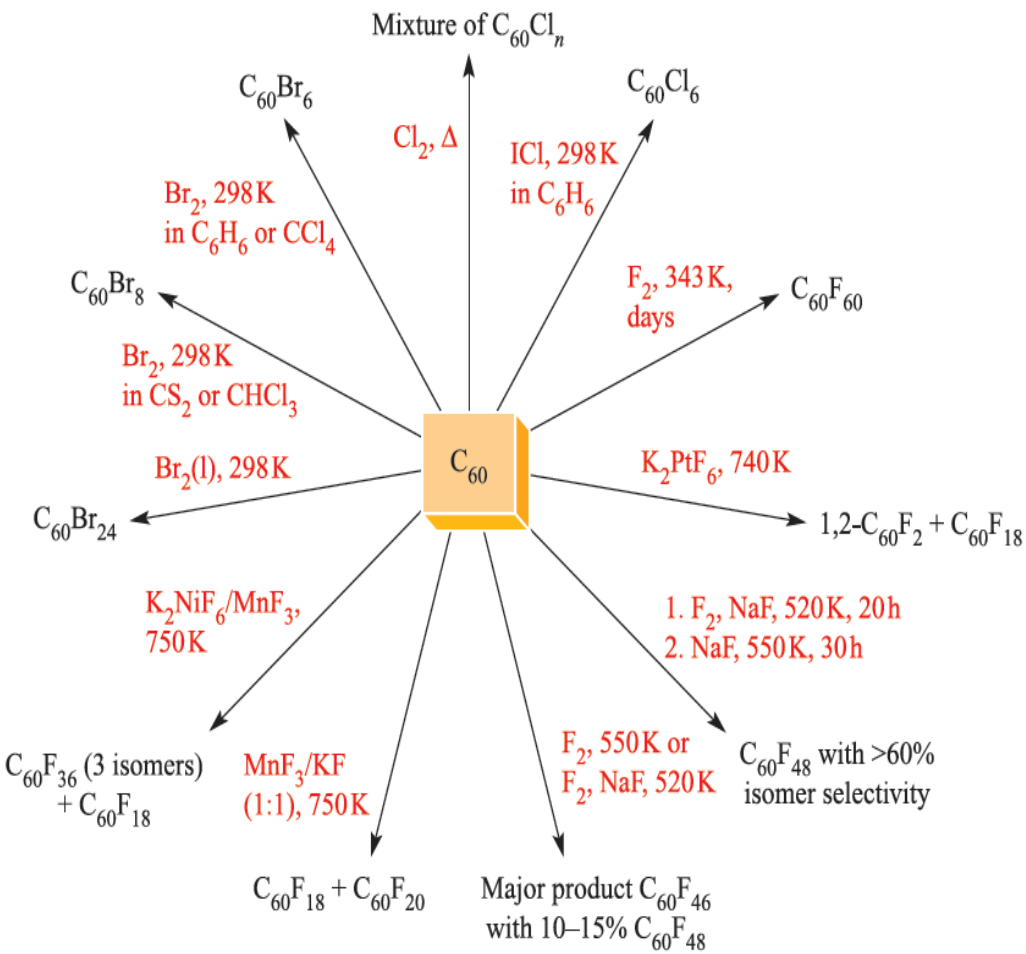
# ***Graphite vs diamond

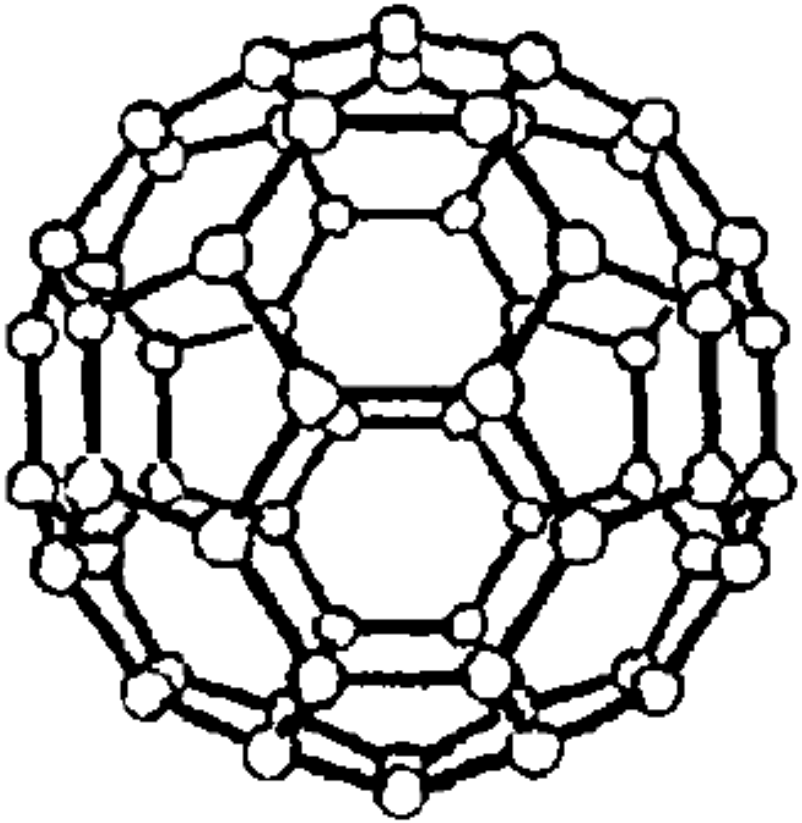
| Property | α-Graphite | Diamond |
|---|---|---|
| Density/g cm$^{-3}$ | 2.266 (ideal) varies from 2.23 (petroleum coke) to 1.48 (activated C) | 3.514 |
| Hardness/Mohs | <1 | 10 |
| MP/K | 4100 ± 100 (at 9 kbar) | 4100 ± 200 (at 125 kbar) |
| $\Delta H_{subl}$/kJ mol$^{-1}$ | 715[a] | ~710[a] |
| Refractive index, $n$ (at 546 nm) | 2.15 (basal)<br>1.81 ($c$-axis) | 2.41 |
| Band gap $E_g$/kJ mol$^{-1}$ | — | ~580 |
| $\rho$/ohm cm | (0.4–5.0) × $10^{-4}$ (basal)<br>0.2–1.0 ($c$-axis) | $10^{14}$–$10^{16}$ |
| $\Delta H_{combustion}$/kJ mol$^{-1}$ | 393.51 | 395.41 |
| $\Delta H_f^\circ$/kJ mol$^{-1}$ | 0.00 (standard state) | 1.90 |

[a]Sublimation to monatomic C(g).



# ***Fullerenes

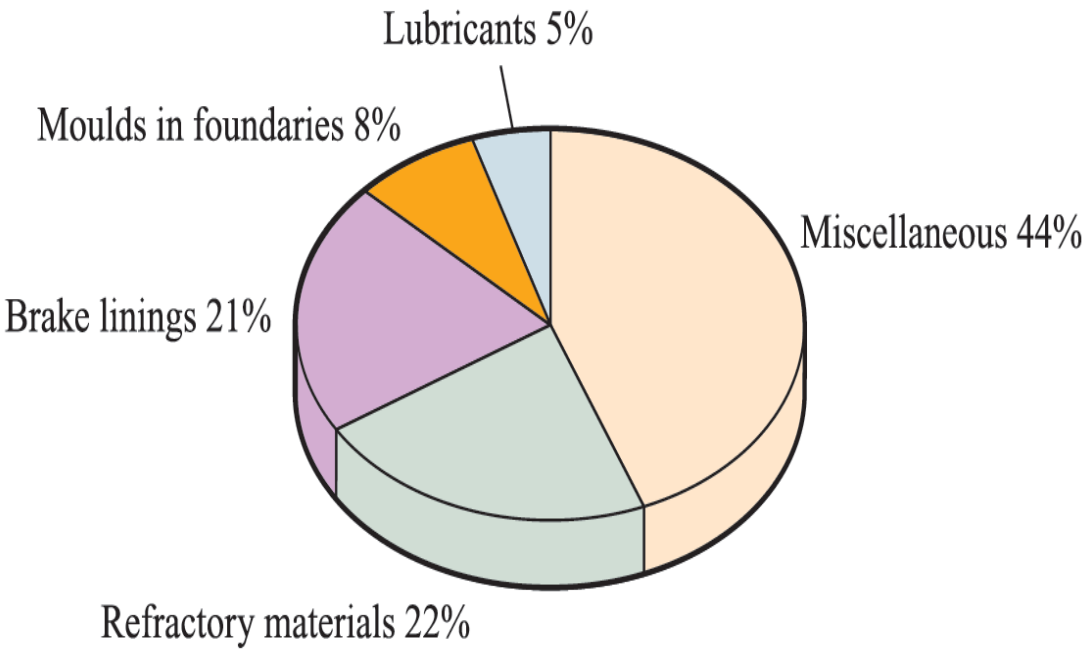

Mixture of $C_{60}Cl_n$
$C_{60}Br_6$
$Cl_2$, Δ
$C_{60}Cl_6$
ICl, 298 K in $C_6H_6$
$Br_2$, 298 K in $C_6H_6$ or $CCl_4$
$C_{60}Br_8$
$F_2$, 343 K, days
$C_{60}F_{60}$
$Br_2$, 298 K in $CS_2$ or $CHCl_3$
$C_{60}$
$Br_2$(l), 298 K
$K_2PtF_6$, 740 K
$C_{60}Br_{24}$
1,2-$C_{60}F_2$ + $C_{60}F_{18}$
$K_2NiF_6/MnF_3$, 750 K
1. $F_2$, NaF, 520 K, 20 h
2. NaF, 550 K, 30 h
$C_{60}F_{36}$ (3 isomers) + $C_{60}F_{18}$
$MnF_3$/KF (1:1), 750 K
$F_2$, 550 K or $F_2$, NaF, 520 K
$C_{60}F_{48}$ with >60% isomer selectivity
$C_{60}F_{18}$ + $C_{60}F_{20}$
Major product $C_{60}F_{46}$ with 10–15% $C_{60}F_{48}$



# *** Coordination Numbers of Carbon

| CN | Examples | Comments |
|---|---|---|
| 0 | C atoms | High-temp, low-press, gas phase |
| 1 | CO | Stable gas |
| | $CH^{\bullet}$ (carbynes) | Reactive free-radical intermediates |
| 2 (linear) | $CO_2$, $CS_2$ | Stable gas, liquid |
| | HCN, HC≡CH, $NCO^-$, $NCS^-$ | The ions are isoelectronic with $CO_2$ and COS respectively |
| | $M(CO)_n$ | Terminal M–CO groups sometimes <180° |
| | RP=C=PR (R = 2,4,6-$Bu^t_3C_6H_2$) | Angle PCP 172.6°[63] |
| 2 (bent) | $Ph_3P{:}C{:}PPh_3$ | A bis(ylide) with angle PCP 130.1° (and 143.8°)[64] |
| | $:CH_2$, $:CX_2$ (carbenes) | Reactive intermediates with 1 lone-pair and 1 vacant orbital; (carbenes are bent for X = H, F, OH, OMe, $NH_2$, but linear if X is less electronegative, e.g. $BH_2$, BeH, Li)[65] |
| | $\bullet CH_2\bullet$, $\bullet CPh_2\bullet$ (methylenes) | Reactive intermediates with 2 unpaired electrons |
| 3 (planar) | COXY (X = H, hal, OH, $O^-$ R, Ar) | Stable oxohalides, carbonates, carboxylic acids, aldehydes, ketones, etc. |
| | $[C(N{=}PCl_3)_3]^+[SbCl_6]^-$ | Colourless crystals prepared from $[C(N_3)_3]^+ + PCl_3$[66] |
| | $M_m(CO)_n$ | Metal carbonyl clusters with bridging CO groups M–C(O)–M |
| | $[PhC(OMe)M(CO)_5]$ | Stable metal — carbene complexes, e.g. M = Cr, W |
| | $CH_3^+$ (carbonium ions) | Unstable reaction intermediates with 1 vacant orbital[67] |
| 3 (pyramidal) | $CH_3^-$, $CPh_3^-$ (carbanions), RMgX | Unstable reaction intermediates with 1 lone pair of electrons |
| | $Ph_3C^{\bullet}$, $R_3C^{\bullet}$ (free radicals) | Paramagnetic species of varying stability |
| 3 (T-shaped) | $[Ta(=CHCMe_3)_2(2,4,6\text{-}Me_3C_6H_2)(PMe_3)_2]$ | The unique H is equatorial and angle Ta=C–$CMe_3$ is 169°[68] |
| 4 (tetrahedral) | $CX_4$, etc. | 4-coord covalent compds such as $CF_4$, $C_2H_6$, CHXYZ, etc. |
| | $M_m(CO)_n$ | Metal carbonyl clusters with triply bridging CO groups (p. 928) |
| 4 (see-saw, $C_{2v}$) | $[Fe_4C(CO)_{13}]$ | The $\mu_4$-carbido C caps $Fe_4$ "butterfly"[69] |
| 5 | $Al_2Me_6$ | Alkyl-bridged organometallics involving 3c–2e, bonds (pp. 259, etc.) |
| | $C_2B_4H_6$, etc. | Several stable carboranes (p. 183) |
| | $[(\eta^5\text{-}C_5H_5)NiRu_3(CO)_9CCHBu^t]$ | The C atom bonds to $CHBu^t$ and to $M_4$ "butterfly"[70] |
| | $[Os_5C(CO)_{13}HL_2]$ | The $\mu_5$-carbido C bonds to all 5 Os[71] |
| | $[C\{AuPPh_3\}_5]^+BF_4^-$ | trigonal bipyramidal cation[72] |
| 6 | $C_2B_{10}H_{12}$, etc. | Several stable carboranes (p. 185) |
| | $[C(AuPPh_3)_6]^{2+}[BF_3(OMe)]_2^-$ | octahedral dication[73] |
| 7 | $(LiMe)_4$ crystals | See structure, p. 104 |
| 8 | $Be_2C$ (antifluorite), | See structure, p. 118 |
| | $[Co_8C(CO)_{18}]^{2-}$ | See structure, p. 1142 |

# ***Uses of natural graphite



# Silicon

**➔Silicon (27.2 wt%) is the most abundant element in the earth's crust after oxygen (45.5%), and together these 2 elements comprise 4 out of every 5 atoms available near the surface of the globe.**

(some common minerals quartz SiO2, olivine (Mg,Fe)2SiO4, biotite mica [(K,H),(Mg,Fe),(Al,Fe),( $SiO_4)_3$], muscovite mica [ $KAl_2$ ($AlSi_3O_{10}(OH)_2$], feldspar [$KAlSi3O_8$],

**➔Industrial production: $SiO_2$ is taken in large excess to prevent SiC formation**

$$SiO_2 + 2C = Si + 2CO$$

**➔Most of Si is used to deoxidize steel**

**➔The chemical properties of Si are defined by three factors:**

**1. Almost always the valence is 4; though valence of 2 is known ( SiO for instance)**

**2. In most compounds Si is tetrahedrally coordinates (CN=4); CN=6 is in $SiF_6^{2-}$**

**3. Si-Si bonding exists but is much weaker than C-C;**

➔At room temperature Si has a diamond structure with coordination 4. Under pressure is undergoes a series of phase transitions with increasing CN (compare with carbon)

$$4(\text{Si-I}) \xrightarrow{8.8\ \text{GPa}} 6(\text{Si-II}) \xrightarrow{16\ \text{GPa}} 8(\text{Si-V}) \xrightarrow{\sim 40\ \text{GPa}} 12(\text{Si-VII})$$

➔bulk Si is shiny gray crystals covered by a thin layer of $SiO_2$.

➔ At room temperature Si is relatively unreactive (except $F_2$). It dissolves in in a mixture of $HNO_3$+HF, hot conc. KOH some organic amines producing hydrogen

$$Si + 4KOH \rightarrow K_4SiO_4(aq) + 2H_2 \uparrow \qquad Si + 4HNO_3 + 6HF \rightarrow H_2SiF_6(aq) + NO_2 \uparrow + 5H_2O$$

➔Upon heating (or molten) Si reacts with $Cl_2$ (300 C) and $Br_2$ and $I_2$ (500 C);

➔ All Si halides hydrolyze

$$2SiF_4 + 4H_2O \rightarrow SiO_2 + 2[H_3O]^+ + [SiF_6]^{2-} + 2HF$$

$$SiO_2 + 4HF = SiF_4\uparrow + 2H_2O \qquad SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

$$SiF_4 + 2HF = H_2SiF_6$$

*** ➔ interesting: K, Cs and Rb salts of $H_2[SiF_6]$ are poorly soluble (<0.2 g/100 gm)

➔Halides (II) can be prepared by they are not stable

➔ Si reacts with C forming SiC. This is the most stable binary compound of Si.

➔At room temperature SiC is resistant to HF ( think why?)

➔ **Upon heating Si reacts with most metals forming silicides. Silicides are often of variable composition from $M_6Si$ to $MSi_6$ (compare with carbides). Silicides are also formed from $SiO_2$**

$$SiO_2 + 2Mg \rightarrow 2MgO + Si \quad SiO_2 + 4Mg \rightarrow Mg_2Si + 2MgO$$

$$Mg_2Si + 2H_2SO_4 \rightarrow MgSO_4 + SiH_4 \uparrow$$

➔**Silicides of groups 1 and 2 are more reactive than those of the transition elements**

$$Na_2Si + H_2O \rightarrow N_2SiO_3 + H_2 \uparrow \qquad Mg_2Si + 2H_2O \rightarrow 2MgO + SiH_4 \uparrow$$

➔ **Si forms a series of silanes from $SiH_4$ to $Si_7H_{14}$ with Si-Si bonds. There are also cyclo-sylanes (compare with carbone).**

➔ **Si forms mixed halide-sylanes:** $Si + 3HCl \xrightarrow{350^\circ} SiHCl_3 + H_2$

➔ **$SiO_2$ exists in a number of modifications (quartz, tridymite etc)**

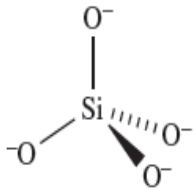
➔ **$SiO_2$ is VERY WEAKLY acidic. $SiO_2$ reacts only with concentrated strong bases;**

➔ **$H_2SiO_3$ is a VERY WEAK acid it is insoluble in water and cannot be prepared anhydrous. Only the alkali metals silicates are soluble. Si forms poly-silicon acids in which Si-O-Si bonds, for instance $[Si_2O_7]^{6-}$**

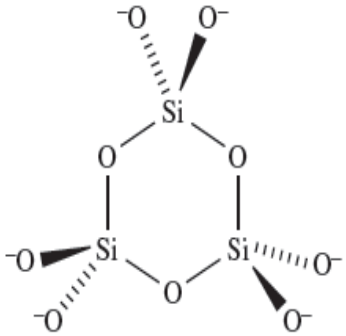
➔ **Ca and Mg silicates constitute a large fraction of cement:**

$$3CaO \cdot SiO_2 + nH_2O = 2CaO \cdot SiO_2 \cdot 2H_2O + Ca(OH)_2 + (n-3)H_2O$$

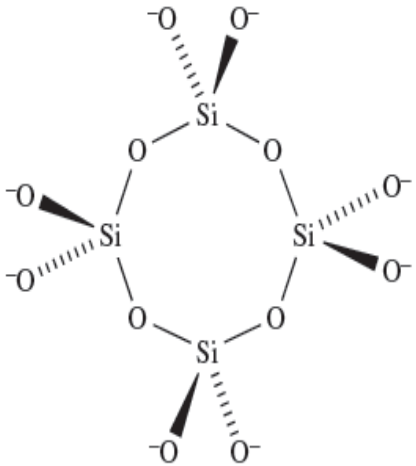
# ***Polysilicon anions



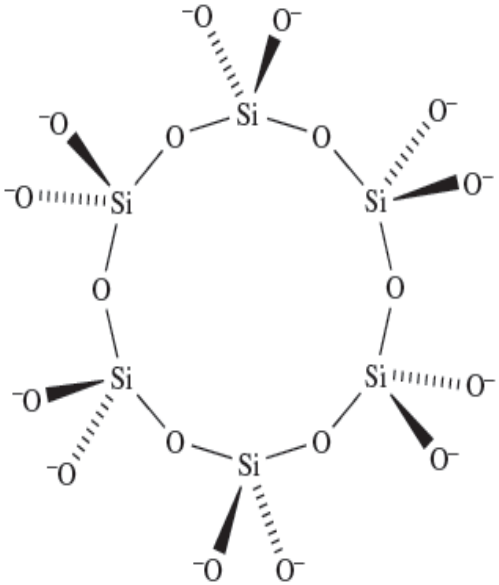
$[SiO_4]^{4-}$



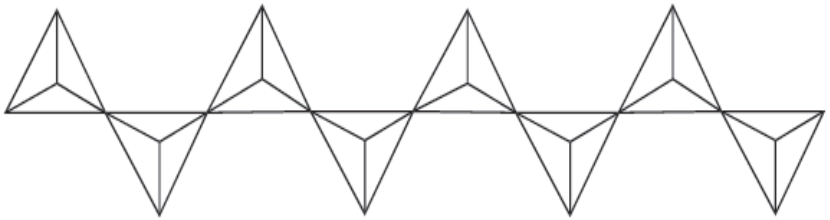
$[Si_3O_9]^{6-}$



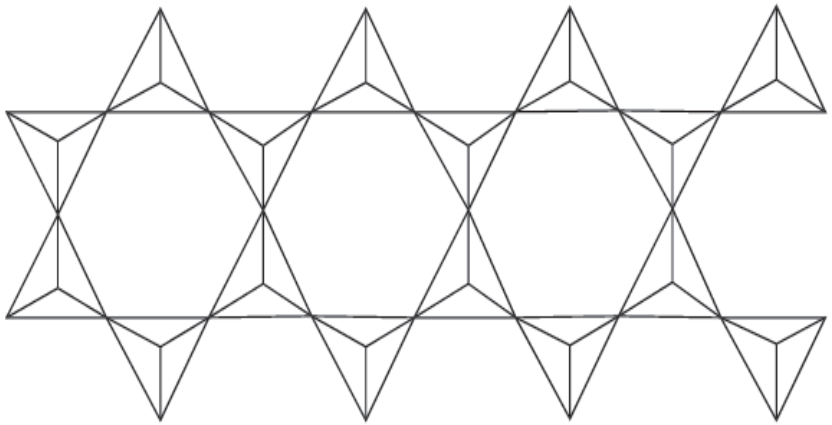
$[Si_4O_{12}]^{8-}$



$[Si_6O_{18}]^{12-}$

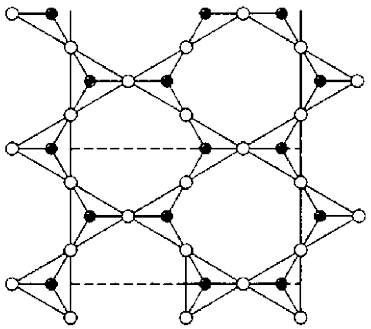
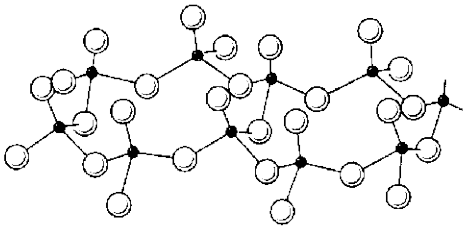
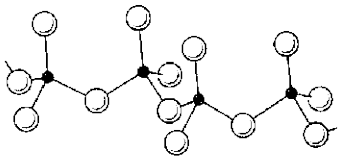
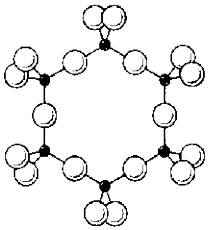
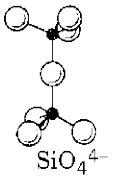


$[SiO_3]_n^{2n-}$



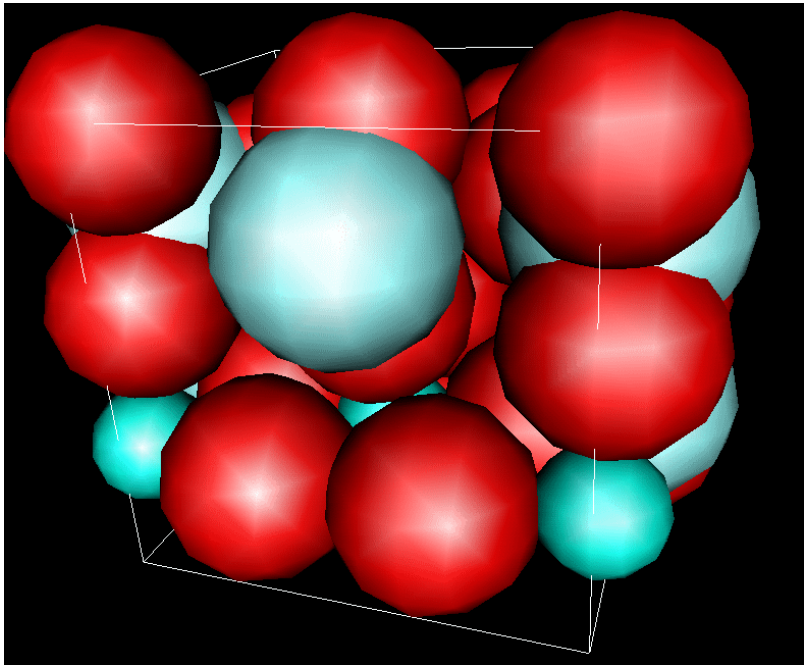
$[Si_4O_{11}]_n^{6n-}$

# Structures of silicates and glasses

| *R* O/Si Ratio | Silicon-Oxygen groups | Silicate structure | Examples |
|---|---|---|---|
| 2 | | $SiO_2$ (completely interconnected tetrahedra) | Quartz, tridymite, cristobalite |
| 2.5 |  | $Si_4O_{10}$ (sheets) | Talc, mica, kaolinite, montmorillonite clays, vermiculite |
| 2.75 |  | $Si_4O_{11}$ (chains) | Amphiboles (asbestos minerals) |
| 3 |  | $SiO_3$ (chains or rings) | Pyroxenes (chains), beryl (rings) |
| |  | | |
| 3.5 |   | $Si_2O_7$ (tetrahedra sharing one oxygen ion) | Pyrosilicates |

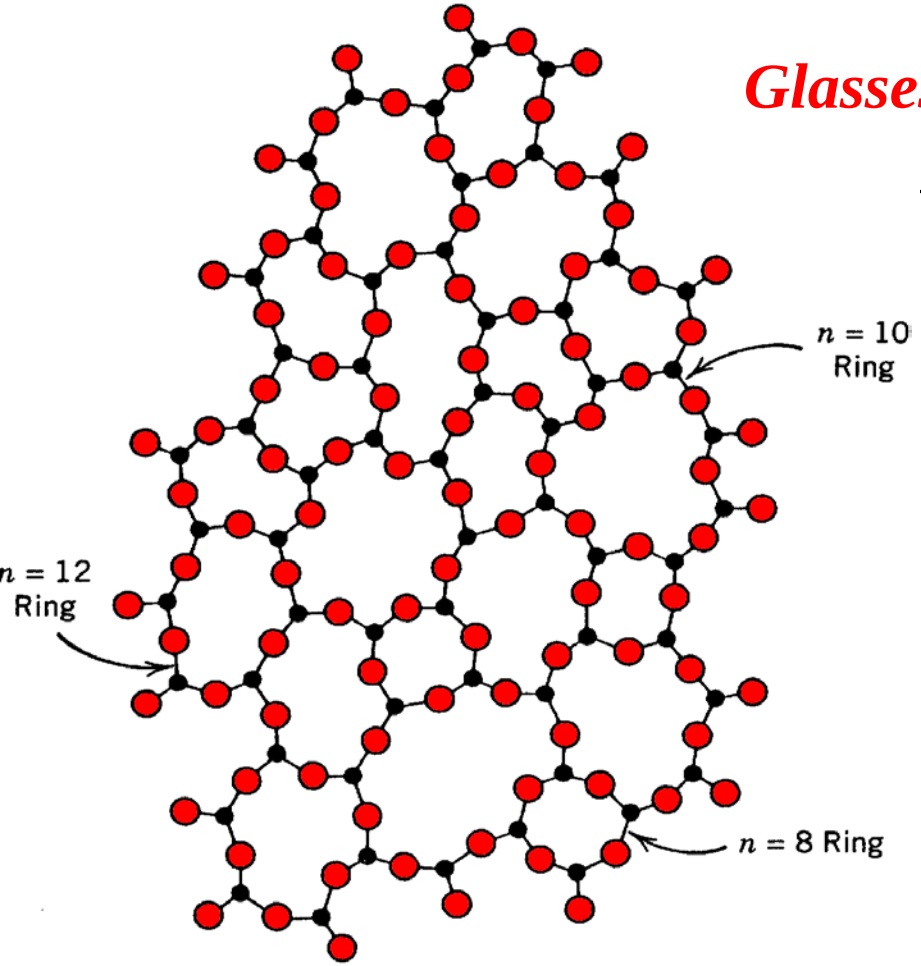
*R=2. Totally interconnected $SiO_4$ tetrahedra*

*R=4. Isolated tetrahedra*



*Zircon, $Zr(SiO_4)$*

# Glasses: Continuous Random Networks




Structural Characteristics of Continuous Random Network Glasses

| | $SiO_2$ | | Si | |
|---|---|---|---|---|
| | Glass | Crystal | Glass | Crystal |
| Number of nearest neighbors | Si : 4<br>O : 2 | Si : 4<br>O : 2 | 4 | 4 |
| Bond angles | 109.5° (O-Si-O)<br>150°+15°rms (Si-O-Si) | 109.5° (O-Si-O)<br>180°(tridymite)<br>150° (quartz, cristobalite) | 109°+9°rms (Si-Si-Si) | 109.5° (Si-Si-Si) |
| Rotation angle between tetrahedra | Random | 0° or 60° | Random | 0° (diamond cubic) |
| Ring counts | 8, 10, 12... | 12 | 5, 6, 7, 8,... | 6, 8, 10.... |

Is oxide glasses directional covalent bonding and ionic bonding in accordance with Pauling's rules promote the formation of tetrahedral ($SiO_4$) basic structural units. Therefore, short-range order is identical in crystalline and glassy $SiO_2$; the coordination of anions around cations is four, and the O-Si-O bond angle within each tetrahedral unit is 109.5°. The O/Si ratio of 2 indicates that all four corners of each tetrahedra are interconnected in glassy $SiO_2$, as is the case in the various crystalline phases of SiO2. However, it is possible for complete connectivity to be maintained without crystalline order; and this is the basis of the *continuous random network* structure first proposed by Zachariesen in 1932 (J *Am. Chem. Soc.*, *54*, 3841).

# *Zachariesen's rules of glass formation*

While cation/anion radius ratios in the correct range (<0.4) for tetrahedral coordination are often found in glass-forming oxides, this is a necessary but not sufficient condition for glass formation (i.e., many tetrahedrally coordinated crystalline oxides are not good glass formers).

Zachariesen's rules state:

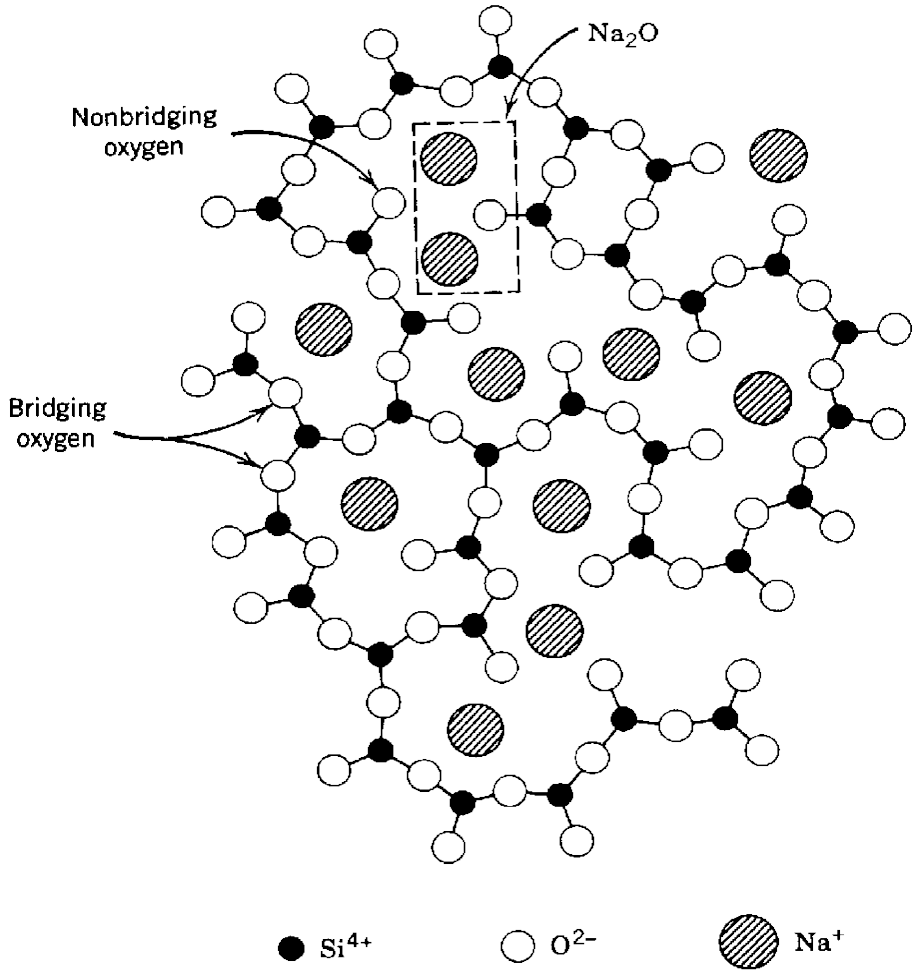
1. Each oxygen atom is linked to no more than two cations.
2. The number of oxygen atoms surrounding the cation must be small, four or less.
3. The oxygen polyhedra share corners rather than edges or faces.
4. At least three corners of each oxygen polyhedra are shared.

These rules correctly predict ease of glass formation for the oxides $B_2O_3$, $SiO_2$, $GeO_2$, $P_2O_5$, and a few others. These oxides are known as *network formers*. Glasses made solely from network formers often have limited utility. For example, pure $B_2O_3$ glass *(Tg~450$^o$C)* is not water resistant, and pure $SiO_2$ glass (fused silica) while valued for its chemical durability, high use temperatures (up to *~1750 $^o$C*), and thermal shock resistance, must be processed above 1750 C. The great majority of useful glasses contain additives that serve to alter processing and properties. These are commonly termed *network modifiers* and *intermediates*. Table at the next slide classifies various cations with respect to their roles as network formers, modifiers, and intermediates in oxide glasses.

***Network modifiers*** ($Na_2O$, $K_2O$, CaO, MgO, PbO, ZnO) provide extra oxygen ions but do not participate in the network, thereby raising the O/Si ratio of the glass. The extra oxygen allows the *bridging* oxygen between two tetrahedra to be disrupted, and two *non-bridging* oxygen to terminate each tetrahedron. For example, in sodium silicates, each $Na_2O$ molecule results in the formation of two *non-bridging* oxygen in SiO, with the $Na^+$ ions providing local charge neutrality. The fraction of non-bridging oxygen is readily determined from the composition. The effects of modifiers are directly analogous to the decreasing $SiO_4$ interconnectivity observed in crystalline silicates with increasing 0/Si ratio described earlier. In glasses the loss of connectivity results in greatly decreased viscosities and $T_g$‘s for modified silicates and reduces the processing temperatures of silicate glasses

***Intermediates*** as the name implies are not clearly modifiers or network formers and may contribute in part to the network structure. They are generally cations with higher valence than the alkalis and alkaline earths, but which do not satisfy Zachariesen's rules for network formers.

| | M in $MO_x$ | Valence | Dissociation Energy per $MO_x$ (kcal/mole) | Coor-dination Number | Single-Bond Strength (kcal/mole) |
|---|---|---|---|---|---|
| Glass formers | B | 3 | 356 | 3 | 119 |
| | Si | 4 | 424 | 4 | 106 |
| | Ge | 4 | 431 | 4 | 108 |
| | Al | 3 | 402–317 | 4 | 108 |
| | B | 3 | 356 | 4 | 89 |
| | P | 5 | 442 | 4 | 111–88 |
| | V | 5 | 449 | 4 | 112–90 |
| | As | 5 | 349 | 4 | 87–70 |
| | Sb | 5 | 339 | 4 | 85–68 |
| | Zr | 4 | 485 | 6 | 81 |
| Intermediates | Ti | 4 | 435 | 6 | 73 |
| | Zn | 2 | 144 | 2 | 72 |
| | Pb | 2 | 145 | 2 | 73 |
| | Al | 3 | 317–402 | 6 | 53–67 |
| | Th | 4 | 516 | 8 | 64 |
| | Be | 2 | 250 | 4 | 63 |
| | Zr | 4 | 485 | 8 | 61 |
| | Cd | 2 | 119 | 2 | 60 |
| Modifiers | Sc | 3 | 362 | 6 | 60 |
| | La | 3 | 406 | 7 | 58 |
| | Y | 3 | 399 | 8 | 50 |
| | Sn | 4 | 278 | 6 | 46 |
| | Ga | 3 | 267 | 6 | 45 |
| | In | 3 | 259 | 6 | 43 |
| | Th | 4 | 516 | 12 | 43 |
| | Pb | 4 | 232 | 6 | 39 |
| | Mg | 2 | 222 | 6 | 37 |
| | Li | 1 | 144 | 4 | 36 |
| | Pb | 2 | 145 | 4 | 36 |
| | Zn | 2 | 144 | 4 | 36 |
| | Ba | 2 | 260 | 8 | 33 |
| | Ca | 2 | 257 | 8 | 32 |
| | Sr | 2 | 256 | 8 | 32 |
| | Cd | 2 | 119 | 4 | 30 |
| | Na | 1 | 120 | 6 | 20 |
| | Cd | 2 | 119 | 6 | 20 |
| | K | 1 | 115 | 9 | 13 |
| | Rb | 1 | 115 | 10 | 12 |
| | Hg | 2 | 68 | 6 | 11 |
| | Cs | 1 | 114 | 12 | 10 |




Schematic representation of the structure of a sodium silicate glass. Each $Na_2O$ addition results in the formation of two non-bridging oxygen terminating silica tetrahedra.

# Germanium, Tin and Lead

➔ Tin and lead are one of the oldest elements known. Romans produced up to 60,000 tons of lead a year.

➔10-15% Tin in Cu is bronze was the first practically important alloy to serve mankind

➔ Ge and Sn are not toxic. Pb is moderately toxic (except for some extremely toxic compounds that are known from the ancient time).

➔ Extraction and production of Ge is expensive (>800 USD/kg $GeO_2$). Mostly it is an impurity in Zn.

➔ Sn is produced from $SnO_2$ (mineral cassiterite ) by carbon reduction (Why???):

$$SnO_2 + C \rightarrow CO_2 + Sn$$

➔Pb is produced from PbS (mineral galena)

$$PbS + 1.5O_2 \longrightarrow PbO + SO_2$$

$$PbS + 2PbO \longrightarrow 3Pb(liq) + SO_2(g)$$

$$PbO + C \longrightarrow Pb(liq) + CO;$$

$$PbO + CO \longrightarrow Pb(liq) + CO_2$$

➔All pure elements look metallic. Ge has a diamond structure. Sn is a shiny metal (tetragonal) at room and becomes a gray powder at -4 C ( diamond); Pb has FCC, typical for metals

# Germanium, Tin and Lead. Chemical properties

➔ **Ge is more reactive than Si. It can be oxidized at low temperatures by strong oxidizing agents: hot conc. $HNO_3$, $H_2SO_4$; Does not react with not oxidizing bases; but dissolves in a mixture of conc NaOH and $H_2O_2$ producing soluble $Na_2GeO_3$**

➔ **Sn is more reactive than Ge. It very slowly dissolves in HCl but reacts fast with hot conc. $HNO_3$, $H_2SO_4$ and hot conc. bases (KOH, NaOH);**

$$Sn + HNO_3 \rightarrow Sn(NO_3)_2 + NH_4NO_3 \qquad Sn + 2H_2SO_4 \rightarrow SnSO_4 + SO_2 + 2H_2O$$

➔ **However:** $Sn + 2H_2O \xrightarrow{\text{hot steam}} SnO_2 + 2H_2$ $\quad Sn + 2KOH + 4H_2O \longrightarrow K_2[Sn(OH)_6] + 2H_2$

➔ **Pb is less reactive than tin. As a fine powder it is pyrophoric. However, it is inert as a bulk covered by PbO. It is stable with respect to HF, dilute HCl, dilute $H_2SO_4$, conc. $HNO_3$.**

**Reacts with dilute $HNO_3$, hot conc. $H_2SO_4$, hot conc HCl, and acetic acid. The products are $Pb^{2+}$ salts.**

➔ **The trend to stabilize 2+ state increases from Ge to Pb.**

**$Pb^{4+}$ does NOT exist in aqueous solutions.**

**All three elements are capable of catenation (making X-X bonds) but the strength decreases quickly from Ge to Pb.**

Approximate average bond energies/kJ $mol^{-1}$

| M– | –M | –C | –H | –F | –Cl | –Br | –I |
|---|---|---|---|---|---|---|---|
| C | 356 | 356 | 416 | 490 | 325 | 279 | 216 |
| Si | 226 | 360 | 323 | 596 | 400 | 325 | 248 |
| Ge | 188 | 255 | 289 | 471 | 339 | 281 | 216 |
| Sn | 151 | 226 | 253 | — | 315 | 261 | 187 |
| Pb | 98 | 130 | 205 | 411 | 308 | — | — |

➔ $GeH_4$ is difficult to produce (GeMg-alloy + anhydrous acids). It decomposes upon heating. $Ge_2H_6$ and $Ge_3H_8$ are known but very unstable.
➔ $SnH_4$ is unstable.

# Germanium, Tin and Lead. Halides

➔All halides including fluorides are not ionic but rather covalent and volatile ( evaporate as molecules). Divalent halides have a shape of $H_2O$, tetravalent have a shape of tetrahedra
➔ Tetrahalides of Ge are similar to those of Si. $GeX_4$ (X=F, Cl, Br or I) is prepared by direct combination of the elements.
➔ Ge forms stable dihalides; $GeF_2$, $GeCl_2$ and $GeBr_2$ are produced when Ge is heated with $GeX_4$. However, $2GeX_2 \xrightarrow{\Delta} GeX_4 + Ge$

➔ $SnF_4$ and $SnCl_4$ are stable but $PbF_4$ and $PbCl_4$ decompose upon heating to halides (II)

➔ $SnF_4$ and $SnCl_4$ very weak acids: $2KCl + SnCl_4 \xrightarrow{\text{in presence of HCl(aq)}} K_2[SnCl_6]$

➔ $SnCl_2$ ($SnCl_2 \cdot 2H_2O$) is used as a strong reducing age $2HgCl_2 + SnCl_2 = Hg_2Cl_2\downarrow + SnCl_4$

➔Although, $PbCl_4$ easily decomposes (especially in water); $PbCl_6^{2-}$ is stable. However, it can be easily reduced to $PbCl_4^{2-}$ . $PbCl_2$ is stable.
➔ Tin and lead have a tendency to form polymorphic anions: $[Pb_3I_{10}]^{4-}$ $[Pb_7I_{22}]^{8}$, $[Pb_{10}I_{28}]^{8-}$.

# Germanium, Tin and Lead. Oxides and hydroxides

➔The dioxides of Ge, Sn and Pb are involatile solids. $GeO_2$ is similar $SiO_2$.

➔ $GeO_2$ dissolves in concentrated HCl forming $[GeCl_6]^{2-}$ and $5GeO_2 + 2Li_2O \xrightarrow{\text{molten}} Li_4[Ge_5O_{12}]$

➔GeO is marginally stable $2GeO \xrightarrow{970\,K} GeO_2 + Ge$

➔ $SnO_2$ is more stable than SnO; Tin hydroxide decomposes to $SnO_2$ after preparation

$$SnCl_4 + 4NH_4OH = H_2SnO_3\downarrow + 4NH_4Cl + H_2O$$

➔ $SnO_2$ and all its hydrates dissolve in bases and in acids

$$H_2SnO_3 + 2NaOH + H_2O = Na_2[Sn(OH)_6]$$
$$H_2SnO_3 + 4HCl \rightleftarrows SnCl_4 + 3H_2O$$

➔$Sn(OH)_2$ precipitates from basic solutions of $Sn^{2+}$. It is amphoteric

$$Sn(OH)_2 + 2NaOH = Na_2[Sn(OH)_4]$$

**Acidity increases** ←

$Ge(OH)_4$ $Sn(OH)_4$ $Pb(OH)_4$

$Ge(OH)_4$ $Sn(OH)_2$ $Pb(OH)_2$

→ **Alkalinity increases**

➔ $PbO_2$ is a strong oxidizer and forms a serious if intermediate phases

$$PbO_2 \xrightarrow{566\,K} Pb_{12}O_{19} \xrightarrow{624\,K} Pb_{12}O_{17} \xrightarrow{647\,K} Pb_3O_4 \xrightarrow{878\,K} PbO$$

**brown** **bright red (pigment)**

**yellow (pigment)**

➔ $Pb(OH)_2$ is amphoteric $Pb(OH)_2 + 4NaOH = Na_4[Pb(OH)_6]$

➔ $Pb(OH)_2$ reacts with molten bases forming salts: $Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O$

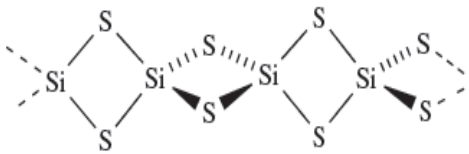
➔ $PbO_2$ has very weak amphoteric properties but it dissolves in NaOH and KOH

➔ $PbO_2$ vs PbO is the basis of the lead battery: During charging both reactions are driven to the left. During the discharge both reaction spontaneously go to the right. Total cell voltage ≈2V

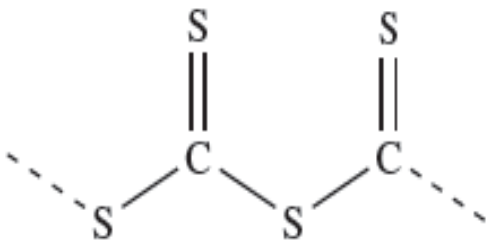
$$Pb(s) + [SO_4]^{2-}(aq) \leftrightarrow PbSO_4(s) + 2e \qquad E^o = -0.36\ V$$

$$PbO_2 + 4H^+(aq) + [SO_4]^{2-}(aq) + 2e \leftrightarrow PbSO_4(s) + 2H_2O \qquad E^o = +1.69\,V$$

# ***Sulfides of $ES_2$ (E=C, Si, Ge, Sn).

| Property | $CS_2$ | $SiS_2$ | $GeS_2$ | $SnS_2$ |
|---|---|---|---|---|
| Melting point / K | 162 | 1363 (sublimes) | 870 (sublimes) | 873 (dec.) |
| Boiling point / K | 319 | – | – | – |
| Appearance at 298 K | Volatile liquid, foul odour | White needle-like crystals | White powder or crystals | Golden-yellow crystals |
| Structure at 298 K | Linear molecule S=C=S | Solid state, chain‡  | Three-dimensional lattice with $Ge_3S_3$ and larger rings with shared vertices.‡ | $CdI_2$-type lattice (see *Figure 5.22*) |

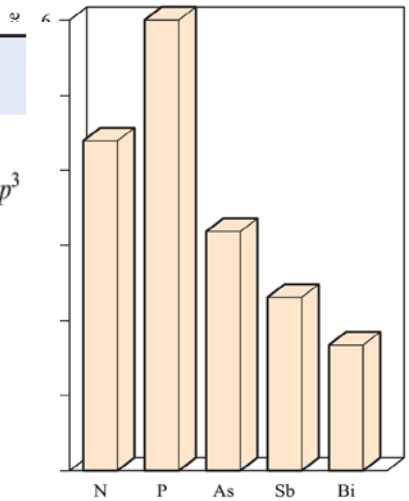
Unlike $CO_2$, $CS_2$ polymerizes under high pressure to give a black solid with the chain structure (why?)



# Group 5A [noble gas]($s^2p^3$): N, P, Sb, As, and Bi

| Property | N | P | As | Sb | Bi |
|---|---|---|---|---|---|
| Atomic number, $Z$ | 7 | 15 | 33 | 51 | 83 |
| Ground state electronic configuration | $[He]2s^22p^3$ | $[Ne]3s^23p^3$ | $[Ar]3d^{10}4s^24p^3$ | $[Kr]4d^{10}5s^25p^3$ | $[Xe]4f^{14}5d^{10}6s^26p^3$ |
| Enthalpy of atomization, $\Delta_a H^o(298\ K)$ / kJ mol$^{-1}$ | 473‡ | 315 | 302 | 264 | 210 |
| Melting point, mp / K | 63 | 317 | 887 sublimes | 904 | 544 |
| Boiling point, bp / K | 77 | 550 | – | 2023 | 1837 |
| Standard enthalpy of fusion, $\Delta_{fus}H^o(mp)$ / kJ mol$^{-1}$ | 0.71 | 0.66 | 24.44 | 19.87 | 11.30 |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 1402 | 1012 | 947.0 | 830.6 | 703.3 |
| Second ionization energy, $IE_2$ / kJ mol$^{-1}$ | 2856 | 1907 | 1798 | 1595 | 1610 |
| Third ionization energy, $IE_3$ / kJ mol$^{-1}$ | 4578 | 2914 | 2735 | 2440 | 2466 |
| Fourth ionization energy, $IE_4$ / kJ mol$^{-1}$ | 7475 | 4964 | 4837 | 4260 | 4370 |
| Fifth ionization energy, $IE_5$ / kJ mol$^{-1}$ | 9445 | 6274 | 6043 | 5400 | 5400 |
| Metallic radius, $r_{metal}$ / pm | – | – | – | – | 182 |
| Covalent radius, $r_{cov}$ / pm* | 75 | 110 | 122 | 143 | 152 |
| Ionic radius, $r_{ion}$ / pm** | 171 ($N^{3-}$) | – | – | – | 103 ($Bi^{3+}$) |
| NMR active nuclei (% abundance, nuclear spin) | $^{14}N$ (99.6, $I = 1$) $^{15}N$ (0.4, $I = \frac{1}{2}$) | $^{31}P$ (100, $I = \frac{1}{2}$) | $^{75}As$ (100, $I = \frac{3}{2}$) | $^{121}Sb$ (57.3, $I = \frac{5}{2}$) $^{123}Sb$ (42.7, $I = \frac{7}{2}$) | $^{209}Bi$ (100, |

‡ For nitrogen, $\Delta_a H^o = \frac{1}{2} \times$ dissociation energy of $N_2$.
* For 3-coordination.
** For 6-coordination.




**Electronegativity**

| | | | |
|---|---|---|---|
| 6 C 2.5 | 7 N 3.0 | 8 O 3.5 | 9 F 4.0 |
| 14 Si 1.8 | 15 P 2.1 | 16 S 2.5 | 17 Cl 3.0 |
| 32 Ge 1.8 | 33 As 2.0 | 34 Se 2.4 | 35 Br 2.8 |
| 50 Sn 1.8 | 51 Sb 1.9 | 52 Te 2.1 | 53 I 2.5 |
| 82 Pb 1.8 | 83 Bi 1.9 | 84 Po 2.0 | 85 At 2.2 |

Minerals: apatites, $Ca_5X(PO_4)_3$, X=F, Cl, OH. Mispickel (arsenopyrite) FeAsS, realgar ($As_4S_4$); orpiment ($As_2S_3$). stibnite ($Sb_2S_3$). bismuthinite ($Bi_2S_3$) and bismite ($Bi_2O_3$).

# The factors defining chemical properties

1. Large differences in size and electronegativity between N and the rest of the elements: five electrons restricted to s and p orbitals only
2. Covalent radius of N is the same as C; however, electronegativity is much larger (equal to Cl and Br);
3. Phosphorus is much larger than N but much smaller than Sb and Bi
4. The inert $s^2$ pair effect becomes strong already for As
5. Small radii and large electro-negativity lead to almost exclusive covalent bonding

1. Chemical properties of N are unique (like B, C, O and F)=> many compounds have electron excess ( compare with B!!!).
2. Although N is a typical non-metal, it may form a number of basic species (why????)
3. Because of (1) N has a WEAK tendency for catenation.
4. N and P are quite different from each other but VERY different from As, Sb and Bi, which are SIMILAR (especially Sb and Bi).
5. Only Bi may form a positive ion $Bi^{3+}$

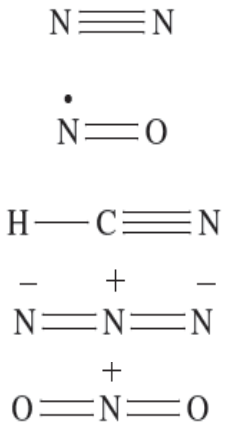
# Chemical properties. Nitrogen.

1. The process $N(g) + 3e^- \rightarrow N^{3-}(g)$ is **endothermic**

2. Bond enthalpy (kJ/mol)

| | | | | | | |
|---|---|---|---|---|---|---|
| N–N 160 | N=N ≈400‡ | N≡N 946 | N–H 391 | N–F 272 | N–Cl 193 | N–O 201 |
| P–P 209 | | P≡P 490 | P–H 322 | P–F 490 | P–Cl 319 | P–O 340 |
| As–As 180 | | | As–H 296 | As–F 464 | As–Cl 317 | As–O 330 |
| | | | | | Sb–Cl 312 | |
| | | | | | Bi–Cl 280 | |

Nitrogen bonding



3. All nitrogen compounds have a tendency to decompose and produce $N_2$

4. **$N_2$ reacts at room temperature only with Li (slow). Upon heating it reacts with alkaline earth metals, Al, Si, Ge and some d-metals producing NITRIDES $N^{3-}$. $2Al+N_2 \rightarrow AlN$**

Nitrides of d-block elements are very hard and quite inert. Often used in cutting tools.

5. Atomic nitrogen (ionized by electrical discharge) is very reactive.

**6. IN ALL COMPOUNDS NITROGEN DOES HAVE FOUR OR LESS NEIGHBORS**

# Chemical properties. Hydrides.

| | $NH_3$ | $PH_3$ | $AsH_3$ | $SbH_3$ | $BiH_3$ |
|---|---|---|---|---|---|
| Name (IUPAC recommended)‡ | Ammonia (azane) | Phosphine (phosphane) | Arsine (arsane) | Stibine (stibane) | Bismuthane |
| Melting point / K | 195.5 | 140 | 157 | 185 | 206 |
| Boiling point / K | 240 | 185.5 | 210.5 | 256 | 290* |
| $\Delta_{vap}H^{o}$(bp) / kJ mol$^{-1}$ | 23.3 | 14.6 | 16.7 | 21.3 | – |
| $\Delta_{f}H^{o}$(298 K) / kJ mol$^{-1}$ | –45.9 | 5.4 | 66.4 | 145.1 | 277* |
| Dipole moment / D | 1.47 | 0.57 | 0.20 | 0.12 | – |
| E–H bond distance / pm | 101.2 | 142.0 | 151.1 | 170.4 | – |
| ∠H–E–H / deg | 106.7 | 93.3 | 92.1 | 91.6 | – |

Estimated value

1. Small quantities can be obtained by

$$Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

$$ECl_3 \xrightarrow{Li[AlH_4]\ \text{in}\ Et_2O} EH_3 \quad E = P,\ As,\ Sb,\ Bi$$

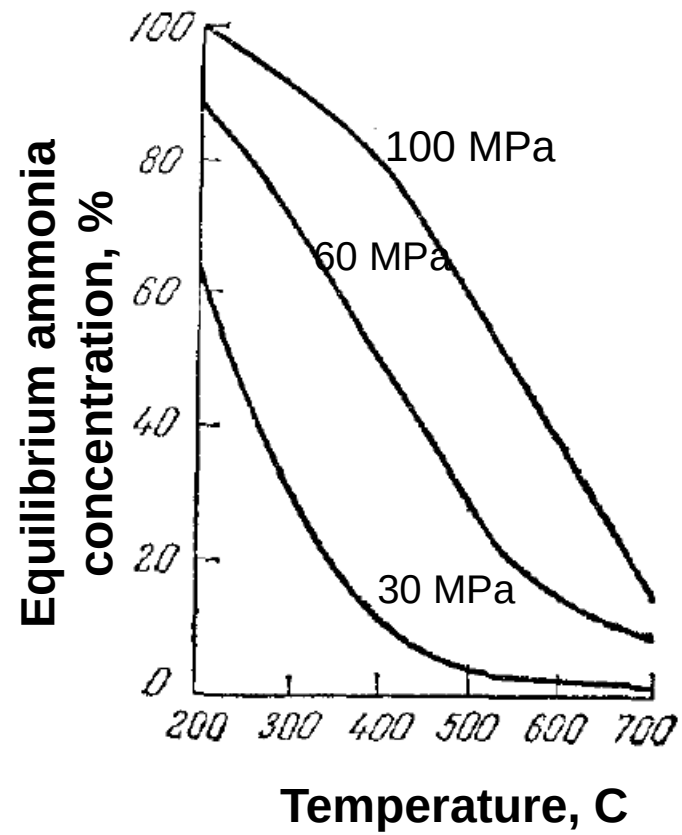
$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$$

$$[PH_4]I + KOH \rightarrow PH_3 + KI + H_2O$$

2. Industrial production called Haber-Bosh process (first produced industrially in 1913, BASF Inc. in Germany) is the **largest chemical industrial process** (109,000,000 metric tons in 2004) (comparable only to cement production 150,000,000 metric tons and steel 1,370,000,000 metric tons in 2009).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \begin{cases} \Delta_r H^o(298\,K) = -92\,kJ\,mol^{-1} \\ \Delta_r G^o(298\,K) = -33\,kJ\,mol^{-1} \end{cases}$$

3. The major problem is the stability of $N_2$ molecule. Therefore, the "art" of ammonia production is in the quality of catalysts. The most commonly used catalysts are based on Fe because of its ability to promote dissociation of $H_2$.




4.*** Prior to Haber-Bosh cycle synthetic ammonia was made via calcium cyan-amide, which decomposes by water and 3 atm

$$CaC_2 + N_2 = CaCN_2 + C \qquad CaCN_2 + 3H_2O = CaCO_3 + 2NH_3\uparrow$$

$CaCN_2$ is a derivative of cyan-amide $H_2N-C\equiv N$

# Chemical properties of ammonia

1. Ammonia is a weak base but it is the strongest base among all the hydrides of the 5A group

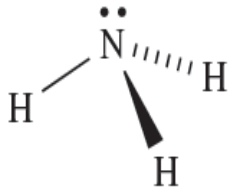
$$NH_3(aq) + H_2O(l) \rightleftharpoons [NH_4]^+(aq) + [OH]^-(aq) \quad K_b = 1.8 \times 10^{-5}$$

$$[NH_4]^+(aq) + H_2O(l) \rightleftharpoons [H_3O]^+(aq) + NH_3(aq) \quad K_a = 5.6 \times 10^{-10}$$

2. Ammonia easily reacts with acids: $NH_3 + HBr \rightarrow NH_4Br$ $\quad NH_3 + HNO_3 \rightarrow NH_4NO_3$

$$CaSO_4 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + [NH_4]_2[SO_4]$$

3. Ammonium salts often crystallize with lattices similar to those of the corresponding K, Rb or Cs salts because ammonia molecule easily accepts a proton.




4. Most salts of ammonia (but not oxidizing anions ) decompose back to ammonia and acid. Therefore, many salts of ammonia “smell” of ammonia.

5. All salts ammonia and oxidizing anions decompose by redox or disproportionation reactions

$$NH_4NO_3(s) \xrightarrow{\text{melts at} \approx 105\ C} N_2O + 2H_2O$$

6. Ammonia salts can reduce many metal oxides upon heating above 200 C

$$CuO(s) + NH_4Cl(s) \xrightarrow{>300\ C} Cu + CuCl_2 + N_2 + 4H_2O$$

7. The vast majority of ammonia salts are water soluble and easily hydrolyze.

8. Ammonia behaves as an acid with respect to pure alkali metals:

$$2NH_3(g) + 2Na(\text{molten}) \xrightarrow{>300\ C} 2NaNH_2(s) + H_2$$

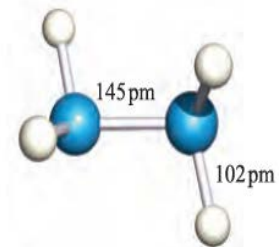
7. Unshared electron pair makes ammonia one of the strongest ligands. Dissolution of semi-noble and many d-metals in ammonia solutions is rapid.

8. Ammonia can be oxidized in two distinctively different routes:

$$4NH_3(g) + 3O_2 \xrightarrow{\text{burning in air}} 2N_2 + 6H_2O$$

$$4NH_3(g) + 5O_2 \xrightarrow{\text{catalitic oxidation}} 4NO + 6H_2O$$

# Hydrazine $H_2N\text{-}NH_2$




1. Hydrazine is kinetically stable: formation enthalpy at 298 K +50:6 kJ/mol.
2. Hydrazine is obtained:

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \quad \textit{fast}$$

$$NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O \quad \textit{slow}$$

**undesirable because** $2NH_2Cl + N_2H_4 \rightarrow N_2 + 2NH_4Cl$

3. The product is hydrazine monohydrate. Dehydration is difficult and it is strategically important process (for rocket fuel). $2NH_3 + [N_2H_5][HSO_4] \rightarrow N_2H_4 + [NH_4]_2[SO_4]$

4. In aqueous solution, $N_2H_4$ forms $[N_2H_5]^+$ (hydrazinium) salts, VERY rare $[N_2H_6]^{2+}$.

5. Hydrazine is far weaker base than ammonia

$$N_2H_4(aq) + H_2O \rightleftharpoons [N_2H_5]^+ + [OH]^- \quad K_b(1) = 8.9 \times 10^{-7}$$

$$[N_2H_5]^+(aq) + H_2O \rightleftharpoons [N_2H_6]^{2+} + [OH]^- \quad K_b(2) \approx 10^{-14}$$

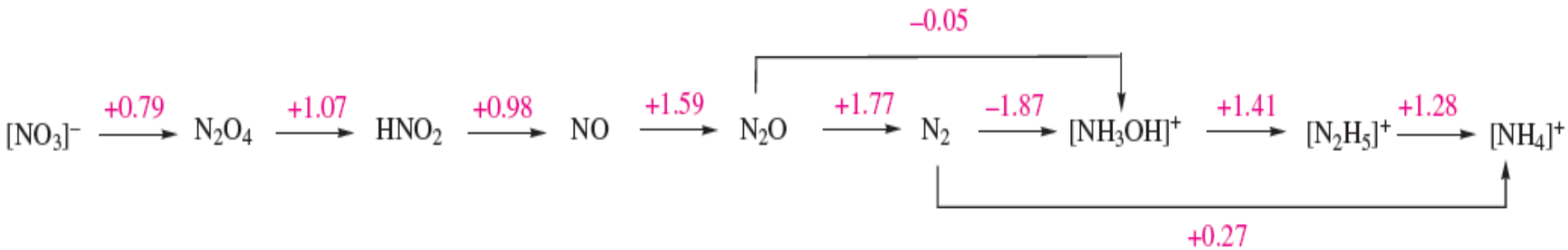
6. Hydrazine is a strong reducer (detection of hydrazine): $N_2H_4 + KIO_3 + 2HCl \rightarrow N_2 + KCl + ICl + 3H_2O$

# Hydroxylamine and Chloramine

1. Chloramine is unstable and forms by reaction: $NH_3(g) + Cl_2(\text{dilute g}) \xrightarrow{<100\ C} ClNH_2 + HCl$

2. Chloramine is used to produce the main component of rocket fuel 1,1-dimethylhydrazine

$$NH_2Cl + 2Me_2NH \rightarrow Me_2NNH_2 + [Me_2NH_2]Cl$$




3. Hydroxylamine can be produced by many routes:

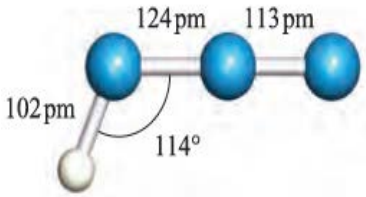
$$2NO + 3H_2 + H_2SO_4 \xrightarrow{\text{platinized charcoal catalyst}} [NH_3OH]_2[SO_4]$$

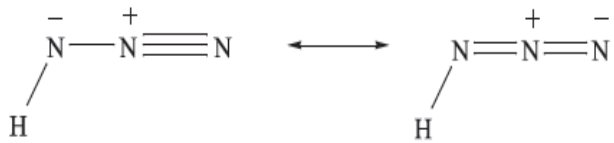
4. Hydroxylamine is a very strong reducer: $2NH_2OH + 4Fe^{3+} \rightarrow N_2O + 4Fe^{2+} + H_2O + 4H^+$

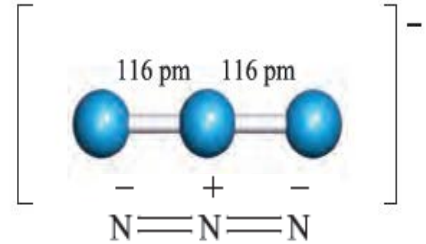
$$NH_2OH + 2Fe(OH)_2 + H_2O \rightarrow NH_3 + 2Fe(OH)_3$$

5. Strong oxidizing agents (bromates and chlorates) oxidize to $HNO_3$ .

# Azides [N=N=N]$^-$






1. Azides are resonance structures and are the simplest among the family of conjugated nitrogen compounds with N=N bonds. They can be obtained by

$$2NaNH_2 + N_2O \xrightarrow{460\,K} NaN_3 + NaOH + NH_3$$

$$NaNH_2\,(\text{or } NH_2OH) + 2HNO_2 \xrightarrow{450\,K} NaN_3 + 2H_2O + N_2$$

$$2NaN_3 + H_2SO_4 \xrightarrow{450\,K} Na_2SO_4 + 2HN_3\uparrow$$

$$H_2N\text{-}NH_2 + HNO_2 \xrightarrow{<30\,C} HN_3 + 2H_2O$$ (dangerous)

1. Hydrazoic acid is very weak explosive and poisonous. $HN_3 + H_2O \rightleftharpoons [H_3O]^+ + [N_3]^-$ $pK_a = 4.75$

2. Azides of alkali metals are stable and decompose upon heating quietly.
Azides of almost all semi-noble metals and many d-metals decompose with explosion.
$Pb(N_3)_2$ is the most commonly used initiator for a gun powder.

# Nitrogen halides

1. Nitrogen forms $NX_3$ (X=F, Cl), $N_2F_4$ and $N_2F_2$ . All of them decompose easily. $NF_3$ is the most stable. $NI_3$ explodes if prepared dry.

$$4NH_3 + 3F_2 \xrightarrow{\text{Cu catalyst}} NF_3 + 3NH_4F$$

2. ***Self-education: cis and trans isomers of $N_2F_4$

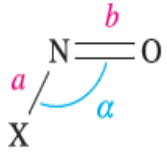
3. ***Nitrogen forms several several oxofluorides and oxochlorides. FNO and ClNO are stable and can be prepared as crystals.

$$2NO + F_2 \leftrightarrow FNO$$

4. $FNO_2$ and $ClNO_2$ can be prepared:

$$N_2O_4 + 2CoF_3 \xrightarrow{570\,K} 2FNO_2 + 2CoF_2$$

5. Reaction of oxohalides with bases may form salts of $[N{=}O]^+$ and $[O{=}N{=}O]^+$




| | X | | |
|---|---|---|---|
| | F | Cl | Br |
| $a$ / pm | 152 | 198 | 214 |
| $b$ / pm | 113 | 114 | 115 |
| $\alpha$ / ° | 110 | 113 | 117 |

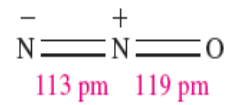
# Oxides of Nitrogen

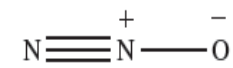
| | $N_2O$ | NO | $N_2O_3$ | $NO_2$ | $N_2O_4$ | $N_2O_5$ |
|---|---|---|---|---|---|---|
| Name | Dinitrogen monoxide‡ | Nitrogen monoxide‡ | Dinitrogen trioxide | Nitrogen dioxide | Dinitrogen tetraoxide | Dinitrogen pentaoxide |
| Melting point / K | 182 | 109 | 173 | – | 262 | 303 |
| Boiling point / K | 185 | 121 | 277 dec. | – | 294 | 305 sublimes |
| Physical appearance | Colourless gas | Colourless gas | Blue solid or liquid | Brown gas | Colourless solid or liquid, but see text | Colourless solid, stable below 273 K |
| $\Delta_f H^o(298\,K)$ / kJ mol$^{-1}$ | 82.1 (g) | 90.2 (g) | 50.3 (l) 83.7 (g) | 33.2 (g) | −19.5 (l) 9.2 (g) | −43.1 (s) |
| Dipole moment of gas-phase molecule / D | 0.16 | 0.16 | – | 0.315 | – | – |
| Magnetic properties | Diamagnetic | Paramagnetic | Diamagnetic | Paramagnetic | Diamagnetic | Diamagnetic |

1. Dinitrogen monoxide, $N_2O$ ( the laughing gas). Dissolves in water but does not react with it

$$NH_4NO_3 \xrightarrow{450-520\,K} N_2O + 2H_2O$$

$$N_2O + H_2O \rightleftharpoons H_2N_2O_2$$



$$NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$$

$N_2O$ easily decomposes upon heating and supports combustions. Mainly used to make azides

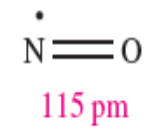
2. Nitrogen monoxide, NO made industrially by millions of tons $4NH_3 + 5O_2 \xrightarrow{600\text{-}750\ °C,\ Pt} 4NO + 6H_2O$

NO produced during reduction of nitrates $[NO_3]^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$

$$2[NO_3]^- + 6Hg + 8H^+ \rightarrow 2NO + 3[Hg_2]^{2+} + 4H_2O$$

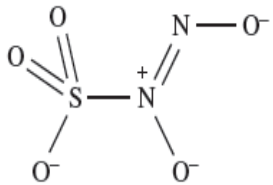
NO is a strong ligand in a large number of nitrosyl complexes $[Fe(NO)(H_2O)_5]^{2+}$ with NO- ions

NO has an unpaired electron, therefore, it is also a radical. Therefore, it is highly reactive.



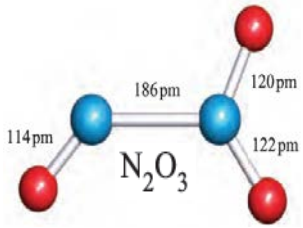

$$2NO + Cl_2 \rightarrow 2ClNO \qquad 2NO + O_2 \rightarrow 2NO_2$$

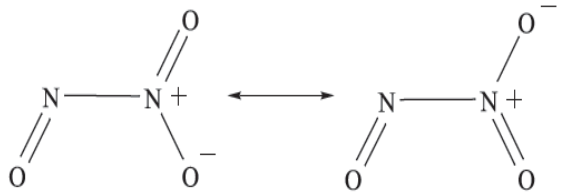
NO reacts with $SO_3^{2-}$ forming $[O_3SNONO]^{2-}$



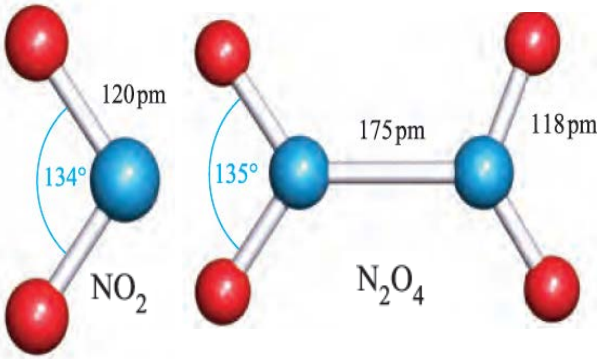
NO reacts with strong oxidizers. The products are typically nitrates.

3. Dinitrogen trioxide, $N_2O_3$ is unstable and forms $2NO + N_2O_4 \rightleftharpoons 2N_2O_3$ It is a is water-soluble anhydride of $HNO_2$, nitrous acid: $N_2O_3 + H_2O \rightarrow 2HNO_2$ . It reacts with strong bases.



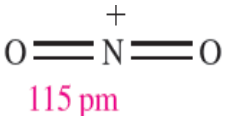
4. Dinitrogen tetraoxide, $N_2O_4$, and nitrogen dioxide, $NO_2$ are at equilibrium $N_2O_4 \rightleftharpoons 2NO_2$




At 293 K $NO_2$ is 15%. At 413 K no $NO_2$ left. Above that $NO_2$ dissociates to NO and $O_2$ .

**$N_2O_4$ is A VERY STRONG OXIDIZER.**

$NO_2$ may form ions $NO_2^+$ (nitryl cation) .

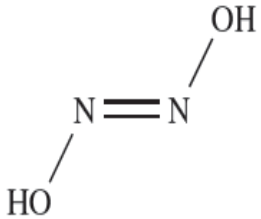



5. Dinitrogen pentaoxide, $N_2O_5$ is nitric anhydride. $2HNO_3 \xrightarrow[\text{(dehydrating agent)}]{P_2O_5} N_2O_5 + H_2O$

Reacts with water to produce nitric acid. $N_2O_5$ **is A VERY STRONG OXIDIZER**

# Oxoacids of nitrogen

1. Hyponitrous acid, $H_2N_2O_2$ is a weak acid. It is unstable ($H_2N_2O_2 \rightarrow N_2O + H_2O$) and potentially explosive, it can be made by the reduction of $NaNO_2$ with sodium amalgam or by reducing organic nitrites. Salts of hyponitrous acids are known and moderately stable $Ag_2N_2O_2$. Only the alkali metal salts are soluble.

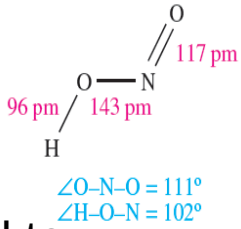



2. **Nitrous acid, $HNO_2$ is known only in solution and in the vapor phase. However its salts are stable and can be easily prepared.

$$Ba(NO_2)_2 + H_2SO_4 \xrightarrow{aqu} BaSO_4 + 2HNO_2$$

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O$$

$$NaNO_3 + Pb \xrightarrow{\Delta} NaNO_2 + PbO$$



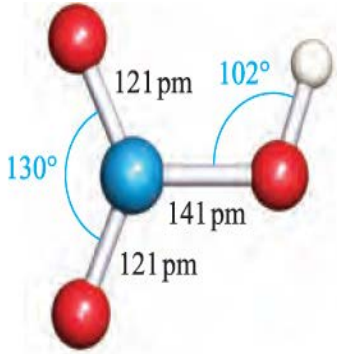

➔ ***Nitrites of alkali metals and alkaline earth metals are soluble in water.

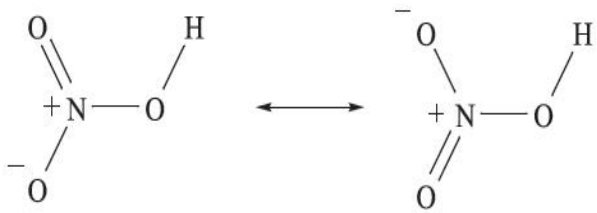
➔*** Strong oxidizers (like $MnO_4^-$) oxidize nitrites to nitrates. Nitrites can be reduced to: NO, $N_2O$ , $NH_2OH$ and $NH_3$ depending on conditions.

3. Nitric acid, $HNO_3$, and its derivatives is one of the most important industrial chemicals. It is produced from water, NO and oxygen that gives 60% acid. Anhydrous acid is obtained by dehydration by $H_2SO_4$

Pure acid easily decomposes: $4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$

$$\left.\begin{array}{l} 2NO + O_2 \rightleftharpoons 2NO_2 \\ 2NO_2 \rightleftharpoons N_2O_4 \\ N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 \\ 2HNO_2 \rightarrow NO + NO_2 + H_2O \\ 3NO_2 + H_2O \rightarrow 2HNO_3 + NO \end{array}\right\}$$



➔ $HNO_3$ is a very strong oxidizer. It reacts almost all elements (except noble metals, F, and Cl). Tin, arsenic and a few d-block metals are converted to oxides by $HNO_3$.. All other metals form nitrates.

Concentrated $HNO_3$ oxidizes $I_2$, $P_4$ and $S_8$ to $HIO_3$, $H_3PO_4$ and $H_2SO_4$ respectively.

$HNO_3$ dissolves all metals except Au, Pt, Ta, Rh and Pd.

Mixture of $HNO_3$ and HCl (3:1) is called *aqua regia* and it is much stronger oxidizing agent than pure $HNO_3$. The mechanism is:

$$HNO_3 + 3HCl = Cl_2 + 2H_2O + NOCl$$

$$NOCl \rightarrow NO + Cl^{\bullet}$$

$$Au + HNO_3 + 4HCl \longrightarrow HAuCl_4 + NO + 2H_2O$$

All nitrates are soluble but only alkaline, $Sr^{2+}$, $Ba^{2+}$, $Ag^{+}$ and $Pb^{2+}$ can be easily made anhydrous.

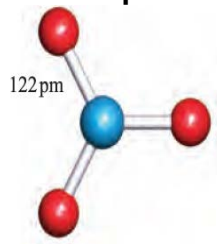
➔ Reminder: the final product of reaction between a reducing agent and $HNO_3$ depends on conditions. It can be, $NO_2$, NO and sometimes ammonia and small quantities of $H_2$.

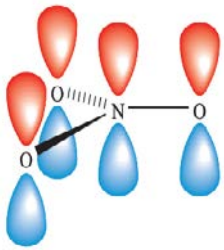
➔ Concentrated $HNO_3$ passivates many metals, including Fe and Al.

➔All nitrates decompose upon heating. Alkali and alkaline earth metals nitrates decompose to nitrites; most d-block nitrates decompose to oxides. Noble metals, Ag and $Hg^{2+}$ nitrates decompose to pure metals.

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2 \qquad 2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

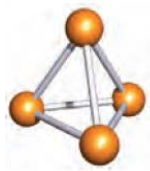
$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$



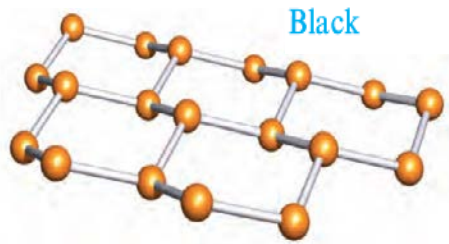
# Phosphides, arsenides, antimonides and bismuthides

1. Chemical reactivity of phosphorus depends on allotropic modification.



**White phosphorus. highly reactive, oxidizes in air at RT producing chemo luminescence.**

$$\underset{\text{Black}}{P} \xleftarrow{\Delta_f H^o = -39.3\ \text{kJ mol}^{-1}} \underset{\text{White}}{\tfrac{1}{4}P_4} \xrightarrow{\Delta_f H^o = -17.6\ \text{kJ mol}^{-1}} \underset{\text{Red}}{P}$$



**black phosphorus. moderately reactive**

**Red phosphorus is a combination of a few phases**

2. Phosphorus reacts with most elements, except Hg, Pb, Sb, Bi and Te ( what else?).

3. Phosphides of active metals (alkali, alkaline earth, Zn, AL) form phosphides with $P^{3-}$ ion. They can hydrolyze producing phosphine $PH_3$ (see the lecture on hydrogen). It is a VERY weak base. It reacts with HX (X=halogen), but only $PH_4I$ is stable. Phosphine acts as a Lewis base: $H_3B{\cdot}PH_3$, $Cl_3B{\cdot}PH_3$

4. Phosphides of the d-block metals tend to be inert, metallic-looking compounds and of variable stoichiometry containing anions like $P_6^{3-}$

5. $AsH_3$ and $SbH_3$ are similar to $PH_3$ but are much less stable. They are even less basic than $PH_3$

$$AsH_3 + HF + AsF_5 \rightarrow [AsH_4]^+ + [AsF_6]^-$$

# Phosphorus halides

1. Phosphorus forms the halides $PX_3$ (X=F, Cl, Br and I) and $PX_5$ (X=F, Cl and Br); $PI_5$ is unknown

2. Most halides can be made directly.

3. Phosphorus trifluoride is a very poisonous, colourless and odourless gas. It easily hydrolizes. Phosphorus trichloride is a colourless liquid.

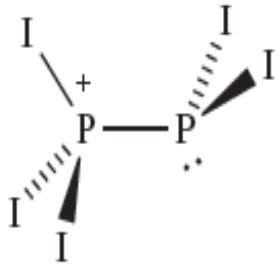
$$PCl_3 \begin{cases} \xrightarrow{O_2} POCl_3 \\ \xrightarrow{X_2\ (X=halogen)} PCl_3X_2 \\ \xrightarrow{NH_3} P(NH_2)_3 \end{cases}$$

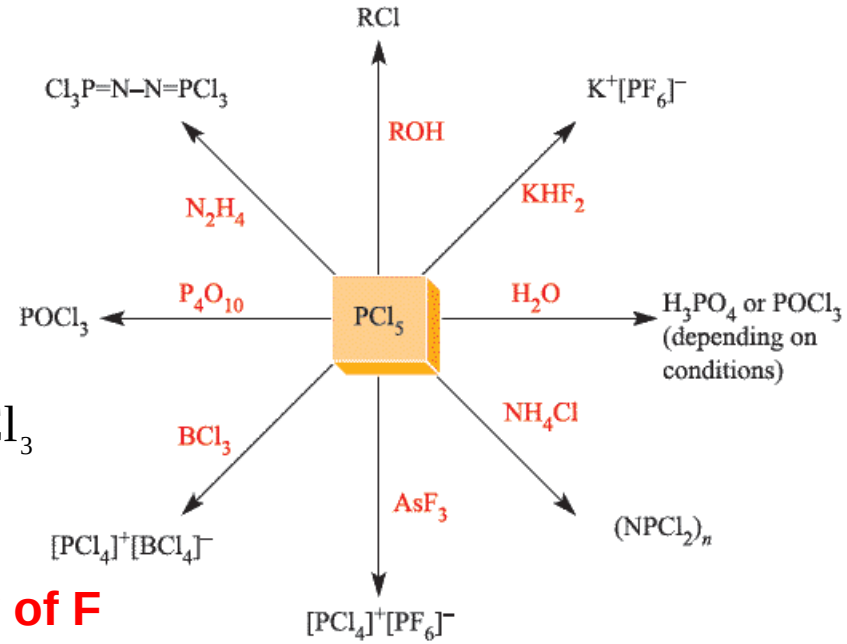
4. There are number of various ions based on $PF_3$: $[PF_4]^-$

5. Phosphorus pentafluoride is a strong Lewis acid and forms stable complexes with amines and ethers, for instance $NH_4PF_6$ and $KPF_6$

6. *** Properties of $PCl_5$

7. ***Phosphorus forms $P_2I_4$




8. Phosphoryl trichloride easily hydrolyzes to HCl:

$$2PCl_3 + O_2 \rightarrow 2POCl_3$$

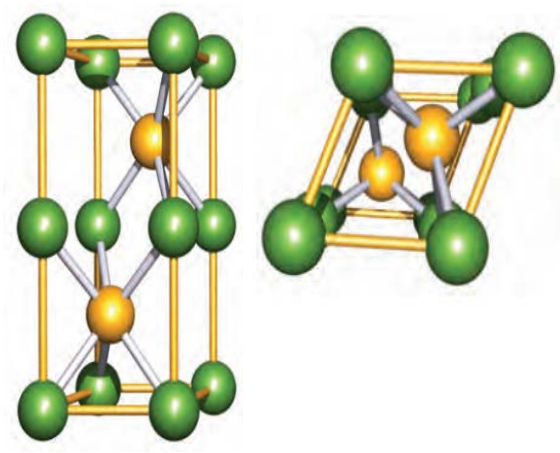
9. ***Arsenic and antimony halides (for self-education).

**10. Bismuth forms tri halides but penta-halide is only of F**

# Arsenic, antimony and bismuth

1. As and Sb form binary compounds with many metals. The degree of iconicity in them varies. One of the most known are the compounds with the group 3A elements: GaAs, InSb. They are important semiconductors with a diamond-like structure.

2. NiAs gives its name to structure type of a number of d-block metal arsenides, antimonides, sulfides, selenides and tellurides.



3. Bi does not form compounds with $Bi^{3-}$

# Oxides of P, Sb, As and Bi

1. **P, Sb, As and Bi form two oxides $E_2O_3$ (or $E_4O_6$) and $E_2O_5$ (or $E_4O_{10}$).**

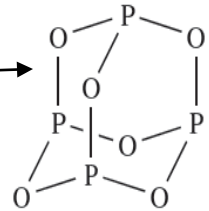
- $E_2O_5$ (E = P, As, Sb, Bi) are acidic;
- $P_4O_6$ is acidic;
- $As_4O_6$ and $Sb_4O_6$ are amphoteric;
- $Bi_2O_3$ is basic.

**$As^{3+}$ $Sb^{3+}$ $Bi^{3+}$ ← — → $As^{5+}$ $Sb^{5+}$ $Bi^{5+}$**

**Increase reducing activity  Increase oxidation activity**

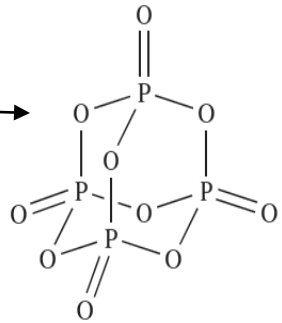
2. Phosphorus (III) oxide, $P_4O_6$, is obtained by burning white phosphorus in a restricted supply of $O_2$. It reacts with water $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

➔ Each P atom in $P_4O_6$ carries a lone pair of electrons and $P_4O_6$ can therefore act as a Lewis base, though very weak.



3. The most important oxide of phosphorus is $P_4O_{10}$ (phosphorus(V) oxide), commonly called phosphorus pentoxide.

➔ is one the best drying agents $\boxed{P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4}$



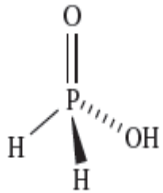
➔ Phosphorus forms number of mixed oxides (III)-(V)

4. Direct reaction of oxygen with As, Sb and Bi yields oxides (III). $As_2O_3$ is weakly acidic and dissolves in based. $Sb_2O_3$ is amphoteric; $Bi_2O_3$ is a metallic oxide.

➔ $As_2O_5$ (and of Sb) can be prepared by oxidation of $As_2O_3$ by strong oxidizers. Both oxides are stable. $Bi_2O_5$ is highly unstable and can be prepared only by very strong oxidizers.

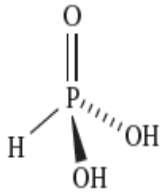
# Oxoacids of phosphorus. Polyphosphates

$H_3PO_2$ Phosphinic acid (hypophosphorous acid)



$pK_a = 1.24$

$H_3PO_3$ Phosphonic acid (phosphorous acid)

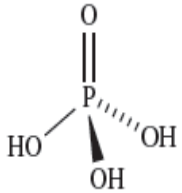


$pK_a(1) = 2.00$; $pK_a(2) = 6.59$

Salts containing the $[HPO_3]^{2-}$ ion are called *phosphonates*

$H_3PO_4$ Phosphoric acid (orthophosphoric acid)

$$Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow{\text{conc}} 2H_3PO_4 + 3CaSO_4$$



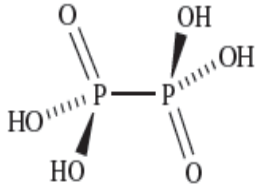
$pK_a(1) = 2.21$; $pK_a(2) = 7.21$; $pK_a(3) = 12.67$

$$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7 + H_2O$$

$$H_3PO_4 + H_4P_2O_7 \xrightarrow{\Delta} H_5P_3O_{10} + H_2O$$

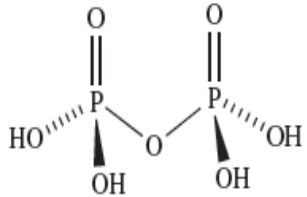
$H_4P_2O_6$ Hypophosphoric acid

$[H_3O]_2[H_2P_2O_6]$



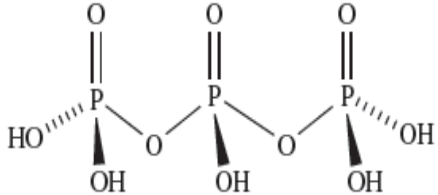
$pK_a(1) = 2.2$; $pK_a(2) = 2.8$; $pK_a(3) = 7.3$; $pK_a(4) = 10.0$

$H_4P_2O_7$ Diphosphoric acid (pyrophosphoric acid)



$pK_a(1) = 0.85$; $pK_a(2) = 1.49$; $pK_a(3) = 5.77$; $pK_a(4) = 8.22$

$H_5P_3O_{10}$ Triphosphoric acid



$pK_a(1) \leq 0$; $pK_a(2) = 0.89$; $pK_a(3) = 4.09$; $pK_a(4) = 6.98$; $pK_a(5) = 9.93$

# ***Oxoacids of arsenic, antimony and bismuth left for self-education…

$$H_3AsO_3 \rightleftarrows H_2O + HAsO_2$$

$$As_2O_3 + 6KOH = 2K_3AsO_3 + 3H_2O$$

$$K_3AsO_3 + I_2 + 2KOH = K_3AsO_4 + 2KI + H_2O$$

$$Sb_2O_3 + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2O$$

$$Sb_2O_3 + K_2SO_4 + H_2O$$

$$Sb_2O_3 + 2NaOH = 2NaSbO_2 + H_2O$$

$$SbCl_3 + 3NaOH = Sb(OH)_3\downarrow + 3NaCl$$

$$SbCl_3 + 2H_2O \rightleftarrows Sb(OH)_2Cl + 2HCl$$

$$Sb(OH)_2Cl = SbOCl\downarrow + H_2O$$

$$Bi(NO_3)_3 + 3NaOH = Bi(OH)_3\downarrow + 3NaNO_3$$

$$Bi(NO_3)_3 + H_2O \rightleftarrows BiONO_3 + 2HNO_3$$

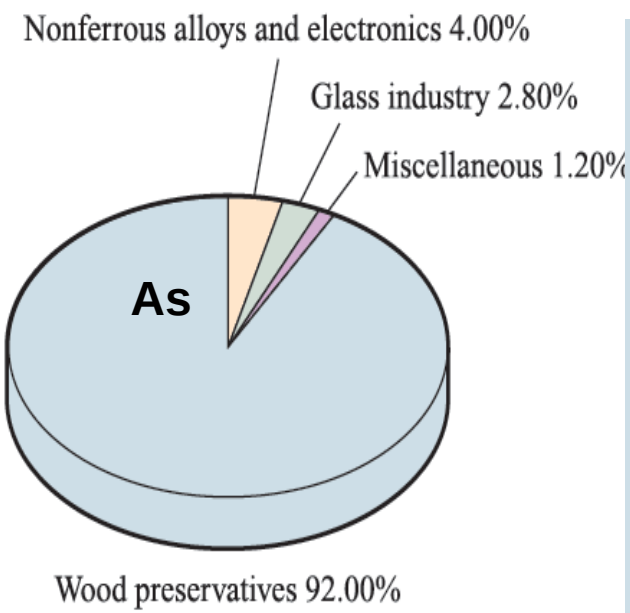
# ***Extraction

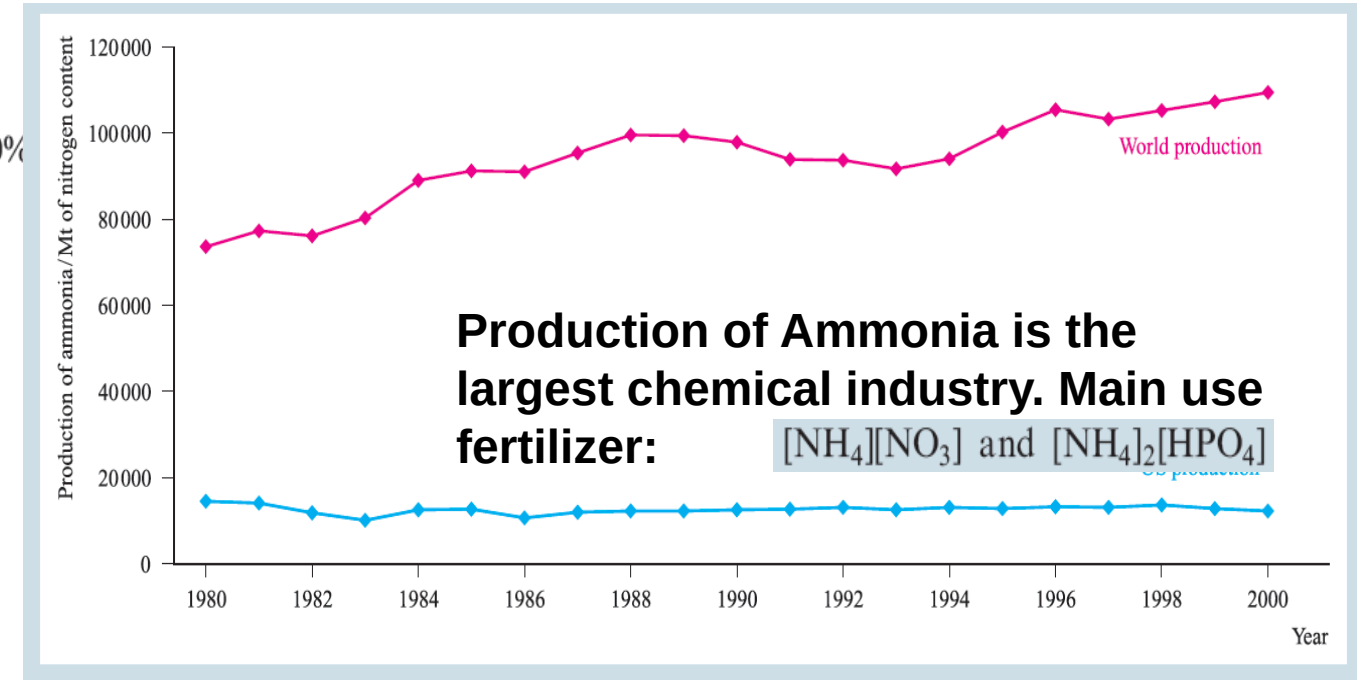
$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{\approx 1700\,K} P_4 + 6CaSiO_3 + 10CO$$

$$FeAsS \xrightarrow{\Delta(\text{in absence of air})} FeS + As$$

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

# ***Uses



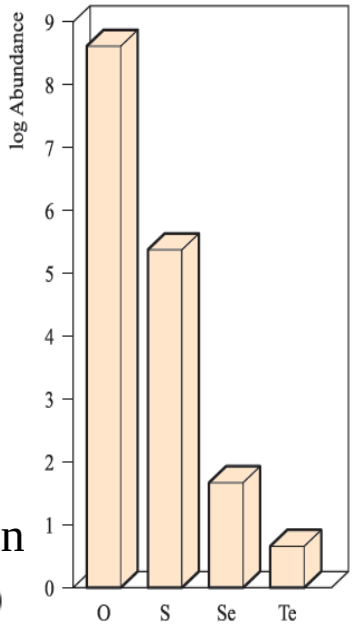



# Group 6A [noble gas]($s^2p^4$): O, S, Se and Te (Po) [chalcogens]

| Property | O | S | Se | Te | Po |
|---|---|---|---|---|---|
| Atomic number, $Z$ | 8 | 16 | 34 | 52 | 84 |
| Ground state electronic configuration | $[He]2s^22p^4$ | $[Ne]3s^23p^4$ | $[Ar]3d^{10}4s^24p^4$ | $[Kr]4d^{10}5s^25p^4$ | $[Xe]4f^{14}5d^{10}6s^26p^4$ |
| Enthalpy of atomization, $\Delta_a H^o(298\,K)$ / kJ mol$^{-1}$ | 249‡ | 277 | 227 | 197 | ≈146 |
| Melting point, mp / K | 54 | 388 | 494 | 725 | 527 |
| Boiling point, bp / K | 90 | 718 | 958 | 1263* | 1235 |
| Standard enthalpy of fusion, $\Delta_{fus}H^o(mp)$ / kJ mol$^{-1}$ | 0.44 | 1.72 | 6.69 | 17.49 | – |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 1314 | 999.6 | 941.0 | 869.3 | 812.1 |
| $\Delta_{EA}H^o{}_1(298\,K)$ / kJ mol$^{-1}$ ** | −141 | −201 | −195 | −190 | −183 |
| $\Delta_{EA}H^o{}_2(298\,K)$ / kJ mol$^{-1}$ ** | +798 | +640 | | | |
| Covalent radius, $r_{cov}$ / pm | 73 | 103 | 117 | 135 | – |
| Ionic radius, $r_{ion}$ for $X^{2-}$ / pm | 140 | 184 | 198 | 211 | – |
| Pauling electronegativity, $\chi^P$ | 3.4 | 2.6 | 2.6 | 2.1 | 2.0 |
| NMR active nuclei (% abundance, nuclear spin) | $^{17}O$ (0.04, $I=\frac{5}{2}$) | $^{33}S$ (0.76, $I=\frac{3}{2}$) | $^{77}Se$ (7.6, $I=\frac{1}{2}$) | $^{123}Te$ (0.9, $I=\frac{1}{2}$) $^{125}Te$ (7.0, $I=\frac{1}{2}$) | |

**Electronegativity**

| | | |
|---|---|---|
| 7 | 8 | 9 |
| N | O | F |
| 3.0 | 3.5 | 4.0 |
| 15 | 16 | 17 |
| P | S | Cl |
| 2.1 | 2.5 | 3.0 |
| 33 | 34 | 35 |
| As | Se | Br |
| 2.0 | 2.4 | 2.8 |
| 51 | 52 | 53 |
| Sb | Te | I |
| 1.9 | 2.1 | 2.5 |
| 83 | 84 | 85 |
| Bi | Po | At |
| 1.9 | 2.0 | 2.2 |




Abundances: sulfur minerals are very common: natural sulfur, sulfides [iron pyrites=fool's gold, $FeS_2$, galena (PbS), sphalerite or zinc blende (ZnS), cinnabar (HgS), realgar ($As_4S_4$), orpiment ($As_2S_3$), stibnite ($Sb_2S_3$), molybdenite ($MoS_2$) and chalcocite ($Cu_2S$), sulfates and silicate-sulfates. Se and Te have very few minerals and they are quite rare.

Pure sulfur was produced by mining the natural sulfur by hot water. Now days, more than 30% of S is obtained from the natural gas $H_2S$: $2H_2S + O_2 \xrightarrow{\text{activated carbon or alumina catalyst}} 2S + 2H_2O$

# The factors defining chemical properties

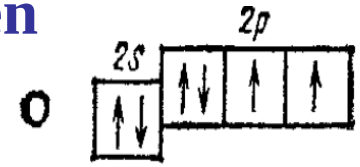
1. **All VIa elements are relatively small atoms with high electronegativity.**
2. **All $X^{2-}$ anions (except $O^{2-}$) are relatively large (>150 nm);**

**1. Chalcogens are much more similar than the elements of groups 3A, 4A and 5A.**

2. **All elements have a strong tendency to catenation. For the case of O it is restricted by the interaction between $s^2$ and p-electron pairs.**
3. **Chalcogens form ANIONS only**
4. **The polarity of the X-H bond quickly decreases down the group.**
5. **Oxygen usually has no more than FOUR neighbors (compare N vs P);**
6. **S, Se, Te may have more than four neighbors (usually with F or Cl).**
7. **S-O; Se-O and Te-O bonds are STRONG and covalent.**
8. **There is some decrease in non-metallic character down the group.**

# Oxygen physical and chemical properties

**➔Oxygen molecule is quite stable. Therefore, although oxygen reacts with many metals and non-metals spontaneously, the reaction requires initiation.**




**➔The rate of oxidation of a certain substance is a strong function of the activation condition ⇒ oxidation by $O_2$ strongly depends on catalysis**

➔Oxygen molecule is paramagnetic (occupied: 2e are on one σ-bonding, 4e on two π bonding; and 2e are unpaired on two π anti-bonding). Liquid oxygen is attracted by a magnet.

| | | | | | |
|---|---|---|---|---|---|
| O–O 146 | O=O 498 | O–H 464 | O–C 359 | O–F 190‡ | O–Cl 205‡ |
| S–S 266 | S=S 427 | S–H 366 | S–C 272 | S–F 326‡ | S–Cl 255‡ |
| Se–Se 192 | | Se–H 276 | | Se–F 285‡ | Se–Cl 243‡ |
| | | Te–H 238 | | Te–F 335‡ | |

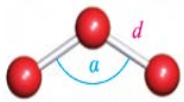
➔Oxygen molecule can be excited if two unpaired electrons on the π anti-bonding orbitals are paired (singlet state). Reactions with singlet oxygen are far more rapid. Singlet state can be prepared either by UV radiation or by $H_2O_2 + NaOCl \rightarrow O_2^* + NaCl + H_2O$

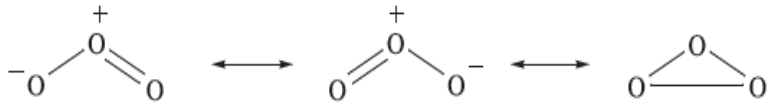
➔ Upon heating oxygen combines with all elements with the exception of: a) halogens; b) noble gases; c) $N_2$; d) noble metals (Au, Pt, slowly with Ir and Pd);

➔ In most of the oxides oxygen is $O^{2-}$. Exceptions: peroxides and super-oxides (see the lecture on alkali and alkaline earth metals).

# ***Ozone and ozonides

➔ Ozone forms under electrical discharge, quenching from 2500 C or by UV



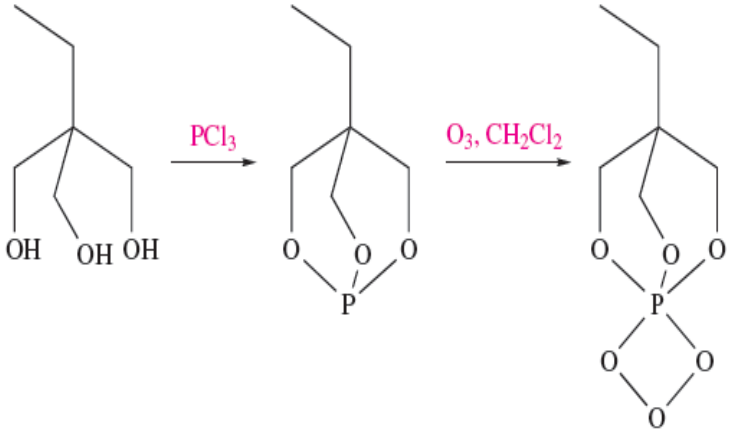
$O_3 \begin{cases} d = 128\,\text{pm} \\ a = 117° \end{cases}$ $[O_3]^- \begin{cases} d = 129\,\text{pm} \\ a = 120° \end{cases}$

$$\tfrac{3}{2}O_2(g) \rightarrow O_3(g) \qquad \Delta_f H^o(O_3, g, 298\,K) = +142.7\,\text{kJ mol}^{-1}$$

➔ Ozone is thermodynamically unstable and it is much stronger oxidizer than $O_2$

➔ Ozonides are salts of $O^{3-}$: $2KOH + 5O_3 \rightarrow 2KO_3 + 5O_2 + H_2O$

➔ Phosphite ozonides, (RO)3PO3 and $[Me_4]NO_3$ are stable



# Hydrogen-oxygen compounds.

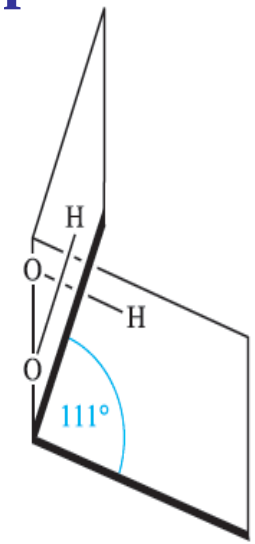
## ➔Hydrogen peroxide H-O-O-H preparation: $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

➔Liquid $H_2O_2$ is heavily hydrogen bonded

➔$H_2O_2$ readily decomposes in the presence of alkali, heavy metal ions or heterogeneous catalysts (e.g. Pt or $MnO_2$)

$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

$$\Delta_r H^o(298\,K) = -98\,kJ \text{ per mole of } H_2O_2$$




Selected properties of $H_2O_2$.

| | |
|---|---|
| Physical appearance at 298 K | Colourless (very pale blue) liquid |
| Melting point / K | 272.6 |
| Boiling point / K | 425 (decomposes) |
| $\Delta_f H^o(298\,K)$ / kJ mol$^{-1}$ | −187.8 |
| $\Delta_f G^o(298\,K)$ / kJ mol$^{-1}$ | −120.4 |
| Dipole moment / debye | 1.57 |
| O–O bond distance (gas phase) / pm | 147.5 |
| ∠O–O–H (gas phase) / deg | 95 |

➔$H_2O_2$ is a weak acid $H_2O_2 + H_2O \rightleftharpoons [H_3O]^+ + [HO_2]^-$ $K_a = 2.4 \times 10^{-12}$ (298 K)

➔$H_2O_2$ is a very strong oxidizer: $I^-$ to $I_2$, $SO_2$ to $H_2SO_4$ and (in alkaline solution) Cr(III) to Cr(VI).

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^o = +1.78\,V$$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^o = +0.70\,V$$

➔$H_2O_2$ can be oxidized to $O_2$ by very strong oxidizers: $2[MnO_4]^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

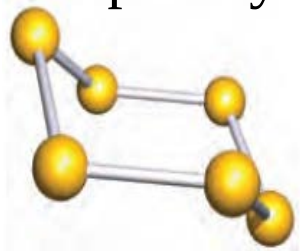
$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

$$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2[OH]^- \quad E^o_{[OH^-]=1} = -0.15\,V$$

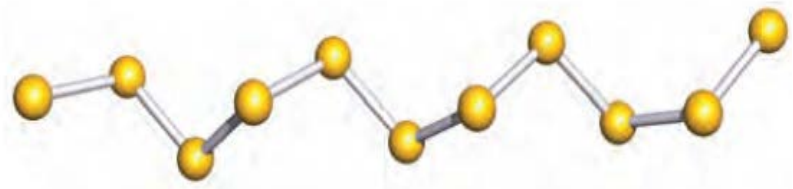
# Sulfur: physical and chemical properties

➔ Sulfur forms a large number of allotropes: cyclic $S_n$ , n=6-12, 18,20 and polymeric $S_\infty$; stable α and β -$S_8$

➔ Sulfur is insoluble in water but soluble in benzene and $CS_2$



$S_6$



Part of the helical chain of $S_\infty$

➔ Sulfur is very reactive. It reacts with many metals either at room temperature (Hg) or upon heating:

$$Zn(powder) + S(powder) \xrightarrow{\text{impact or ignition}} \text{explosion} + ZnS(s)$$

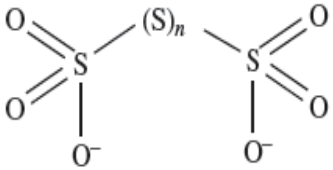
$$Hg(l) + S(s) \xrightarrow{\text{Shaking or grinding at RT}} HgS(s)$$

➔ Sulfur burns (if ignited) in air producing $SO_2$ and with halogens:

$$S_8 \begin{cases} \xrightarrow{F_2} SF_6 \\ \xrightarrow{Cl_2} S_2Cl_2 \\ \xrightarrow{Br_2} S_2Br_2 \end{cases}$$

➔ S reacts with hot alkali solutions producing a mixture of polysulfides, $[S_x]^{2-}$, and polythionates.

**➔Sulfur has a strong tendency to catenation.**




➔ Saturated hydrocarbons are dehydrogenated when heated with sulfur, and further reaction with alkenes occurs (used to make rubber).

➔ Sulfur reacts with electron donors like C=O: $O{=}C{=}S$ and $CN^-$: $^{-}N{=}C{=}S \longleftrightarrow N{\equiv}C{-}S^-$

➔ Sulfur reacts with sulfites ( at boiling ) $Na_2SO_3 + \frac{1}{8}S_8 \xrightarrow{H_2O,\ 373\,K} Na_2S_2O_3$

# Se and Te: physical and chemical properties

➔ Thermodynamically stable allotrope is grey selenium: contains helical chains -Se-; red monoclinic Se exists in three forms, each containing rings $Se_8$. black selenium consists of large polymeric rings;

➔ Tellurium has only one crystalline form: a silvery white metallic-looking solid. The structure is similar to that of grey selenium.

**➔ Chemical properties of Se and Te are quite similar to that of S.**

# Hydrides $H_2E$ (E=S, Se, Te)

| | $H_2S$ | $H_2Se$ | $H_2Te$ |
|---|---|---|---|
| Name‡ | Hydrogen sulfide | Hydrogen selenide | Hydrogen telluride |
| Physical appearance and general characteristics | Colourless gas; offensive smell of rotten eggs; toxic | Colourless gas; offensive smell; toxic | Colourless gas; offensive smell; toxic |
| Melting point / K | 187.5 | 207 | 224 |
| Boiling point / K | 214 | 232 | 271 |
| $\Delta_{vap}H^o$(bp) / kJ mol$^{-1}$ | 18.7 | 19.7 | 19.2 |
| $\Delta_f H^o$(298 K) / kJ mol$^{-1}$ | −20.6 | +29.7 | +99.6 |
| p$K_a$(1) | 7.04 | 4.0 | 3.0 |
| p$K_a$(2) | 19 | – | – |
| E–H bond distance / pm | 134 | 146 | 169 |
| ∠H–E–H / deg | 92 | 91 | 90 |

→$H_2S$ is obtained in industry from natural gas (and removed). Small amounts of hydrides can be obtained by $FeS(s) + 2HCl(aq) \rightarrow H_2S(g) + FeCl_2(aq)$ ; similarly $Al_2Se_3 + 6H_2O \rightarrow 3H_2Se + 2Al(OH)_3$

→$H_2S$ is a weak acid. All sulfides except alkali metals are insoluble. Sulfides of d-elements and metallic p- elements have very low solubility products. $H_2S + Pb(O_2CCH_3)_2 \rightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3CO_2H$

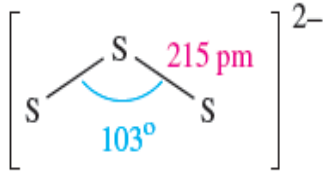
CuS, PbS, HgS, CdS, $Bi_2S_3$, $As_2S_3$, $Sb_2S_3$ and SnS SP<$10^{-30}$ precipitate from asides.
ZnS, MnS, NiS and CoS $10^{-15}$<SP<$10^{-10}$ precipitated only from neutral or alkaline solutions

→Sulfur forms a number of **polysulfanes** H-$S_n$-H: $2H_2S + S_nCl_2 \rightarrow H_2S_{n+2} + 2HCl$

➔Sulfides of many d-elements contain $[S_2]^{2-}$ ions like $FeS_2$ (iron pyrites). $[S_2]^{2-}$ is an analogue of the superoxide ion and has been detected in solutions of alkali metal sulfides in acetone or dimethyl sulfoxide.

➔ Polysulfides with $[S_n]^{2-}$ can be formed by adding sulfur to sulfides: $2Cs_2S + S_8 \xrightarrow{\text{aq medium}} 2Cs_2[S_5]$

➔ Polysulfides of the alkali and alkaline earth metals usually contain




➔Se and Te have much lower tendency to catenation. Properties of $H_2Se$ and $H_2Te$ are similar to that of $H_2S$. **Both are STRONGER acids than $H_2S$** (Think why???) . Salts tellurides and selelnides are similar to sulfides.

➔ Only $H_2Se_2$ and $H_2Te_2$ are known among poly-hydrides.

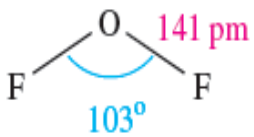
➔Polyselenides, polytellurides and their metal complexes are well known $3Se + K_2Se_2 \xrightarrow{\text{DMF}} K_2[Se_5]$

# Halides, oxohalides and complex halides

| Property | $OF_2$ | $O_2F_2$ | $S_2F_2$ | $F_2S{=}S$ | $SF_4$ | $SF_6$ | $S_2F_{10}$ |
|---|---|---|---|---|---|---|---|
| Physical appearance and general characteristics | Colourless (very pale yellow) gas; explosive and toxic | Yellow solid below 119 K; decomposes above 223 K | Colourless gas; extremely toxic | Colourless gas | Colourless gas; toxic; reacts violently with water | Colourless gas; highly stable | Colourless liquid; extremely toxic |
| Melting point / K | 49 | 119 | 140 | 108 | 148 | 222 (under pressure) | 220 |
| Boiling point / K | 128 | – | 288 | 262 | 233 | subl. 209 | 303 |
| $\Delta_f H^\circ(298\ K)$ / kJ mol$^{-1}$ | +24.7 | +18.0 | | | −763.2 | −1220.5 | |
| Dipole moment / D | 0.30 | 1.44 | | | 0.64 | 0 | 0 |
| E–F bond distance / pm‡ | 141 | 157.5 | 163.5 | 160 | 164.5 (ax)<br>154.5 (eq) | 156 | 156 |

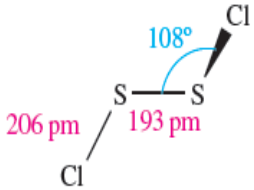
➔Oxygen difluoride, $OF_2$ forms if $2NaOH + 2F_2 \rightarrow OF_2 + 2NaF + H_2O$

➔ It is a very strong oxidizer and hydrolyzes: $H_2O + OF_2 \rightarrow O_2 + 2HF$




➔$SF_4$ and $S_2F_2$ are unstable. $SF_6$ is stable and kinetically chemically inert. It hydrolyzes by steam above 400 C. Direct reaction of S and $F_2$ results in $SF_6$

➔Sulfur forms a number of chlorides and oxychlorides. Molten sulfur reacts with $Cl_2$ producing $S_2Cl_2$




$2SO_2 + S_2Cl_2 + 3Cl_2 \rightarrow 4SOCl_2$

$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$

$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$

$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$

$SO_2 + Cl_2 \xrightarrow{\text{activated charcoal}} SO_2Cl_2$

# Oxides oxo-acides and derivatives

➔Sulfur forms a number of oxides ($S_2O$, $S_8O$ …$S_nO$) but only $SO_2$ and $SO_3$ are stable.

➔ Burning of sulfur or sulfides in air yields $SO_2$. $4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$

| Property | $SO_2$ | $SO_3$ |
|---|---|---|
| Physical appearance and general characteristics | Colourless, dense gas; pungent smell | Volatile white solid, or a liquid |
| Melting point / K | 198 | 290 |
| Boiling point / K | 263 | 318 |
| $\Delta_{vap}H^o$(bp) / kJ mol$^{-1}$ | 24.9 | 40.7 |
| $\Delta_f H^o$(298 K) / kJ mol$^{-1}$ | −296.8 ($SO_2$, g) | −441.0 ($SO_3$, l) |
| Dipole moment / D | 1.63 | 0 |
| S–O bond distance / pm ‡ | 143 | 142 |
| ∠O–S–O / deg ‡ | 119.5 | 120 |

➔ $SO_2$ reacts with $O_2$, $F_2$ , $Cl_2$. $SO_2 + X_2 \rightarrow SO_2X_2$ (X = F, Cl)

➔ $SO_2$ forms addicts with alkali metal fluorides and azides: $SO_2 + MF \xrightarrow{258\ K} M^+[SO_2F]^-$ (M = K, Rb, Cs)

➔ $SO_2$ is a weak reducing agent in acidic solution and a slightly stronger one in basic media.

$$[SO_4]^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l) \quad E^o = +0.17\,V$$

$$[SO_4]^{2-}(aq) + H_2O(l) + 2e^- \rightleftharpoons [SO_3]^{2-}(aq) + 2[OH]^-(aq) \quad E^o_{[OH^-]=1} = -0.93\,V$$

➔In a very strongly acidic environment $SO_2$ is an oxidizer $SO_2 + 4H^+ + 4Fe^{2+} \rightarrow S + 4Fe^{3+} + 2H_2O$

$$H_2SO_3 + 2H_2S = 3S\downarrow + 3H_2O$$

➔<u>The oxidation of $SO_2$ by atmospheric $O_2$ is very slow, but it is catalyzed by $V_2O_5$</u>

$\Delta_r H^o = -96$ kJ per mole of $SO_2$

➔Solution of $SO_2$ in water is a fairly strong acid. $SO_2 + H_2O \rightleftarrows H_2SO_3$

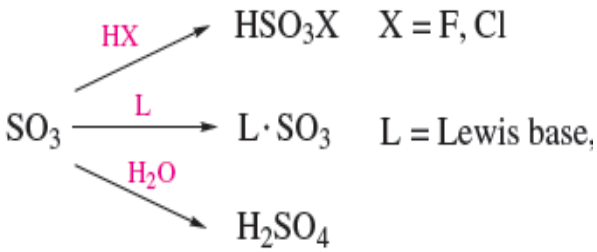
➔Sulfurous acid cannot be isolated but its alkali salts (sulfites) are stable. In solutions $SO_2$ slowly oxidizes. $2H_2SO_3 + O_2 = 2H_2SO_4$

➔ <u>Alkali salts of sulfurous acid are stable</u>. Upon heating they disproportionate:

$$4Na_2SO_3 = Na_2S + 3Na_2SO_4$$

➔*** solution of $Ca(HSO_3)$ (solid does not exist) is a very important product for paper production.

# ➔Sulfur trioxide is a typical anhydride:




➔Solubility of sulfates is difficult to predict. Most sulfates are soluble. Alkali sulfates are soluble. Most divalent d-metals sulfates are soluble. All hydro-sulfates $(HSO_4)^-$ are soluble. Insoluble sulfates of Ca, Ba, Sr, Pb

➔Hot concentrated $H_2SO_4$ is a very strong oxidizer: $8HI + H_2SO_4 = 4I_2 + H_2S\uparrow + 4H_2O$

$2HBr + H_2SO_4 = Br_2 + SO_2\uparrow + 2H_2O$

$C + 2H_2SO_4 = CO_2\uparrow + 2SO_2\uparrow + 2H_2O$

$S + 2H_2SO_4 = 3SO_2\uparrow + 2H_2O$

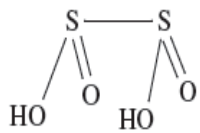
$Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$

➔Diluted sulfuric acid oxidizes by $H^+$ only.

➔Electrolysis of 50% solution of $H_2SO_4$ produces peroxi-sulfuric acid: $2HSO_4^- = H_2S_2O_8 + 2e^-$

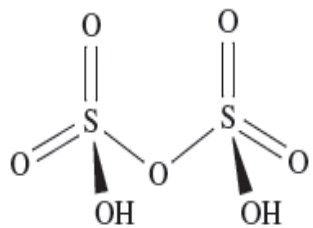
➔Sulfur forms a line of acids with S-S, S-O-S and S=S bonds. They can be produced by reduction of sulfites. Most of them are known only in solutions.

$H_2S_2O_4$ Dithionous acid (tetraoxodisulfuric acid)



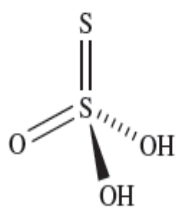
$pK_a(1) = 0.35$; $pK_a(2) = 2.45$

$H_2S_2O_7$ Disulfuric acid (μ-oxo-hexaoxodisulfuric acid)



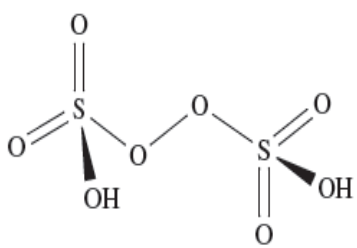
$pK_a(1) = 3.1$

$H_2S_2O_3$ Thiosulfuric acid (trioxothiosulfuric acid)



$pK_a(1) = 0.6$; $pK_a(2) = 1.74$

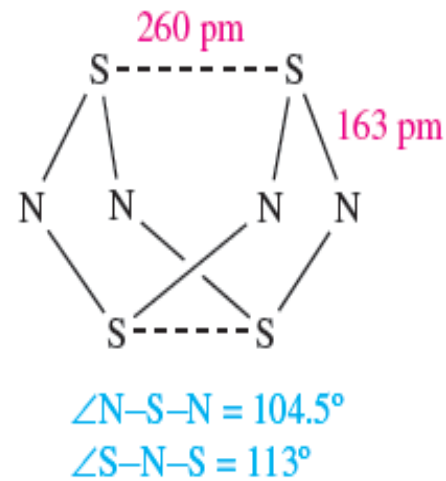
$H_2S_2O_8$ Peroxodisulfuric acid (μ-peroxo-hexaoxodisulfuric acid)



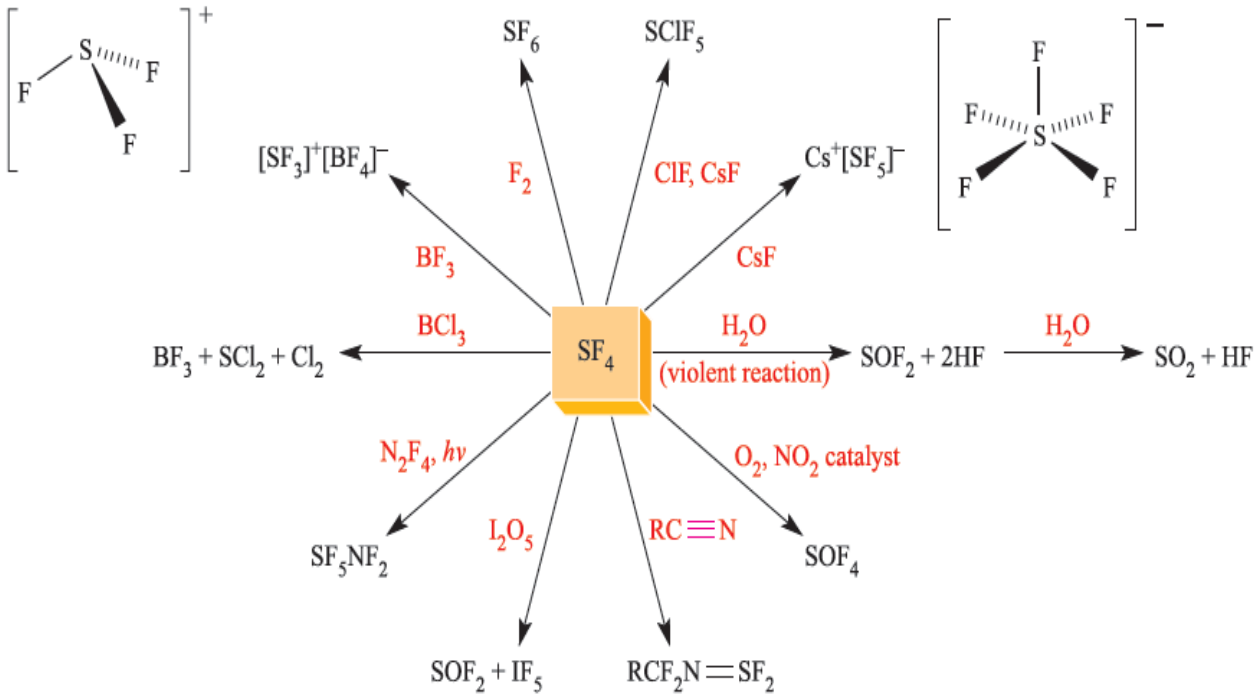
➔Selenium and tellurium also form two line of acid +4 and +6. They are quite similar to the corresponding sulfates.

➔*** Sulfur forms a number of nitrides. The best known is $S_4N_4$

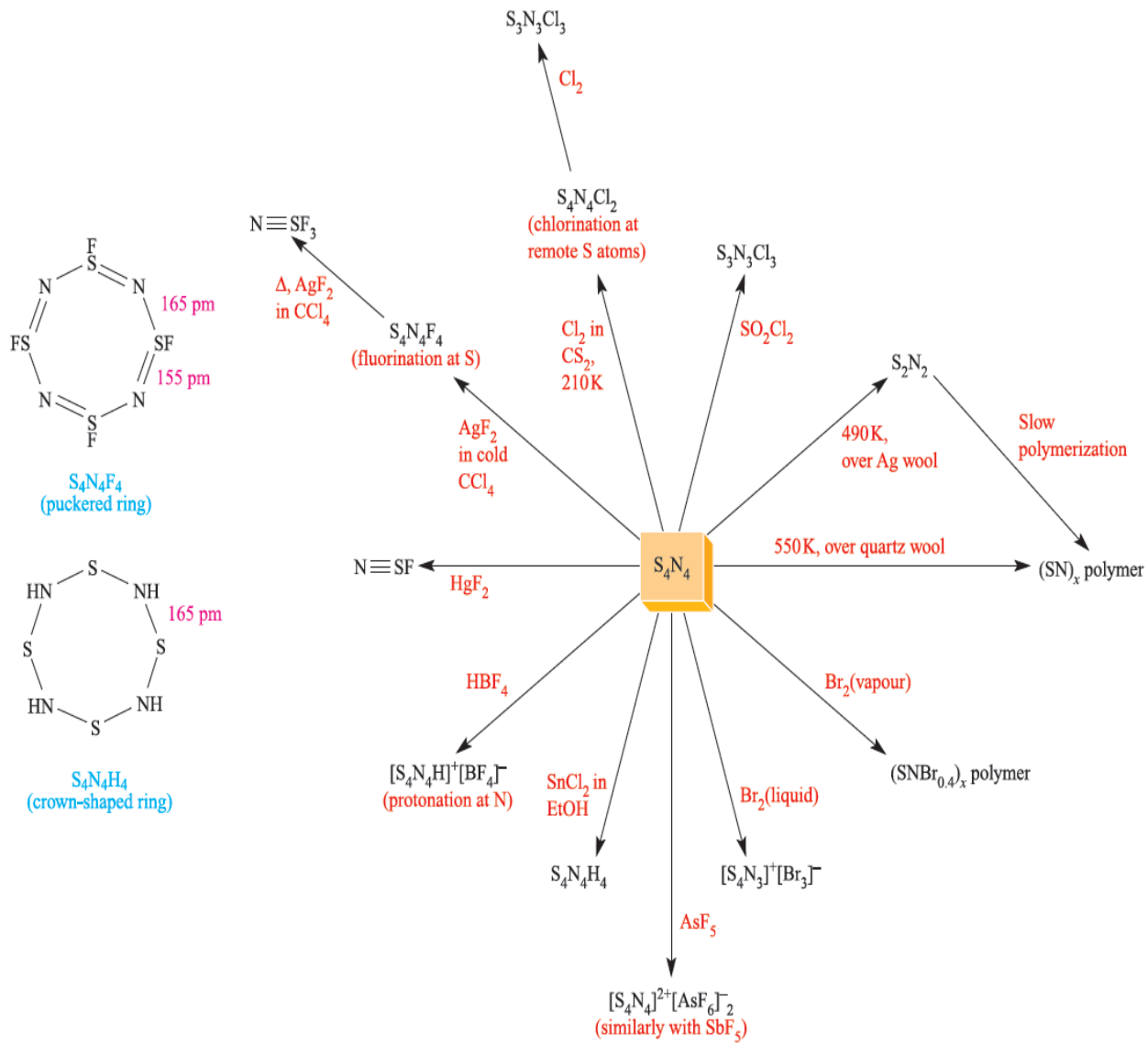
$$6S_2Cl_2 + 16NH_3 \xrightarrow{CCl_4,\ 320\ K} S_4N_4 + 12NH_4Cl + S_8$$



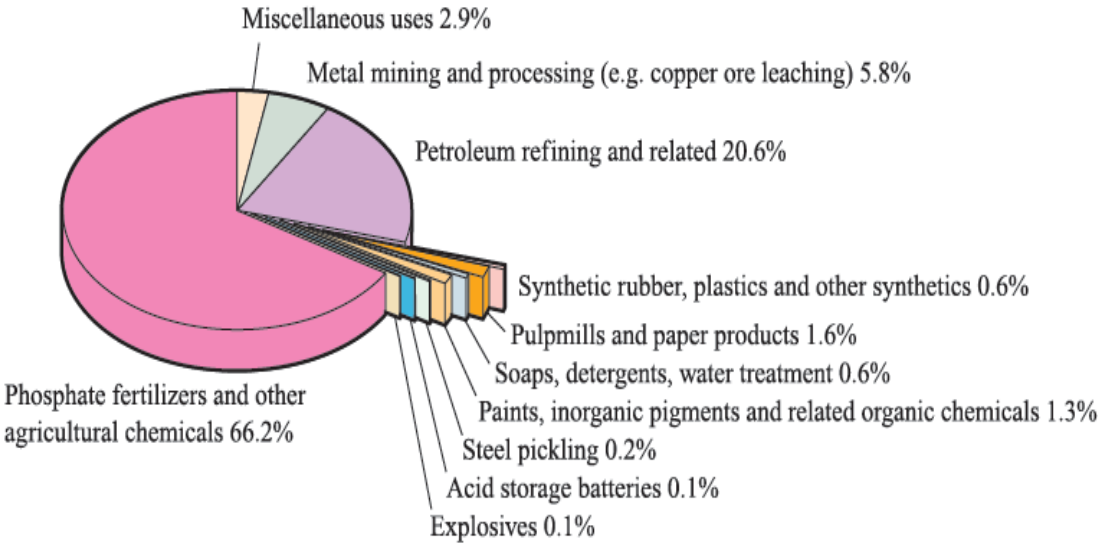
# ***Selected reactions of sulfur tetrafluoride



# ***Selected reactions of $S_4N_4$; the rings in $S_4N_4H_4$ and $S_4N_4F_4$ are non-planar

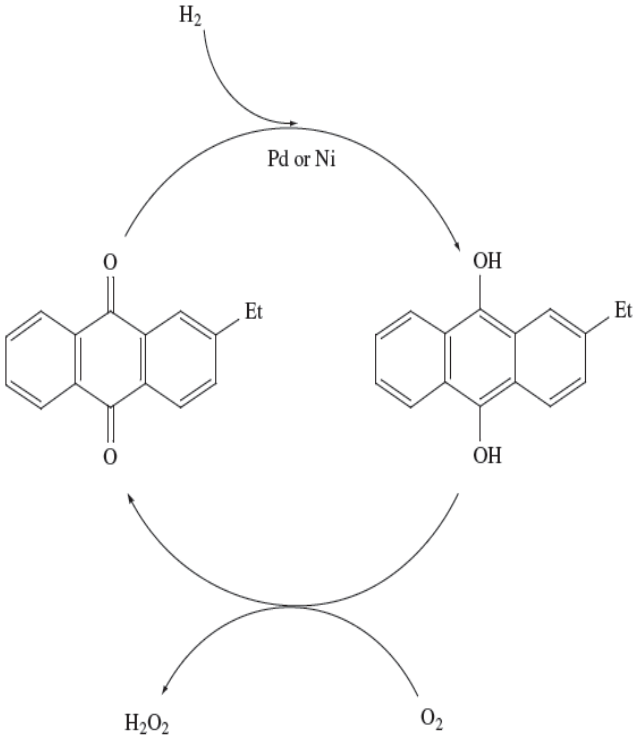


# ***Uses




Uses of sulfur and sulfuric acid

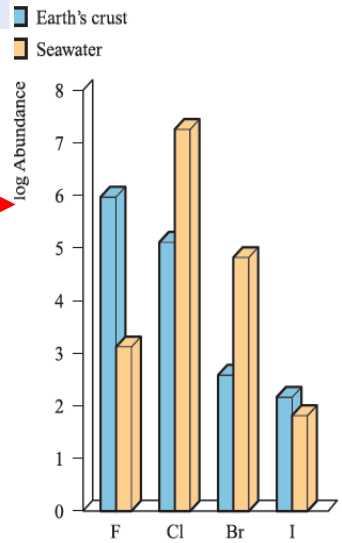
# The catalytic cycle used in the industrial manufacture of hydrogen peroxide




$O_2$ is converted to $H_2O_2$ during the oxidation of the organic alkylanthraquinol. The organic product is reduced by $H_2$ in a Pd- or Ni catalyzed reaction.

# Group 7A [noble gas]($s^2p^4$): F, Cl, Br, I [halogens]

| Property | F | Cl | Br | I |
|---|---|---|---|---|
| Atomic number, $Z$ | 9 | 17 | 35 | 53 |
| Ground state electronic configuration | $[He]2s^22p^5$ | $[Ne]3s^23p^5$ | $[Ar]3d^{10}4s^24p^5$ | $[Kr]4d^{10}5s^25p^5$ |
| Enthalpy of atomization, $\Delta_a H^o(298\ K)$ / kJ mol$^{-1}$ ‡ | 79 | 121 | 112 | 107 |
| Melting point, mp / K | 53.5 | 172 | 266 | 387 |
| Boiling point, bp / K | 85 | 239 | 332 | 457.5 |
| Standard enthalpy of fusion of $X_2$, $\Delta_{fus}H^o(mp)$ / kJ mol$^{-1}$ | 0.51 | 6.40 | 10.57 | 15.52 |
| Standard enthalpy of vaporization of $X_2$, $\Delta_{vap}H^o(bp)$ / kJ mol$^{-1}$ | 6.62 | 20.41 | 29.96 | 41.57 |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 1681 | 1251 | 1140 | 1008 |
| $\Delta_{EA}H_1^o(298\ K)$ / kJ mol$^{-1}$ * | −328 | −349 | −325 | −295 |
| $\Delta_{hyd}H^o(X^-, g)$ / kJ mol$^{-1}$ | −504 | −361 | −330 | −285 |
| $\Delta_{hyd}S^o(X^-, g)$ / J K$^{-1}$ mol$^{-1}$ | −150 | −90 | −70 | −50 |
| $\Delta_{hyd}G^o(X^-, g)$ / kJ mol$^{-1}$ | −459 | −334 | −309 | −270 |
| Standard reduction potential, $E^o(X_2/2X^-)$ / V | +2.87 | +1.36 | +1.09 | +0.54 |
| Covalent radius, $r_{cov}$ / pm | 71 | 99 | 114 | 133 |
| Ionic radius, $r_{ion}$ for $X^-$ / pm ** | 133 | 181 | 196 | 220 |
| van der Waals radius, $r_v$ / pm | 135 | 180 | 195 | 215 |
| Pauling electronegativity, $\chi^P$ | 4.0 | 3.2 | 3.0 | 2.7 |
| | pale yellow gas | pale green - yellow gas | dark orange liquid | dark purple crystals |




**Electronegativity**

| | | |
|---|---|---|
| 7<br>N<br>3.0 | 8<br>O<br>3.5 | 9<br>F<br>4.0 |
| 15<br>P<br>2.1 | 16<br>S<br>2.5 | 17<br>Cl<br>3.0 |
| 33<br>As<br>2.0 | 34<br>Se<br>2.4 | 35<br>Br<br>2.8 |
| 51<br>Sb<br>1.9 | 52<br>Te<br>2.1 | 53<br>I<br>2.5 |
| 83<br>Bi<br>1.9 | 84<br>Po<br>2.0 | 85<br>At<br>2.2 |

Halogens form a number of minerals:

F: ( fluorite, $CaF_2$), cryolite ($Na_3(AlF_6)$) and fluorapatite, ($Ca_5F(PO_4)_3$);

Cl: rock salt (NaCl), sylvite (KCl) and carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$);

Bromine is extracted from salt lakes; Iodine is extracted from seaweed.

Flouring is produced by electrolysis of KF·2HF (m.p. 70 °C);

HF is produced from fluorite: $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

Chlorine is produced by electrolysis of conc water solution of NaCl or KCl

# The factors defining chemical properties

1. **There is a great similarity between the corresponding compounds of all group members.**
2. **The electronegativities are very high (F-the highest possible)**
3. **All $X^-$ radii are large**
4. **Molecule dissociation energies are small**

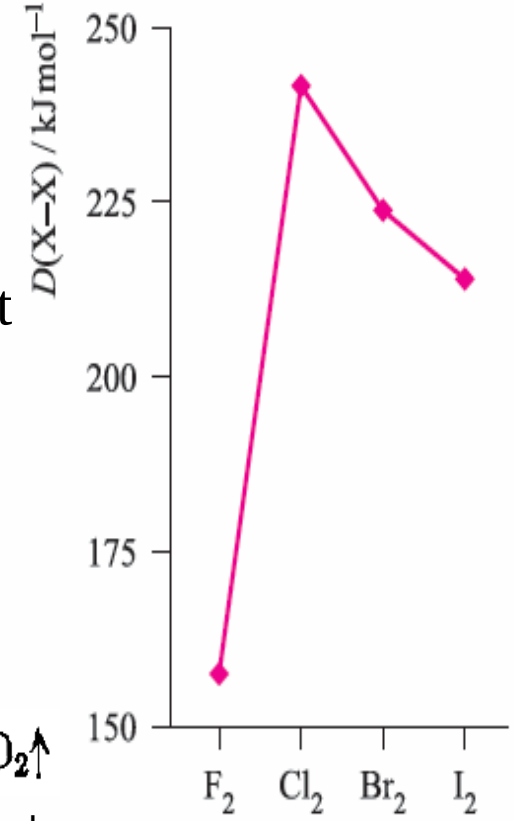
1. **All elements in free forms are strong oxidizers**
2. **All elements form anions only ( [there are exception])**
3. **Low dissociation energy: Chemical activity of halogens at room temperature is defined by the stability of the $X_2$ molecules.**
4. **F is somewhat different from the other halogens because:**

a) **F has only one state -1; b) the strongest oxidizer.**

5. **Large number of possible positive oxidation states: +1, 3, 5 and 7 but <u>almost</u> never 2, 4 or 6.**

*****Halogens (except F) are poorly soluble in water, but soluble in organic solvents (methanol, ethanol) and $CS_2$ and $CCl_4$**

# Chemical properties.




➔ **$F_2$** a pale yellow gas, extremely corrosive (most active known); **$F_2$ combines directly with all elements except $O_2$, $N_2$,** C-diamond, He and Ne; In many cases, the reaction starts at RT (alkali metals, Fe, Ni, $H_2$, $S_8$, $I_2$, $Br_2$, $P_4$, Sb, C, Si, B…)

➔Upon heating $F_2$ oxidizes $Cl_2$, Kr, Xe $Xe + F_2 = XeF_2$

➔ Many metals (Fe, Ni) are passivated by the formation of a layer of nonvolatile metal fluoride;

➔ $F_2$ reacts with water and many oxides displacing oxygen:

➔Reaction with $SiO_2$ is catalyzed by water $2F_2 + 2H_2O = 4HF + O_2\uparrow$

$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$ slow

$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$
$2H_2O + 2F_2 \rightarrow 4HF + O_2$ } fast

➔ **Chemical reactivity decreases from $Cl_2$ to $I_2$ but $I_2$ reacts more readily. Most reactions require heating.**

$F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

$I_2 + 2ClO_3^- \longrightarrow 2IO_3^- + Cl_2$

➔$Cl_2$ reacts with $H_2$ with explosion, $Br_2$ slower, $I_2$+$H_2$ reacts only partially.

# Hydrogen halides and their salts

| Property | HF | HCl | HBr | HI |
|---|---|---|---|---|
| Physical appearance at 298 K | Colourless gas | Colourless gas | Colourless gas | Colourless gas |
| Melting point / K | 189 | 159 | 186 | 222 |
| Boiling point / K | 293 | 188 | 207 | 237.5 |
| $\Delta_{fus}H^o(mp)$ / kJ mol$^{-1}$ | 4.6 | 2.0 | 2.4 | 2.9 |
| $\Delta_{vap}H^o(bp)$ / kJ mol$^{-1}$ | 34.0 | 16.2 | 18.0 | 19.8 |
| $\Delta_f H^o(298\,K)$ / kJ mol$^{-1}$ | −273.3 | −92.3 | −36.3 | +26.5 |
| $\Delta_f G^o(298\,K)$ / kJ mol$^{-1}$ | −275.4 | −95.3 | −53.4 | +1.7 |
| Bond dissociation energy / kJ mol$^{-1}$ | 570 | 432 | 366 | 298 |
| Bond length / pm | 92 | 127.5 | 141.5 | 161 |
| Dipole moment / D | 1.83 | 1.11 | 0.83 | 0.45 |

➔ All water solutions of HX are acids. Acidity quickly increases from HF to HI because of the ionic radius increase $F^-$ to $I^-$

➔ HF has a tendency to form $HF_2^-$ ion (why???) $[F—H—F]^-$

➔ HCl, HBr and HI can be oxidized, HCl with difficulties, HBr and HI easier.

$$4HCl + O_2 \xrightarrow{CuCl2\,(400K)} 2Cl_2 + 2H_2O$$

$$2HBr + H_2SO_4(conc) \xrightarrow{heating} Br_2 + SO_2\uparrow + 2H_2O$$

$$8HI + H_2SO_4(conc) \xrightarrow{heating} 4I_2 + H_2S\uparrow + 4H_2O$$

$$16HCl + 2KMnO_4(conc) \xrightarrow{aq.\,solution} 5Cl_2 + 2KCl + 2MnCl_2 + 8H_2O$$

$$2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + I_2 + 2HCl$$

➔ Most fluorides are insoluble, with the exception of Na, K, Al, Sn and Ag. (and $NH_3$)

➔ Most salts of Cl, Br and I are soluble. Insoluble chlorides are of Ag, Pb(II), CuCl, $Hg_2Cl_2$. Practical importance have: NaCl, KCl, $CaCl_2 \cdot 6H_2O$, AgCl.

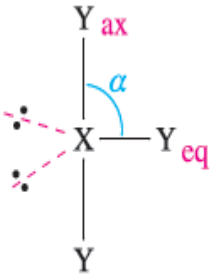
➔ Halogen salts of noble metals and Ag slowly decompose (especially in presence of visible light) to metals and halogen.

# Interhalogen compounds and polyhalogen ions

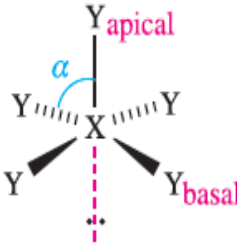
most stable

| Compound | Appearance at 298 K | Melting point / K | Boiling point / K | $\Delta_f H^o(298\,K)^{***}$ / kJ mol$^{-1}$ | Dipole moment for gas-phase molecule / D | Bond distances in gas-phase molecules except for $IF_3$ and $I_2Cl_6$ / pm[§] |
|---|---|---|---|---|---|---|
| ClF | Colourless gas | 117 | 173 | −50.3 | 0.89 | 163 |
| BrF | Pale brown gas | ≈240* | ≈293* | −58.5 | 1.42 | 176 |
| BrCl | ‡ | – | – | +14.6 | 0.52 | 214 |
| ICl | Red solid | 300 (α)<br>287 (β) | ≈373** | −23.8 | 1.24 | 232 |
| IBr | Black solid | 313 | 389** | −10.5 | 0.73 | 248.5 |
| $ClF_3$ | Colourless gas | 197 | 285 | −163.2 | 0.6 | 160 (eq), 170 (ax) |
| $BrF_3$ | Yellow liquid | 282 | 399 | −300.8 | 1.19 | 172 (eq), 181 (ax) |
| $IF_3$ | Yellow solid | 245 (dec) | – | ≈ −500 | – | 187 (eq), 198 (ax)[§§] |
| $I_2Cl_6$ | Orange solid | 337 (sub) | – | −89.3 | 0 | 238 (terminal)[§§]<br>268 (bridge) |
| $ClF_5$ | Colourless gas | 170 | 260 | −255 | – | 172 (basal),<br>162 (apical) |
| $BrF_5$ | Colourless liquid | 212.5 | 314 | −458.6 | 1.51 | 178 (basal),<br>168 (apical) |
| $IF_5$ | Colourless liquid | 282.5 | 373 | −864.8 | 2.18 | 187 (basal),<br>185 (apical) |
| $IF_7$ | Colourless gas | 278 (sub) | – | −962 | 0 | 186 (eq), 179 (ax) |

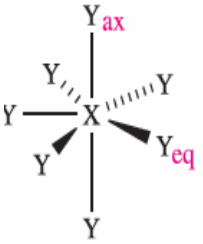
➔ Interhalogens form by direct reaction.




T-shaped




Square-based pyramid




Pentagonal bipyramid

➔ Many interhalogens disproportionate: $3BrF \rightarrow Br_2 + BrF_3$ $5IF \rightarrow 2I_2 + IF_5$

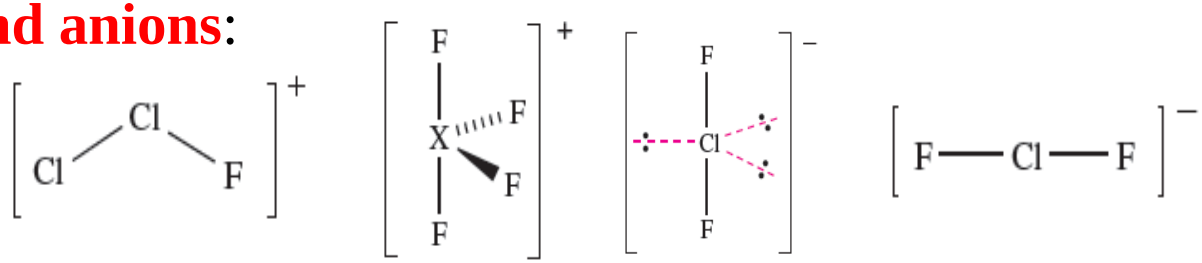
➔ClF acts as a powerful fluorinating and oxidizing agent. $W + 6ClF \rightarrow WF_6 + 3Cl_2$

# ***Poly-halogen ions (useful to know)

➔ interhalogens form **cations and anions**:

$$2ClF + AsF_5 \rightarrow [Cl_2F]^+[AsF_6]^-$$

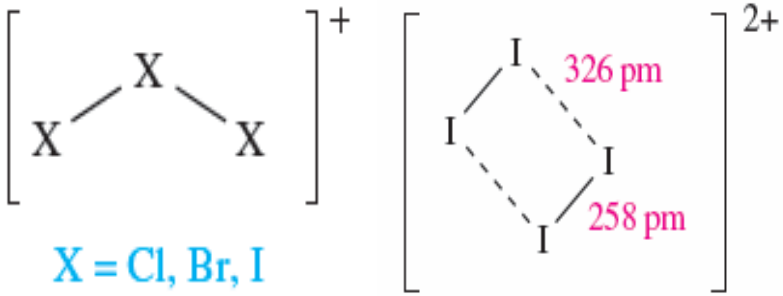
$$ClF + CsF \rightarrow Cs^+[ClF_2]^-$$




These cations and anions can be viewed an interhalogen molecule with missing electron and distributed charge.

➔ Halogens form a number of homo-nuclear **cations** $[Br_2]^+$, $[I_2]^+$, $[Cl_3]^+$, $[I_3]^+$, $[Cl_5]^+$, $[Br_5]^+$, $[I_5]^+$, $[I_4]^+$

$$Br_2 + SbF_5 \xrightarrow{BrF_5} [Br_2]^+[Sb_3F_{16}]^-$$




➔ Iodine forms a number of homo-nuclear **anions** $[I_n]^-$ n=3,4,5,7,8,9,10,12,16,

There are also data about $[Br_3]^-$ . The best known poly-iodine is used in medicine:

$$I^-(aq.) + I_2(solid) \rightarrow I_3^-$$

Interesting fact: Solution of $KI_3$ dissolves gold.

# Oxygen-containing compounds (except F). Part 1. Cl

➔The only thermodynamically stable oxide of halogen is $I_2 + \frac{5}{2}O_2 \rightarrow I_2O_5$

$\Delta_f H^o(298\,K) = -158.1\,kJ\,mol^{-1}$

➔Bromine oxides can be obtained by oxidation by ozone: $\underset{\text{Brown}}{Br_2} \xrightarrow{O_3,\ 195\,K} \underset{\text{Orange}}{Br_2O_3} \xrightarrow{O_3,\ 195\,K} \underset{\text{Colourless}}{Br_2O_5}$

➔Chlorine oxides have a tendency to decompose explosively.

➔Chlorine oxides and oxo-acids can be obtained by disproportionation reactions.

➔In cold water solutions Chlorine disproportionates. In bases the reaction is complete

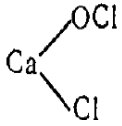
$Cl_2 + H_2O \longrightarrow HCl + HClO + 25kJ/mol$ $\quad Cl_2 + KOH \xrightarrow{aq.\,sol.} KCl + KClO + H_2O$

➔ **HOCl** (hypochlorous, known in solutions) is a weak acid pK=5×10$^{-8}$. It decomposes slowly: $2HClO \longrightarrow 2HCl + O_2$

The acid and its salts (hypochlorites) is VERY STRONG oxidizer, especially in acid environment because: $KClO + CO_2 + H_2O \xrightarrow{aq.\,sol.} KHCO_3 + HClO$

➔Chlorine reacts with alkali earth bases forming mixed salts that hydrolyze with time to HClO

$$Cl_2 + Ca(OH)_2 \longrightarrow CaOCl_2 + H_2O$$




HCl acting on the mixed salts release chlorine $CaOCl_2 + 2HCl = CaCl_2 + Cl_2 + H_2O$

➔Solutions of HClO may decompose in three distinctive ways depending on conditions

$$2HClO \xrightarrow{cold\ aq.solution} 2HCl + O_2$$ (sun light, some d-metal ions)

$$2HClO \xrightarrow{\text{dehydrating agent } (P_2O_5)} H_2O + Cl_2O$$ ➔$Cl_2O$ is an unstable gas

$$3HClO \xrightarrow{\text{hot aq.solutions}} 2HCl + HClO_3$$

➔$Cl_2$ disproportionate to chlorates ($ClO_3^-$) directly in hot bases:

$$3Cl_2 + 6KOH \xrightarrow{\text{aq. solution, } 90\,^oC} 5KCl + KClO_3 + 3H_2O$$

➔$HClO_3$ (chlorous acid) can be prepared as 50% solution at most. It is a very strong acid (as HCl or $HNO_3$). It is a very strong oxidizer ($HClO_3$ ignites wood or cotton).

➔ Upon strong heating all **chlorates** (salts of $HClO_3$ ) decompose to:

$$2KClO_3 \xrightarrow{>200\,^oC} 2KCl + 3O_2$$

➔$HClO_3$ does not have an anhydride. Upon dehydration it gives:

$$2KClO_3 + H_2SO_4(conc) \longrightarrow 2K_2SO_4 + ClO_2 + H_2O + \frac{1}{2}O_2$$

➔$ClO_2$ is a yellow-brown gas, highly unstable with tendency to explode. It reacts with basis giving the salts of TWO acids: $2ClO_2 + 2KOH \xrightarrow{\text{cold water}} KClO_3 + KClO_2 + H_2O$

Although $ClO_2$ is a radical, it shows only minor (if any) tendency to make dimers

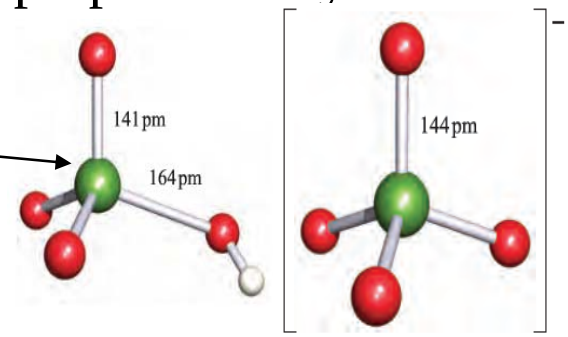
➔$HClO_2$ acid is unstable, but its alkali salts (**chlorites**) are stable

Cl—O = 157 pm; ∠O–Cl–O = 111°

➔Heating dry alkali chlorates causes their disproportionation into perchlorates

$$4KClO_3 \xrightarrow{100\ ^oC,\ slow} 3KClO_4 + KCl$$

➔Perchlorates are the salts of chloric acid $HClO_4$ which can be prepared anhydrous (by concentrated $H_2SO_4$). $HClO_4$ is a very strong acid.




➔Anhydride of $HClO_4$, $Cl_2O_7$ (yellow liquid) can be prepared as a pure substance: $2HClO_4 + P_2O_5 \xrightarrow{<50\,C} 2HPO_3 + Cl_2O_7$

➔$Cl_2O_7$ is stable unless heated or detonated.

➔Stability of the oxo-chloride acids and their salts increases in the line:

**Increased stability and strength of the acid** →

**$HClO$ $HClO_2$ $HClO_3$ $HClO_4$**

← **Increased oxidation activity**

➔ **$HClO_4$ reacts with metals releasing $H_2$**

➔Explanation: large anions are stable because of the resonance effects; Their acidity increases because the electrostatic interaction with $H^+$ decreases.

➔Solubility of the oxo-chloride salts increases from $HClO$ to $HClO_4$

# Oxo-acids of I and Br

➔For Br and I the equilibrium $X_2 + H_2O \longrightarrow HX + HXO$ is shifted to the left

➔$HXO_3$ (X=Br, I) can be obtained by oxidation with $Cl_2$

$$Br_2 + 5Cl_2 + 6H_2O \longrightarrow 2HBrO_3 + 10HCl$$

➔$HBrO_3$ is very similar to $HClO_3$, $HIO_3$ is different from them by the fact that it is a weak oxidizer. $HIO_3$ can be easily dehydrated: $HIO_3 \xrightarrow{P_2O_5} I_2O_5 + H_2O$

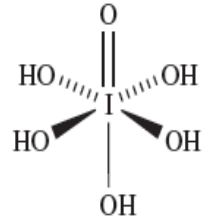
$I_2O_5$ is a stable solid that decomposes only above 300 C.

➔Oxidation of $HBrO_3$ into per-bromates can be achieved only by very strong oxidizers and the resulting product is poorly studied.

$$KBrO_3 + XeF_2 + H_2O \longrightarrow KBrO_4 + Xe + 2HF$$

➔ $HIO_4$ is stable and can be obtained as: $2HClO_4 + I_2 \longrightarrow 2HIO_4 + Cl_2$

➔ $HIO_4$ precipitates as $HIO_4 \cdot 2H_2O$, which should be viewed as $H_5IO_6$ because it makes salts $Ag_5IO_6$. $HIO_4 \cdot 2H_2O$ can be dehydrated




I–O(terminal) = 178 pm
I–OH = 189 pm

---

➔Hypofluorous acid, HOF is unstable and does not ionize in water: $HOF + H_2O \rightarrow H_2O_2 + HF$

$$F_2 + H_2O \xrightarrow{230\ K} HOF + HF$$

# Oxo-acids summary

| Oxoacids of chlorine | | Oxoacids of bromine | | Oxoacids of iodine | |
|---|---|---|---|---|---|
| Hypochlorous acid | $HOCl$ | Hypobromous acid | $HOBr$ | Hypoiodous acid | $HOI$ |
| Chlorous acid | $HOClO$ ($HClO_2$) | | | | |
| Chloric acid | $HOClO_2$ ($HClO_3$) | Bromic acid | $HOBrO_2$ ($HBrO_3$) | Iodic acid | $HOIO_2$ ($HIO_3$) |
| Perchloric acid | $HOClO_3$ ($HClO_4$) | Perbromic acid | $HOBrO_3$ ($HBrO_4$) | Periodic acid | $HOIO_3$ ($HIO_4$) |
| | | | | Orthoperiodic acid | $(HO)_5IO$ ($H_5IO_6$) |

**Strengths of the acids increases;**
**Stability increases;**
**Oxidation ability decreases;**

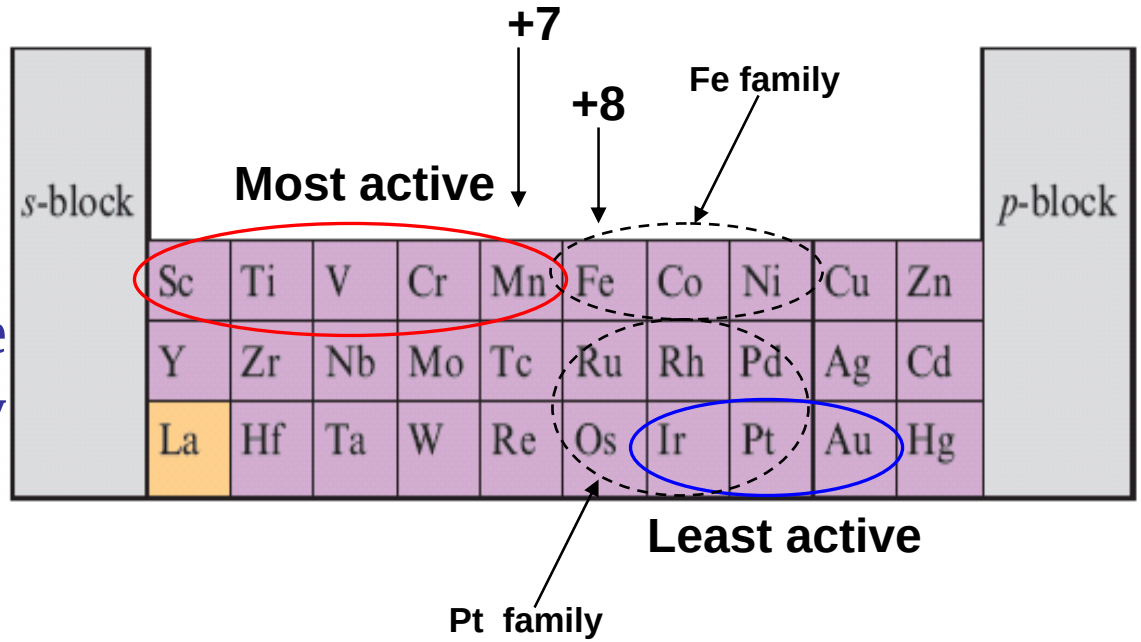
**Stability decreases;**
**Oxidation ability Increases strongly;**
**Strengths of the acids does not change;**

# Transition metals (d-metals). VERY brief overview

# Part 1.

There are a number of <u>clear tendencies</u> among d-block.. metals.

1. The highest oxidation state of most metals with ($d^n$ n=1-6) in the same column is the same and may reach +8. The lowest oxidation states are +1 or +2.




2. Chemical reactivity in the rows <u>decreases from $d^5$ to $d^{10}$</u>

3. The first row elements are significantly different from the second and third row elements. The chemical reactivity quickly decreases from the first row (n=4) to the third row (n=6)

Summary: the most active are the elements in the top left corner. The least active are the elements in the right bottom corner.

Oxidation states of the d-block metals; the most stable states are marked in blue.

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | [0] | |
| | | 1 | 1 | 1 | 1 | 1 | 1 | **1** | |
| | 2 | 2 | **2** | **2** | **2** | **2** | **2** | **2** | **2** |
| **3** | 3 | **3** | **3** | 3 | **3** | **3** | 3 | 3 | |
| | **4** | **4** | 4 | 4 | 4 | 4 | 4 | [4] | |
| | | **5** | 5 | 5 | | | | | |
| | | | **6** | 6 | 6 | | | | |
| | | | | **7** | | | | | |

| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 0 | 0 | 0 | 0 | | |
| | | | | 1 | | 1 | | **1** | |
| | 2 | 2 | 2 | [2] | 2 | 2 | **2** | 2 | **2** |
| **3** | 3 | 3 | 3 | 3 | **3** | **3** | | 3 | |
| | **4** | 4 | 4 | **4** | 4 | 4 | 4 | | |
| | | **5** | 5 | **5** | 5 | 5 | | | |
| | | | **6** | 6 | 6 | 6 | | | |
| | | | | **7** | 7 | | | | |
| | | | | | 8 | | | | |

| La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 0 | 0 | 0 | 0 | [0] | |
| | | | | 1 | | 1 | | 1 | **1** |
| | 2 | 2 | 2 | 2 | 2 | 2 | **2** | [2] | **2** |
| **3** | 3 | 3 | 3 | **3** | 3 | **3** | | **3** | |
| | **4** | 4 | **4** | **4** | **4** | **4** | **4** | | |
| | | **5** | **5** | **5** | 5 | 5 | 5 | 5 | |
| | | | **6** | **6** | 6 | 6 | 6 | | |
| | | | | **7** | 7 | | | | |
| | | | | | 8 | | | | |

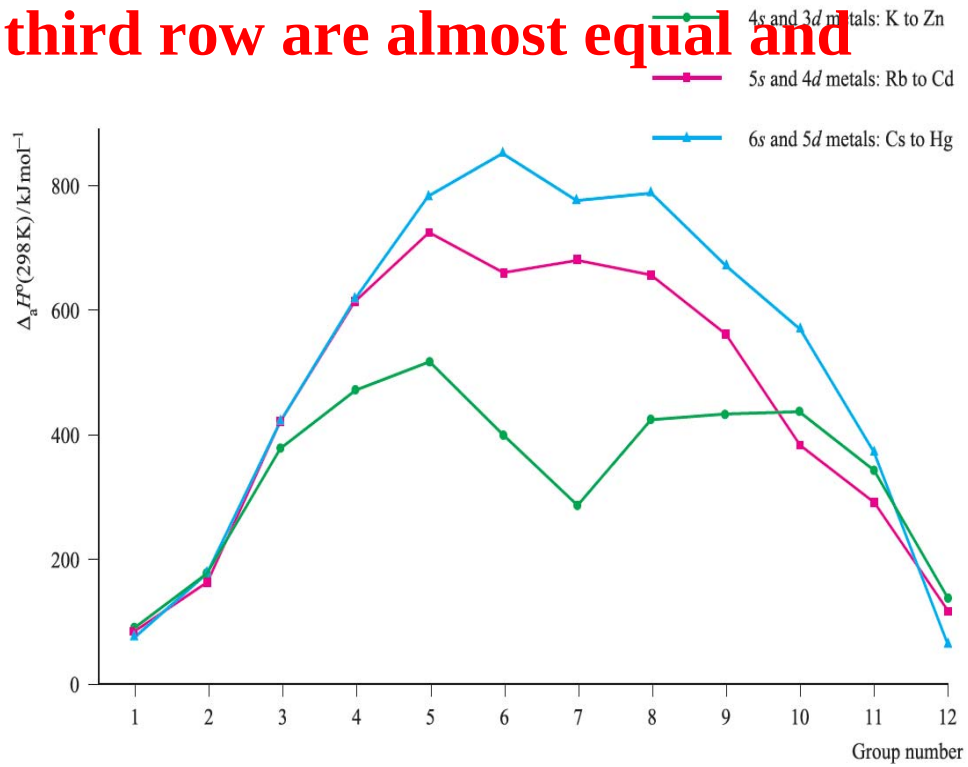
4. All d-block metals are hard, ductile and malleable, with high electrical and thermal conductivities.

5. At room temperature, the metals possess either FCC, HCP or BCC structure-typical for metals. The exceptions are Mn (I4-double cube), Hg (rhombohedral 70°);

6. Ionic radii of d-block metals are smaller than those of the s-block metals of comparable atomic numbers:

a) along the row the radii almost do not change;

b) the radii of the second row and the third row are almost equal and larger than those of the first row




7. Most d-block metals have a tendency to form complexes and some of them (Pt, Hg, Ru, Re) have a tendency to catenation.

# Selected physical properties of the metals of the first row of the d-block

| Property | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Atomic number, $Z$ | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Physical appearance of pure metal | Soft; silver-white; tarnishes in air | Hard; lustrous silver coloured | Soft; ductile; bright white | Hard; blue-white | Hard; lustrous silver-blue | Quite soft; malleable; lustrous, white | Hard; brittle; lustrous blue-white | Hard; malleable and ductile; grey-white | Malleable and ductile; reddish | Brittle at 298 K; malleable 373–423 K; lustrous blue-white |
| Melting point / K | 1814 | 1941 | 2183 | 2180 | 1519 | 1811 | 1768 | 1728 | 1358 | 693 |
| Boiling point / K | 3104 | 3560 | 3650 | 2945 | 2235 | 3023 | 3143 | 3005 | 2840 | 1180 |
| Ground state valence electronic configuration (core = [Ar]): | | | | | | | | | | |
| Atom | $4s^2 3d^1$ | $4s^2 3d^2$ | $4s^2 3d^3$ | $4s^1 3d^5$ | $4s^2 3d^5$ | $4s^2 3d^6$ | $4s^2 3d^7$ | $4s^2 3d^8$ | $4s^1 3d^{10}$ | $4s^2 3d^{10}$ |
| $M^+$ | $4s^1 3d^1$ | $4s^2 3d^1$ | $3d^4$ | $3d^5$ | $4s^1 3d^5$ | $4s^1 3d^6$ | $3d^8$ | $3d^9$ | $3d^{10}$ | $4s^1 3d^{10}$ |
| $M^{2+}$ | $3d^1$ | $3d^2$ | $3d^3$ | $3d^4$ | $3d^5$ | $3d^6$ | $3d^7$ | $3d^8$ | $3d^9$ | $3d^{10}$ |
| $M^{3+}$ | [Ar] | $3d^1$ | $3d^2$ | $3d^3$ | $3d^4$ | $3d^5$ | $3d^6$ | $3d^7$ | $3d^8$ | $3d^9$ |
| Enthalpy of atomization, $\Delta_a H^\circ(298\,K)$ / kJ mol$^{-1}$ | 378 | 470 | 514 | 397 | 283 | 418 | 428 | 430 | 338 | 130 |
| First ionization energy, $IE_1$ / kJ mol$^{-1}$ | 633.1 | 658.8 | 650.9 | 652.9 | 717.3 | 762.5 | 760.4 | 737.1 | 745.5 | 906.4 |
| Second ionization energy, $IE_2$ / kJ mol$^{-1}$ | 1235 | 1310 | 1414 | 1591 | 1509 | 1562 | 1648 | 1753 | 1958 | 1733 |
| Third ionization energy, $IE_3$ / kJ mol$^{-1}$ | 2389 | 2653 | 2828 | 2987 | 3248 | 2957 | 3232 | 3395 | 3555 | 3833 |
| Metallic radius, $r_{metal}$ / pm‡ | 164 | 147 | 135 | 129 | 137 | 126 | 125 | 125 | 128 | 137 |
| Electrical resistivity ($\rho$) $\times 10^8$ / $\Omega$ m (at 273 K)* | 56** | 39 | 18.1 | 11.8 | 143 | 8.6 | 5.6 | 6.2 | 1.5 | 5.5 |
| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |

# Triad [$d^1$]: Sc, Y and La. Lanthanodes.

## 1. Electron structure: $d^1s^2$

## 2. The only oxidation state +3

## 3. Electrode potentials: -2.4….-2 V

All metals of the groups are white-white in a pure form. They melt above 1000 °C. All of them react with air and water at ambient conditions and form purely basic oxides $Me_2O_3$ (except Sc).

## Scandium

Sc is VERY similar to Al however, it reacts with water because $Sc_2O_3$ does not protect it. Sc dissolves both in bases and acids, combines with halogens, N2, and S. In all cases it shows oxidation state +3. Similar to Al, In and Ga, Sc has a tendency to form poly-halogenides (like $ScVCl_{12}$); forms complex $[ScF_6]^{3-}$. In most of the cases, the coordination number of 6.

# Yttrium

Yttrium is quite very similar to lanthanides but exhibit only +3 oxidation state

1. Yttrium is partially passivated in air by $Y_2O_3$. Y reacts rapidly with hot water (but slowly reacts with cold water), most dilute acids and hot solution of KOH liberating $H_2$. Interesting: Y does not dissolve in HF ( $YF_3$ is completely insoluble). Yttrium reacts with oxygen upon heating and with halogens.

$$4Y + 3O_2 \xrightarrow{\Delta} 2Y_2O_3 \qquad 2Y + 3X_2 \xrightarrow{\Delta} 2YX_3 \qquad (X = F, Cl, Br, I)$$

2. In most compounds Y has an oxidation state +3 with CN=6. Interesting: no complex with F. $3KCl + YCl_3 \rightarrow K_3[YCl_6]$

3. $Y_2O_3$ is insoluble in water but soluble in acids. It is exclusively basic.

# Lanthanum and lanthanides (La to Lc)

**1. Electron structure:** $f^{1-14}d^{1}s^{2}$ *(La, Ce,Gd,Lu)*

*and* $f^{1-14}d^{0}s^{2}$ *(all the rest)*

**2. *4f*-electrons do not participate in chemical bonding, with the exception of Ce ⇒**

**All lanthanides except Ce exhibit +3 oxidation state.**

(Eu, Sm and Lu sometimes exhibit +2; Pr, Tb and Dy sometimes exhibit +4 ).

**3. Ce, Pr, Tb and Dy may be +4, however, except for Ce, this oxidation state is not stable at ambient conditions.**

**4. Atomic size shrinks from La to Lc**

**5. All lanthanides have $E^{o}$ within the range –(2-2.4)V**

1. All lanthanides are soft white metals. All of them react with dilute acids and water (hot and cold) liberating $H_2$.

2. All lanthanides react with halogens and other non-metals.

3. All lanthanides from a number of complex compounds. The coordination number may vary 6-8.

4. **All lanthanide oxides exhibit exclusively basic properties.**

## Brief note about actinides

1. *5f*-electrons PARTICIPATE in bonding. Therefore, actinides exhibit a range of high oxidation state.

**Actinides are substantially different from each other.**

Oxidation states of actinium and the actinoids. The most stable states are shown in red.

| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 2 | | | 2 | 2 | 2 | 2 | 2 | |
| 3 | | | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | | | | | |
| | | 5 | 5 | 5 | 5 | 5 | | | | | | | | |
| | | | 6 | 6 | 6 | 6 | | | | | | | | |
| | | | | 7 | 7 | | | | | | | | | |

# Triad [$d^2s^2$]: Ti, Zr and Hf

1. Electrode potential $Ti/Ti^{2+}$ is -1.63=> should be very reactive. Ti is covered in air by $TiO_2$, which protects it from cold bases and many acids. Ti reacts with **hot water**, hot acids (HF, HCl, $HNO_3$, $H_3PO_4$ , $H_2SO_4$), dissolves in $H_2O_2$

2. Stable oxidation state +4, though +2 and +3 are known. $TiO_2$ (rutile or anatase), $Ti_2O_3$ and TiO. Exposure to air or water convert all compounds of $Ti^{+3}$ and $Ti^{2+}$ to $Ti^{4+}$. In most +4 compounds Ti has CN=6. $TiO_2$ is the most commonly used white pigment.

3. Titanium forms stable tetra-halides; they and most titanium salts hydrolyze except for very acidic environment.

$$TiF_4 + 2H_2O \Leftrightarrow TiO_2 + 4HF$$

4. Ti and $TiO_2$ react with hot strong bases (NaOH, $Ba(OH)_2$), forming titanates ($BaTiO_3$) that are poorly soluble.

| Ti | Zr | Hf |
|---|---|---|
| 0 | | |
| 2 | 2 | 2 |
| 3 | 3 | 3 |
| 4 | 4 | 4 |

1. Zr and Hf have similar chemical tendencies as Ti, however, they are far less chemically active. The stable oxidation state for both is +4. The lower oxidation states are far less stable than that of Ti.

2. Fine powders Hf and Zr metals are pyrophoric.

$$M^{4+} + 4e^- \rightleftharpoons M \qquad \begin{cases} M = Zr, & E^o = -1.70\,V \\ M = Hf, & E^o = -1.53\,V \end{cases}$$

However, both metals are covered by $ZrO_2$ and $HfO_2$ and do not react with bases at all; They do not react with most diluted acids.

3. Zr and Hf dissolve in $HNO_3$/HCl, conc. HF forming complexes of +4 oxidation state.

4. Halides can be produced directly but similar to Ti halides hydrolyze.

5. The specific ability of Zr and Hf to form clusters: complex poly-nuclear – poly-ligand complexes like $Zr_6Cl_{14}C$.

6. $ZrO_2$ and $HfO_2$ are very inert and dissolve only in concentrated HF and hot 100% $H_2SO_4$

# Triad [$d^3s^2$]: V, Nb and Ta

**1. V, Nb and Ta may exhibit any oxidation state from +2 to +5 ( V also 0 and +1). In the higher oxidation state they are quite similar to P and Sb. In the lower oxidation states they have metallic (amphoteric character).**

V
0
1
2
3
4
5

1. Pure V does not react with water, HCl and bases. However, it reacts easily with HF, $HNO_3$ and $H_2SO_4$.

Nb

2. V forms 4 oxides: VO, $V_2O_3$, $VO_2$ and $V_2O_5$. Heating in air results in a mixture of oxides.

$$V^{2+} + 2e^- \rightleftharpoons V \qquad E^o = -1.18\ V$$

2
3
4
5

3. VO and $V_2O_3$ are purely basic and dissolve in acids only. Salts of $V^{2+}$ can be easily oxidized into $V^{3+}$ or $V^{4+}$. ($V^{2+}$/ $V^{3+}$ E=-0.26 V).

4. $VO_2$ is amphoteric and dissolves in both acids ($[VO]^{2+}$) and bases $[V_{12}O_{42}]^{12-}$. It is weak acid and a weak base.

Ta

All V-halognedies are molecular liquids or solids.

$$V \begin{cases} \xrightarrow{F_2} VF_5 \\ \xrightarrow{Cl_2} VCl_4 \\ \xrightarrow{X_2} VX_3 \quad (X = Br \text{ or } I) \end{cases}$$

2
3
4
5

$$2VF_4 \xrightarrow{\geq 298\ K} VF_5 + VF_3 \qquad 2VCl_4 \rightarrow 2VCl_3 + Cl_2$$

$$V_2O_5 + VCl_3 \rightarrow VOCl_2 \rightarrow VOCl_3 + VOCl$$

5. $V_2O_5$ is mostly acidic and the salts of $HVO_3$ are usually soluble. However, there is an equilibrium (compare with $NO_2^+$):

| | |
|---|---|
| pH 14 | $[VO_4]^{3-}$ |
| | $[VO_3(OH)]^{2-}$ in equilibrium with $[V_2O_7]^{4-}$ |
| | $[V_4O_{12}]^{4-}$ |
| pH 6 | $[H_nV_{10}O_{28}]^{(6-n)-}$ |
| | $V_2O_5$ |
| pH 0 | $[VO_2]^+$ |

$$[VO_4]^{3-} + H^+ \rightleftharpoons [VO_3(OH)]^{2-}$$

$$2[VO_3(OH)]^{2-} \rightleftharpoons [V_2O_7]^{4-} + H_2O$$

$$[VO_3(OH)]^{2-} + H^+ \rightleftharpoons [VO_2(OH)_2]^-$$

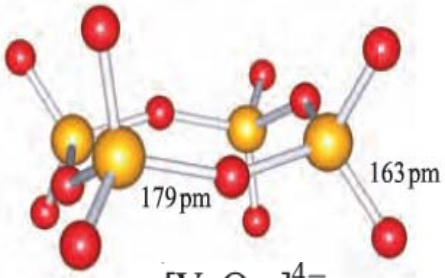
$$4[VO_2(OH)_2]^- \rightleftharpoons [V_4O_{12}]^{4-} + 4H_2O$$

$$10[V_3O_9]^{3-} + 15H^+ \rightleftharpoons 3[HV_{10}O_{28}]^{5-} + 6H_2O$$

$$[HV_{10}O_{28}]^{5-} + H^+ \rightleftharpoons [H_2V_{10}O_{28}]^{4-}$$

$$[H_2V_{10}O_{28}]^{4-} + 14H^+ \rightleftharpoons 10[VO_2]^+ + 8H_2O$$

6. Vanadium forms poly-vanadic acids (polyoxometallates), which a common property of $V^{5+}$, $Mo^{6+}$ and $W^{6+}$ . Some weak tendency to form polyoxometallates also exists in $Ta^{5+}$ and $Cr^{6+}$




$[V_4O_{12}]^{4-}$

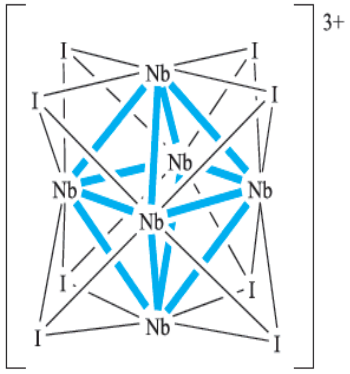
1. Nb and Ta are very similar and both are far less chemically active than V. They do not react with $H_2O$, HCl and $HNO_3$ (passivated). They dissolve in HF, hot concentrated $H_2SO_4$.

2. Upon heating in air both oxidize forming $Nb_2O_5$ and $Ta_2O_5$. The most stable oxidation state of both is +5. The oxides are fairly inert and dissolve only in concentrated HF. They do not dissolve in basis but react with molten basis or carbonates. In presence of water complex anions form: $[Nb_6O_{19}]^{8-}$

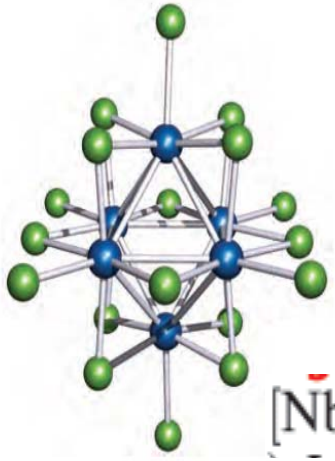
With carbonates one can obtain insoluble in basis and acids (except HF) salts:

$$LiNbO_3,\ NaNbO_3,\ LiTaO_3,\ NaTaO_3 \text{ and } CaNb_2O_6$$

3. The halides of both metals are molecular solids that easily hydrolyze. However, many poly-halides with low oxidation states are known:




$[Nb_6I_8]^{3+}$



$[Nb_6Cl_{18}]^{3-}$

# Triad [$d^4$]: Cr, Mo and W

## 1. Electron structure: *$d^5s^1$(Cr, Mo), ; $d^4s^2$ (W)*

## 2. Maximum oxidation state +6

## 3. Electrode potentials: -0.74, -0.15, -0.12

# Chromium

1. Cr is shiny metal, melts 1890 °C and its alloys are stable in air, salt water, $HNO_3$, *aqua regia*, and bases. Cr dissolves in HF, HCl, $H_2SO_4$ forming salts of $Cr^{2+}$ (mostly soluble). Heating in air produces CrO. CrO is a blue-black powder soluble in acids. From basic solutions of $Cr^{2+}$ precipitates as yellow $Cr(OH)_2$, which has only basic properties, reminiscent of alkali earth metals

2. All salts of $Cr^{2+}$ are unstable in air and quickly oxidize into the salts of $Cr^{3+}$.

Halogenides and sulfates of $Cr^{3+}$ are soluble. $Cr^{3+}$ forms a green oxide $Cr_2O_3$, which crystallographically and chemically is very similar to $Al_2O_3$.

Cr
0
1
2
3
4
5
6

Mo
0
2
3
4
5
6

W
0
2
3
4
5
6

3. From basic solutions of $Cr^{3+}$ precipitates as $Cr(OH)_3$ . Freshly prepared, it readily dissolves in acids and in basis.

$$Cr(OH)_3 + 3OH^- \Leftrightarrow [Cr(OH)_6]^{3-}$$

4. Smelting $Cr_2O_3$ with oxides of divalent metals produces chromites: $M(CrO_2)_2$ . ( the most important is natural mineral $Fe(CrO_2)_2$ , the source of Cr);

**all properties of $Cr^{3+}$ are VERY similar to $Al^{3+}$**

5. Strong oxidizers transform $Cr^{3+}$ into $Cr^{6+}$. In water solutions it requires basic environment.

$$2K_3[Cr(OH)_6] + Br_2 + 4KOH \rightarrow 2K_2CrO_4 + 6KBr + 8H_2O$$

6. Melting $Cr_2O_3$ in with bases and strong oxidizers yields similar results

$$Cr_2O_3 + 4KOH + KClO_3 \rightarrow 2K_2CrO_4 + KCl + 2H_2O$$

7. Chromic acid is not known as a pure substance. Action of strong acids on solutions of $Cr^{6+}$ precipitates $CrO_3$ (red crystals), which can be re-dissolved in water.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 7H_2O; E_o = 1.33 \text{ V}$$

two anions $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ (chromates and di-chromates). Chromates are yellow. The tendency for poly-anions is weak (see W and Mo). Dichromates are red. Change in pH transforms them into each other reversibly. Dichromates are very strong oxidizers, especially in acidic environment.

8. Examples of the oxidation reactions with dicromates

$$K_2Cr_2O_7 + 3H_2S + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S\downarrow + K_2SO_4 + 7H_2O$$

$$K_2Cr_2O_7 + 14HCl + H_2SO_4 \rightarrow 2Cr_2Cl_3 + 3Cl\uparrow + 2KCl + 7H_2O$$

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

# Molybdenum and Tungsten (IUPAC recommended name wolfram)

1. Mo and W are a shiny metals, melt 2620 °C and 3420 °C (respectively). Both are stable in air, water, HF, cold HCl, cold $H_2SO_4$. Dissolves in diluted $HNO_3$ (Mo only), aqua regia, hot conc. $H_2SO_4$ and HCl (Mo only). Heating in air produces $MoO_3$ and $WO_3$ (compare with Cr!!!). Mo and react with C forming extremely hard MoC carbide (excess of C yields Mo(C≡C));

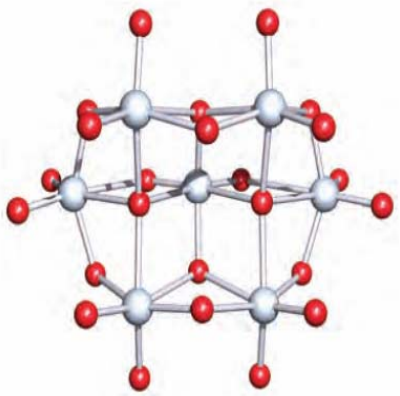
$$M + 3F_2 \rightarrow MF_6 \quad (M = Mo, W) \qquad M + 2S \xrightarrow{\Delta} MS_2 \quad (M = Mo, W)$$

2. Mo and W in the 6+ oxidation state have many characteristics of S. $H_2(Mo, W)O_4$ are strong acids

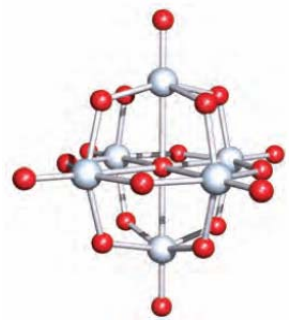
$$\left.\begin{array}{l} M + O_2 + F_2 \\ MOCl_4 + HF \\ MO_3 + F_2 \end{array}\right\} \rightarrow MOF_4 \quad (M = Mo, W)$$

3. $MoO_3$ and $WO_3$ are insoluble in acids (except HF) but react with bases producing salts with $MeO_4^{2-}$ anions, their alkali salts are soluble.

4. Upon heating above 800 °C $MoO_3$ and $WO_3$ lose oxygen and form $MoO_2$ and $WO_2$. Reduction of $MeO_4^{2-}$ anions produces poly-anions win which there are combination of +4 and +6 cations. For instance $[M_6O_{19}]^{2-}$ or $[M_7O_{24}]^{6-}$ (M=W,Mo)



$[Mo_7O_{24}]^{6-}$



$[W_6O_{19}]^{2-}$

# Triad [$d^5$]: Mn, (Tc) and Re

**1. Electron structure: $d^5s^2$**

**2. Maximum oxidation state +7**

**3. Electrode potentials: -1.18, +0.3**

| Mn | Re |
|---|---|
| 0 | 0 |
| 1 | 1 |
| 2 | 2 |
| 3 | 3 |
| 4 | 4 |
| 5 | 5 |
| 6 | 6 |
| 7 | 7 |

4. Tc has no long-living isotopes and has very little practical imporatnce.

**Manganese may exhibit any oxidation state form (+1)+2 to +7.**

The most stable oxidation states in air are +2 and +4. Naturally occurs $MnO_2$ – pyrolusite). (+1 is extremely rare)

1. Mn is a shiny-white metals, stable in air but reacts with hot water, easily dissolves in acids producing $Mn^{+2}$ salts releasing $H_2$. Finely divided, Mn is pyrophoric.

2. Mn easily reacts with most non-metals (halogens, sulfur, oxygen). The oxidation state in each reaction depends on the conditions: with oxygen upon heating $Mn_2O_3$, $Mn_3O_4$ or $MnO_2$ may formed. With $N_2$ upon heating $Mn_2N_3$ is formed. Reaction with $Cl_2$ produces $MnCl_2$. Being oxidized by strong oxidizers, Mn forms $Mn_2O_7$.

3. $Mn^{2+}$ is similar to alkali earth: all halides are known (F, Cl, Br, I) and soluble; sulfate is moderately soluble; carbonate is insoluble. MnO is has a green color and the structure of NaCl. **MnO is purely basic.** In water, $Mn^{2+}$ exists as $[Mn(H_2O)_6]^{2+}$ complex. Large numbers of $Mn^{2+}$ complexes exist. This oxidation state is relatively stable with respect to both oxidation and reduction. However, $Mn(OH)_2$ (white) oxidizes in air into $Mn(OH)_4$ (brown). MnO can be obtained by dehydration of $Mn(OH)_2$ without oxidizers.

4. $Mn^{3+}$ is relatively rare and less stable than $Mn^{2+}$ and $Mn^{4+}$. $Mn_2O_3$ can be obtained by: oxidizing $Mn^{2+}$ in basic environment ($H_2O_2$) or by heating $MnO_2$ above 750-850 °C. Heating above 850 °C forms $Mn_3O_4$. $Mn_2O_3$ is basic and soluble in acids. Only one halide known $MnF_3$:

$Mn^{3+}$ has a strong tendency to disproportionate. $2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$

$Mn^{3+}$ is stabilized by "hard" ligands $F^-$, $PO_4^{3-}$, $SO_4^{2-}$

5. $Mn^{3+}$ compounds are often non-stoichiometric containing some $Mn^{3+}$ and $Mn^{4+}$ . The only known halide $MnF_4$ decomposes upon heatin $2MnF_4 \rightarrow 2MnF_3 + F_2$

6. $MnO_2$ is polymorphic and often markedly non-stoichiometric. It is farily strong oxidizer: $MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$ (conc). Most $Mn^{4+}$ derivatives of are insoluble (except $[Mn(CN)_6]^{2-}$ and $[MnF_6]^{2-}$ )

7. $Mn^{6+}$ are not stable and easily disproportionate into $Mn^{7+}$ and $Mn^{4+}$.

$$3[MnO_4]^{2-} + 4H^+ \rightarrow 2[MnO_4]^- + MnO_2 + 2H_2O$$

$K_2MnO_4$ can be obtained by melting: $MnO_2 + KNO_3 + K_2CO_3 \rightarrow KMnO_4 + N_2 + K_2O$

$K_2MnO_4$ is soluble in water (bright green solution). It disproportionates:

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^-$$

Potassium manganate $K_2MnO_4$ can be complete converted into permanganate:

$$K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

8. $Mn^{7+}$ does not form binary halides or sulfides but forms oxy-halides $MnO_3F$ and $MnO_3Cl$.

$MnO_4^-$ ion is a very strong oxidizer. The final product is a strong function of the pH: strongly acidic→$Mn^{2+}$ ; neutral, weakly basic →$Mn^{4+}$ ($MnO_2$); strongly basic → $MnO_4^{2-}$;

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ = 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

$$2MnO_4^- + 3SO_3^{2-} + H_2O = 2MnO_2\downarrow + 3SO_4^{2-} + 2OH^-$$

$$2MnO_4^- + SO_3^{2-} + 2OH^- = 2MnO_4^{2-} + SO_4^{2-} + H_2O$$

Upon heating: $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2\uparrow$

$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O$$

$Mn_2O_7$ is an unstable liquid

# Rhenium

1. Re is a shiny-white metals, melts at 3190 C, stable in air, water, most non-oxidizing acids (HCl, HF, cold $H_2SO_4$). Rh are far less reactive than Mn.

It dissolves slowly in aqueous bases, actively reacts with $HNO_3$, hot conc. $H_2SO_4$, hot $HClO_4$, $H_2O_2$, molten alkali. Dissolution of Re produces the salts of Rhenium acid $HReO_4$ (per-rhenates).

2. Most common oxidation state of Re is +7. Rhenium acid and $Re_2O_7$ oxide are known as pure substances. $Re_2O_7$ can be obtained by heating Re in air.

Re forms a line of oxides (and fluorides and chlorides) similar to Mn.

All oxidations states except +4 and +7 have a strong tendency to disproportionate.

$$3ReO_3 + 2[OH]^- \xrightarrow{\Delta} 2[ReO_4]^- + ReO_2 + H_2O$$

conc

Re
0
1
2
3
4
5
6
7

| Ox. state | +7 | +6 | +5 | +4 | +3 | +2 |
|---|---|---|---|---|---|---|
| Mn | $Mn_2O_7$ | | | $MnO_2$ | $Mn_2O_3$ $Mn_3O_4$ | MnO |
| Tc | $Tc_2O_7$ | $TcO_3$(?) | | $TcO_2$ | | |
| Re | $Re_2O_7$ | $ReO_3$ | $Re_2O_5$ | $ReO_2$ | | |

# Family of Iron [$d^{6-8}$]: Fe, Co, Ni

**1. Fe, Co and Ni share a lot of similar chemical properties with the prevalent oxidation states +2 and +3, though other oxidation states are possible.**

**2. Electrode potential $M^{2+}/Me$ -0.44, -0.28, -0.25**

| Fe | Co | Ni |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 1 | 1 |
| 2 | 2 | 2 |
| 3 | 3 | 3 |
| 4 | 4 | 4 |
| 6 | | |

Fe, Co and Ni are shiny-white metals. They do not react with water directly but easily oxidized by atmospheric oxygen in wet conditions. All three metals dissolve in dilute acids forming +2 ions.

# Iron

Iron has BCC (below 912 °C and above 1394 °C) and FCC structure.

1. Oxidation by $H^+$ produces $Fe^{2+}$, which can be oxidized by atmospheric oxygen to $Fe^{3+}$. Dilute $HNO_3$ and other oxidation acids produces $Fe^{3+}$. Concentrated oxidizers (conc. $HNO_3$ and $H_2SO_4$) passivated Fe.

$E^o(Fe^{3+}/Fe^{2+})$=+0.33 V $\Rightarrow$concentrated $Fe^{3+}$ is a fairly strong oxidizer.

$Fe^{2+}$ is fairly strong reducer.

$$FeCl_3 + Cu \rightarrow FeCl_2 + CuCl$$

2. Iron reacts directly with all halogens, sulfur (FeS, though natural mineral pyrite is $FeS_2$), phosphorus and other non-metals. Halogenides: $FeX_3$, except $FeI_2$.

3. Iron forms a line of stable oxides: FeO, $Fe_3O_4$, $Fe_2O_3$, all of which are BASIC and dissolve in acids only.

4. Iron forms an interstitial carbide $Fe_3C$, which is a component of many steels.

5. $Fe^{3+}$ and $Fe^{2+}$ are strong complex formers, typical CN=6;

6. Hydroxides of $Fe^{3+}$ and $Fe^{2+}$ are insoluble in water. All salts of $Fe^{3+}$ are strongly hydrolyzed.

7. Both $Fe^{3+}$ and $Fe^{2+}$ have strong affinity to $CN^-$. $Fe^{2+} + 2CN^- \rightarrow Fe(CN)_2$

$Fe^{2+} + 2CN^- \rightarrow Fe(CN)_2$ $Fe(CN)_2 + 4CN^- \rightarrow [Fe(CN)_6]^{4-}$

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]_3 \quad 3Fe^{2+} + 2[Fe(CN)_6]^{3-} = Fe_3[Fe(CN)_6]_2$$

**Prussian blue**
**(*Berlin blue* )**

**Turnbull's blue**

8. Cyanide complexes of Fe are one of the most stable. Prussian blue and Turnbull's blue are close to identical. Prussian blue was one of the first synthetic pigments. It was synthesized for the first time in Berlin around 1706

8. Iron exhibits +4, +5 and +6 oxidation states, containing anions:

$$[FeO_4]^{2-}, [FeO_4]^{3-}, [FeO_4]^{4-} \text{ and } [FeO_3]^{2-}$$

9. Iron can be oxidized above +3 only by very strong oxidizers

$$Fe_2O_3 + 3[OCl]^- + 4[OH]^- \rightarrow 2[FeO_4]^{2-} + 3Cl^- + 2H_2O$$

10. Iron with the oxidation state above +3 is a very strong oxidizer. All ferrates decompose.

$$4[FeO_4]^{2-} + 6H_2O \rightarrow 4FeO(OH) + 8[OH]^- + 3O_2$$

# Cobalt

Cobalt is less reactive than Fe; Co does not react with $O_2$ unless heated, however, it easily dissolves in acids.

1. Cobalt forms CoO, $Co_2O_3$ and $Co_3O_4$ and families of salts +2 and +3. Oxidation to +3 requires strong agents:

$$2Co(OH)_2 + NaClO + H_2O = 2Co(OH)_3 + NaCl$$

All salts of +3 are unstable and revert to +2.

$$2Co(OH)_3 + 6HCl = 2CoCl_2 + Cl_2\uparrow + 6H_2O \qquad 4Co(OH)_3 + 4H_2SO_4 = 4CoSO_4 + 10H_2O + O_2\uparrow$$

Both oxides and hydroxides are purely basic and dissolve in acids only.

2. There are very a few compounds in which Co is +4 $Cs_2[CoF_6]$

# Nickel

1. Ni closely resembles Co. The prevalent oxidation state is +2. The states +1 and +3 are extremely rare. Ni forms insoluble and coherent $NiF_2$ which makes stable with respect to fluorine gas.

2. NiO and $Ni(OH)_2$ are purely basic and dissolve only in acids.

3. Ni forms a large variety of complexes with different coordination numbers.

# Pt family: Ru, Os, Rh, Ir, Pd, Pt

All Pt-family have similar atomic and ionic (+2) radius 134-138 nm, similar electronegativity. All metals of these groups react with molten alkali oxides (most common way to oxidize them)

## Ru and Os

1. Ru and Os do not react with non-oxidizing acids but dissolve in <u>aqua regia</u>. Os slowly reacts with $HNO_3$. Both metals react with oxygen upon heating producing $OsO_4$ and $RuO_2$. Both metals react with $F_2$ and $Cl_2$.
2. Ru and Os have a tendency to form poly-metal anions containing Me-O-Me bridges.
3. Both metals form a line of halides and sulfides. Halides easily hydrolyze and disproportionate. The oxidation state in each case depends on the conditions, amount of the regents and temperature.
4. Both metals have a rich family of various complexes with a great variety of oxidation states. Though $OsO_4$ is stable, only $OsF_n$ n=2-6 is known. $RuF_6$ is unstable. Oxo-flourides of Os and Ru +8 are known. The oxidation state +8 is unstable. All compounds corresponding to the states above +4 are acidic (form anions). The states +2 and +3 are basic (form cations).

Ru
0
2
3
4
5
6
7
8

Os
0
2
3
4
5
6
7
8

# Rh and Ir

1. Rhodium and iridium are **unreactive metals**; they react with $O_2$ or the halogens only at high temperatures and **neither rapidly is attacked by aqua regia** (Rh slowly reacts but very slow).

**Ir is the least reactive (most noble) metal known.**

2. Both metals have a tendency to revert to the state +3 from higher oxidation states. Oxidation state +6 and +5 can be obtained by heating with $O_2$ or $F_2$ and then quenching the volatile products.

3. The state +4 only exists as unstable $MeF_4$ fluorides, which disproportionate into +5 and +3.

4. The oxidation state +3 is the most common. It appears in halides (all known and can be obtained directly) and in oxides.

5. In each oxidation state Rh and Ir form a large variety of complex products that can stabilize very exotic oxidation states (like 0, +1, and +2).

Rh
0
1
2
3
4
5
6

Ir
0
1
2
3
4
5
6

# Pd and Pt

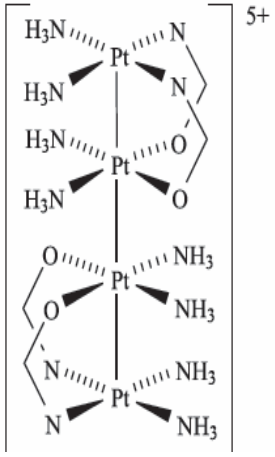
1. Pd is considerably more reactive than Pt. Pd directly combines with O2, F2 and Cl2. Both metals react with hot concentrated $HNO_3$ and aqua regia.

2. The high oxidation state +6 and +5 are restricted to Pt fluorides only and highly unstable with respect to decomposition and disproportionation (+5).

3. The oxidation state +4 is represented by $PdF_4$ and all halides of Pt (+4); Oxides $PtO_2$ and $PdO_2$ are also known but easily(>600 C) decompose back to metals and oxygen. Both metals form complex halide cations $[MeX_6]^{2-}$ and a large variety of complexes. Pd(+4) is far less stable that Pt(+4).

4. Oxidation state +3 corresponds to a mixture of +2 and +4 or to the complexes containing metal-metal bond.

5. Oxidation state +2 is the most stable. All halides (except $PtF_2$) are known. Oxides PdO and PtO are amphoteric and form both positively and negatively charged complexes with CN=6 and CN=4. Hexa- and tetra-chloro-acids are strong acids, which indicates covalent Pt-Cl and Pd-Cl bonds




Pd
0
2
4

Pt
0
2
4
5
6

# Triad [$d^9$]: Cu, Ag and Au

**1. Electron structure: $d^{10}s^1$ is more stable than $d^9s^2$;**

**2. Electrode potentials: 0.52 0.8 1.7 V⇒ none of these metals can be oxidized by $H^+$**

1. Cu is stable in dry air. In wet air it is oxidized by $O_2$ forming $(CuOH)_2CO_3$
2. Upon heating in air Cu forms two oxides CuO and $Cu_2O$.

$$2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$$

3. Cu may be +1, +2 and +3. The most stable +2, however in solutions

$$CuCl_2 + Cu = 2CuCl$$

4. CuO dissolves in acids. $Cu(OH)_2$ is a very weak base: $[Cu(H_2O)_4]^{2+}$. It dissolves in acids but may dissolve in a very strong base:

$$Cu(OH)_2 + 2NaOH \rightleftarrows Na_2[Cu(OH)_4]$$

5. Cu is a very strong complex-forming ion with CN=4; It may form anions and cations. $Cu^{2+} + 4NH_3 = [Cu(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$
6. Cu dissolves in complex-forming acids, sometimes oxidized by $H^+$ (HCN, HCl). Oxidation by $O_2$ is also accelerated by ligands.

Cu
[0]
1
2
3
[4]

Ag
1
2
3

Au
[0]
1
[2]
3
5

1.Ag is stable in air even upon heating. It is stable in diluted acids but

$$Ag + 2HNO_3 = AgNO_3 + NO_2\uparrow + H_2O$$

2. In all stable compounds silver is $Ag^+$, although AgO and $Ag_2O_3$ exist.

3. $Ag_2O$ is poorly soluble (0.017g/l) but it is a fairly strong base and silver salts do not hydrolyze.

4. Ag is a strong complex-forming agent with a typical CN=2; Especially stable complexes are $[Ag(NH_3)_2]^+$ and with $CN^-$.

5. Many insoluble salts of Ag dissolve in solutions with ligands ($CN^-$, $NH_3$ ) sometimes displacing hydrogen

$$AgBr + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaBr$$

6. Interesting fact: all silver halides (except AgF) are insoluble.

1. Au is stable towards heating in air and towards ALL pure acids and dissolves only in a mixture of $HNO_3$ and HCl. However, it dissolves in HCN in presence of $O_2$ ( main extraction technique)

$$4Au + 8CN^- + O_2 + 2H_2O = 4[Au(CN)_2]^- + 4OH^-$$
$$2[Au(CN)_2]^- + Zn = [Zn(CN)_4]^{2-} + 2Au$$

2. Au has only TWO oxidation states +1 and +3. The state +3 is more stable.

Two oxides are $Au_2O$ and $Au_2O_3$

3. Dissolution of Au in ($HNO_3$/HCl) results in $HAuCl_4$, which is a strong acid.

4. $AuCl_4^-$ is a strong oxidizer and can be reduced to AuCl. Most salts of $Au^{+1}$ are insoluble. $Au_2O$ is inert but dissolves in strong acids.

# Triad $d^{10}$: Zn, Cd and Hg

## 1. Electron structure: $d^{10}s^2$

## 2. Electrode potentials: -0.76 -0.4 0.85 ⇒ Zn and Cd dissolve in acids ($H^+$), Hg only in oxidizing acids ($HNO_3$)

1. In all compounds Zn (and Cd) exhibit the oxidation state of +2;
2. Zn easily dissolves in acids ($H^+$) and in strong bases (NaOH) forming $[Zn(OH)_4]^{2-}$ or $[Zn(OH)_6]^{4-}$ (compare with Cu). Note CN of Zn is almost always CN=4 and rarely CN=6.
3. ZnO and $Zn(OH)_2$ are a very weak base and acid. Therefore, all Zn salts hydrolyze unless stabilized by high or low pH ( in Zn+ state or a complex);
4. Pure Zn is a strong reducing agent and used as such in metallurgy and some organic synthesis. It reacts with many non-metals with a flash.
5. Interesting fact: ZnO ( and Zn ) dissolves in solutions of amino-acids (for instance glycine). (THINK WHY?)

1. Chemical properties of Cd are strongly reminiscent of Zn. However

a) Cd is far less chemically active and reacts slowly with acids;

b) Cd has no acidic (amphoteric) tendencies and does not dissolve in bases.

2. Cd similar to Zn forms variety of complexes with CN=4.

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1. Hg exhibits a number of differences from Zn and Gd. It is far less chemically active and has a tendency for catenation forming $[Hg\text{-}Hg]^{2+}$ ion.

2. Hg dissolves many metals forming amalgams. Energy of their formation may be very high. For instance electrolysis of NaCl with Hg electrode results in reduction of Na into amalgam.

3. Most known mineral of Hg is cinnabar HgS, bright red ( used as a pigment until 20$^{th}$ century);

4. Oxidation of Hg by strong oxidizers ($HNO_3$, $KMnO_4$, S) leads to $Hg^{2+}$. Upon heating many salts and HgO transform into $[Hg\text{-}Hg]^{2+}$ compounds;

$HgO \rightarrow Hg_2O+O_2$; $HgCl_2 \rightarrow Hg_2Cl_2+Cl_2$ but: $HgCl_2 + Hg = Hg_2Cl_2$

5. Hg hydroxide is unknown. Action of bases on Hg salts yields oxides.

6. Most mono-base acids salts of $Hg^{2+}$ are soluble. Most $[Hg\text{-}Hg]^{2+}$ are not;

7. Hg is a poor complex former. However, halogen-anion complexes exist: $K_2[HgI_4]$