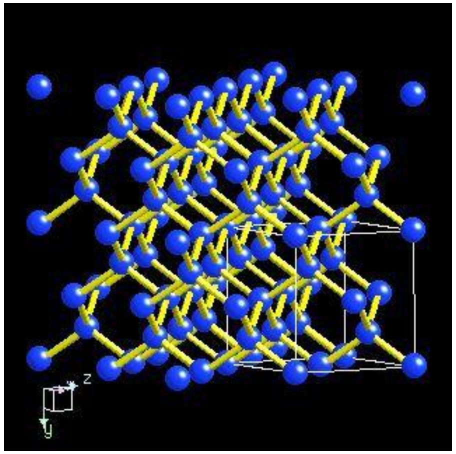
Silicon

- Silicon is the 7th most abundant element in the universe and the second most abundant element in the earth's crust.

- Two allotropes of silicon exist at room temperature: **amorphous** and **crystalline**. Amorphous appears as a brown powder while crystalline silicon (**diamond lattice**) has a metallic luster and a grayish color.



Synthesis of Silicon

- For the synthesis of technical Si, SiO_2 is reduced with C in an electric oven:

$$SiO_2 + 2\,C \xrightarrow{1800\ ^\circ C} Si + 2\,CO$$

- In the laboratory, Mg or Al is used as the reducing agent:

$$3\,SiO_2 + 4\,Al \longrightarrow 3\,Si + 2\,Al_2O_3$$

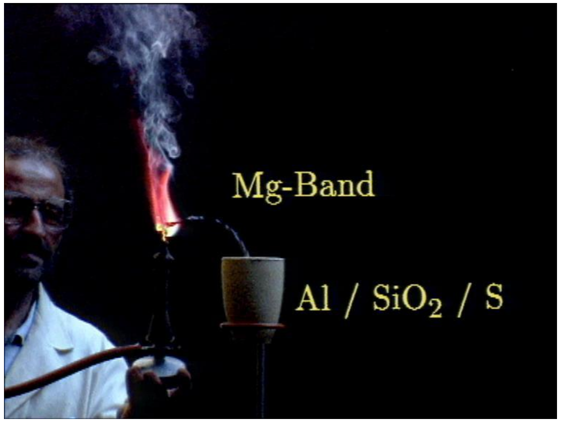
- In order to obtain high purity Si, technical Si is converted to trichlorosilane which is purified by distillation and then reduced back to Si. This way, one can obtain polycrystalline Si with a purity of 10^{-8} %.

$$Si + 3\,HCl \underset{1100\ ^\circ C}{\overset{300\ ^\circ C}{\rightleftarrows}} \underset{\Big|}{HSiCl_3 + H_2}$$

Distillation!

- Single crystalline Si is obtained by the CZ process (see below).

Aluminothermic Preparation of Silicon



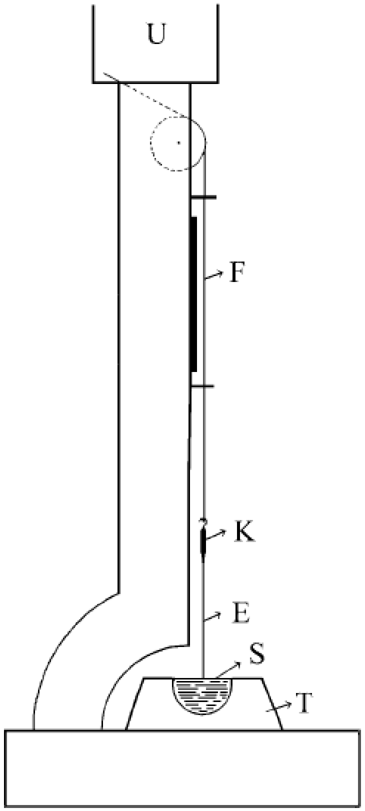
For the aluminothermic production of crystalline silicon, in which quartz is reduced by aluminum. Sulfur is added, in order to further increase the temperature of the reaction. This reacts with excess aluminum to produce aluminum sulfide.

$$3\ SiO_2 + 4\ Al \longrightarrow 3\ Si + 2\ Al_2O_3 \qquad -\ 619\ \text{kJ/mol}$$

$$4\ Al + 6\ S \longrightarrow 2\ Al_2S_3 \qquad -\ 1448\ \text{kJ/mol}$$

Jan Czochralski's Creative Mistake

- The first synthesis of a crystal (Sn) from a crucible with molten tin was made by accident.
- The procedure was published in 1918.
- The apparatus shown on the left can be used to prepare single crystals of tin, lead and zinc.
- The length of the single crystals of tin drawn in the first Czochralski apparatus was about 15 cm with a diameter of about 1 mm and a mass of about 1 g.
- See: *Angew. Chem. Int. Ed.* **2003**, *42*, 5684.



Czochralski's crystal drawing apparatus of 1916. The clockwork motor (U) draws the single crystal (E) out of the melt (S) which sits in the crucible (T). The seed crystal resides in a capillary (K), which is attached to a thread (F).

The Czochralski (CZ) Process

- About 95 % of the world's production of silicon single crystals is manufactured by the Czochralski (CZ) procedure.

- In the 1970s, the technology was at 50 mm. In 1980 this had reached 100 mm, then 200 mm by 1995, and by 2002 the technology was at a diameter of 300 mm.

- The single crystal (3) is drawn from the melt (1) on a seed (2) at about 1420 °C. The SiO_2 crucible and the Si single crystal may be rotated and each is adjustable upwards or downwards. External magnetic coils (7) can be attached at the furnace chamber so that the single crystal may also be drawn from the melt under the influence of a magnetic field. During the growth period the furnace chamber is filled with argon as protective gas. The growth process may be monitored and controlled directly with an optical sensor (13).

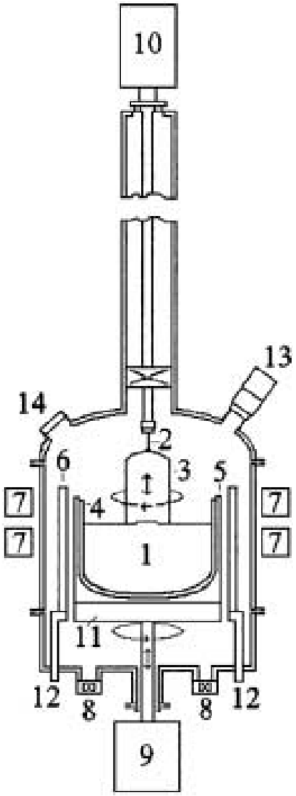
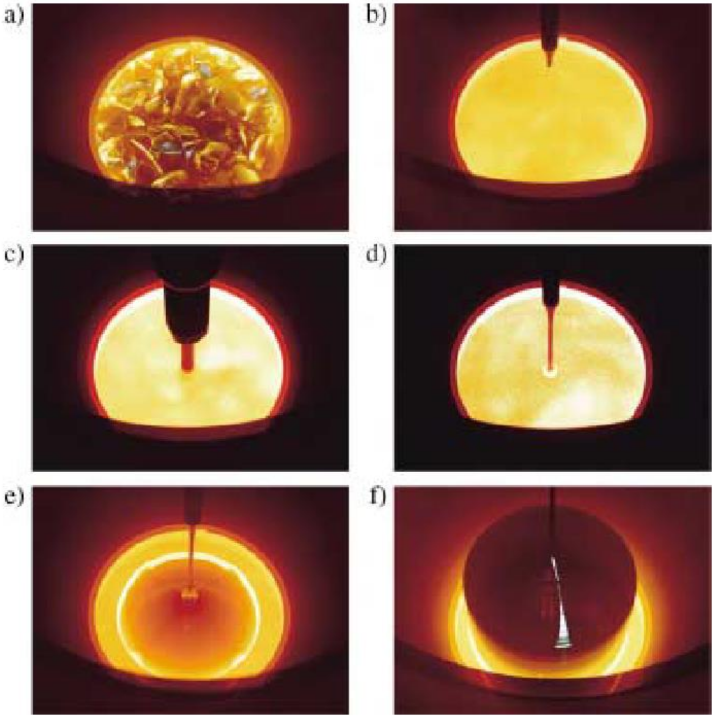


Diagram of a CZ drawing plant for 300-mm diameter silicon single crystals. The total height of the drawing plant is about 15 m.

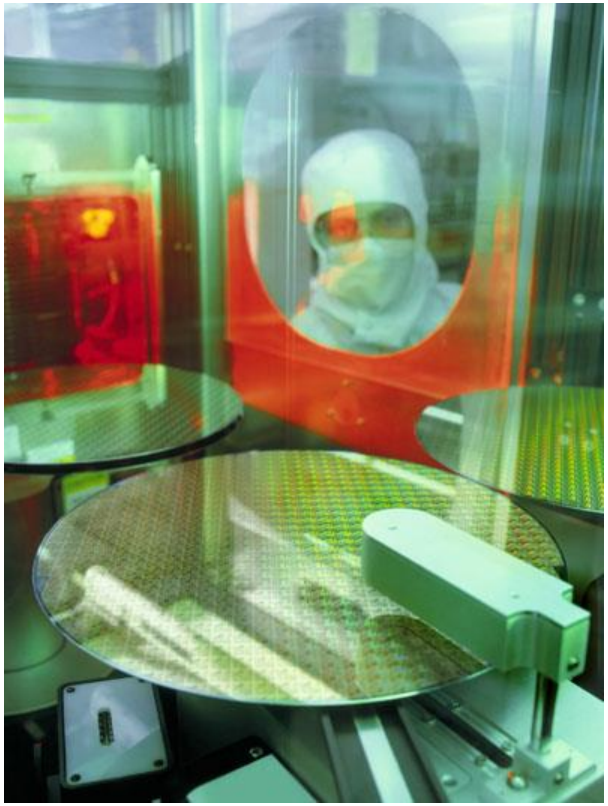
Synthesis of Silicon Single Crystals

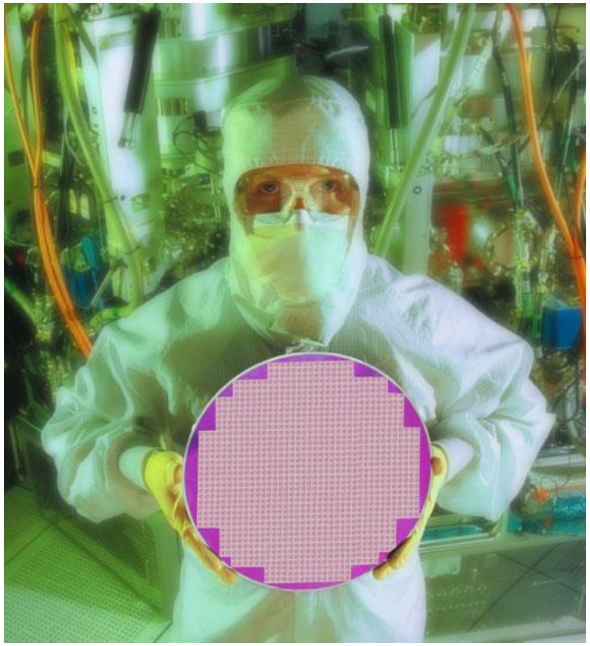


For the 300-mm single crystal shown, a total time of 3-4.5 days is needed for a crystal length of 2 m. The drawing rate in the cylindrical part is 0.4-1.2 mm min^{-1}.

A single crystal of silicon, 300 mm in diameter, 2 m long, and weighing 265 kg, drawn using the CZ process (Photograph: Wacker-Chemie).

The Basis for Modern Chip Technology



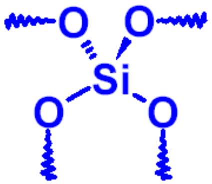


Today’s most advanced semiconductor manufacturing takes place on 300 mm (12-inch) wafers.

Carbon vs. Silicon

$O=C=O$

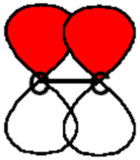
gas



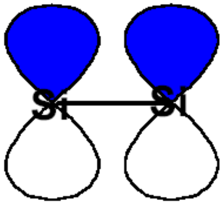
SiO_2

network solid

Strong
pπ-pπ bonding



Weak
pπ-pπ bonding



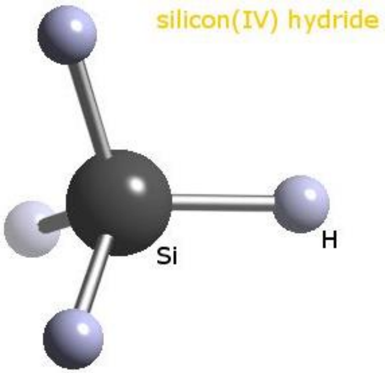
D (C-O)	358 kJ/mol
D (C=O)	799
D (Si-O)	452

Silanes

- Silicon forms chain hydrogen compounds of **the general formula Si_nH_{2n+2}** which are analogous to alkanes.

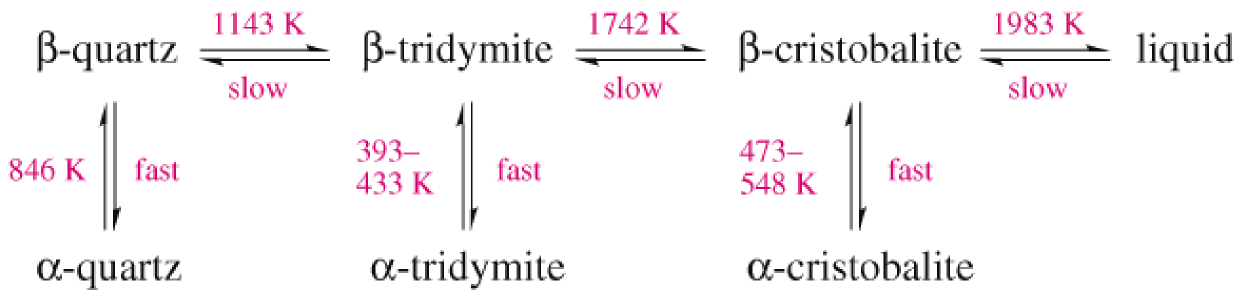
- Upon heating silanes **decompose to give Si and H_2**.

- In air they immediately **burn to give SiO_2 and H_2O**.



Silicon Dioxide (SiO_2)

- SiO_2 exists in several allotropes. They differ in the relative orientation of the SiO_4 tetrahedrons.
- The transformation between **quartz** and **tridymite/cristobalite** occurs very slowly because bonds have to be broken. Transformations between α and β forms only require modifications of the Si-O-Si angles.
- At room temperature **α-quartz is the thermodynamically most stable form**. All others are metastable.



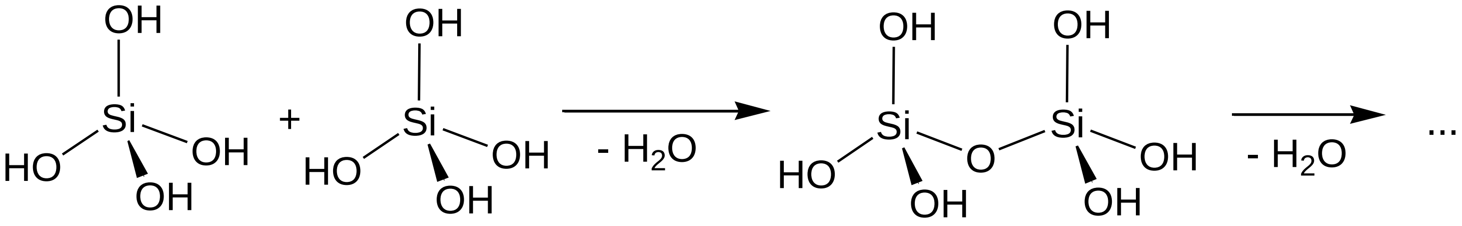
$$\begin{tikzcd}
\beta\text{-quartz} \arrow[r, shift left, "1143\text{ K}"] \arrow[d, shift left, "\text{fast}"] & \beta\text{-tridymite} \arrow[l, shift left, "\text{slow}"] \arrow[r, shift left, "1742\text{ K}"] \arrow[d, shift left, "\text{fast}"] & \beta\text{-cristobalite} \arrow[l, shift left, "\text{slow}"] \arrow[r, shift left, "1983\text{ K}"] \arrow[d, shift left, "\text{fast}"] & \text{liquid} \arrow[l, shift left, "\text{slow}"] \\
\alpha\text{-quartz} \arrow[u, shift left, "846\text{ K}"] & \alpha\text{-tridymite} \arrow[u, shift left, "393\text{–}433\text{ K}"] & \alpha\text{-cristobalite} \arrow[u, shift left, "473\text{–}548\text{ K}"] &
\end{tikzcd}$$

Silicic Acid (H_4SiO_4)

- The simplest oxo.acid of silicon. It is formed from SiO_2 and water:

$$SiO_2 + 2\,H_2O \rightleftharpoons H_4SiO_4$$

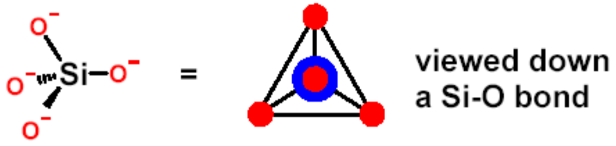
- Only stable at very low concentrations. Above 2 mmol/l: condensation to give polysilicic acids:

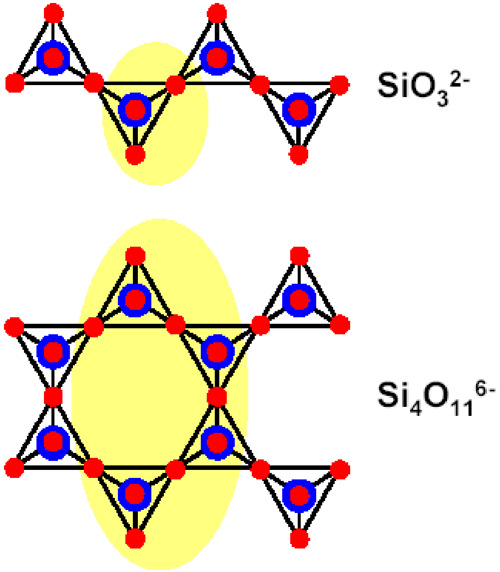


- Extensive dehydration leads to silica gel.

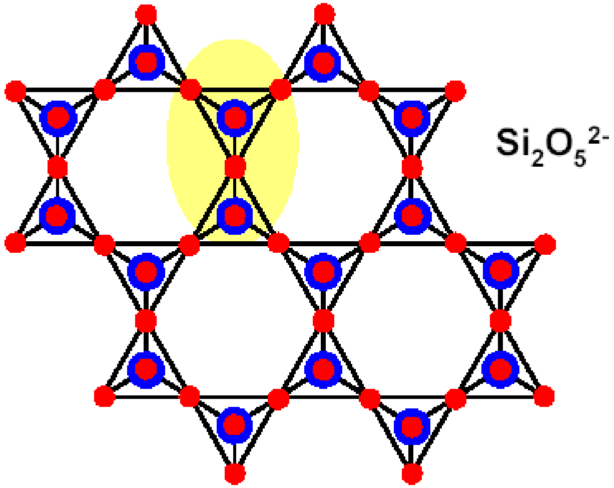
Silicates

- Anionic Si-O compounds based on SiO_4^{4-} and its condensates.
- Many minerals are insoluble metal salts of silicates.
- Intermediate levels of condensation give single and double strand chains and sheet structures (next slide).



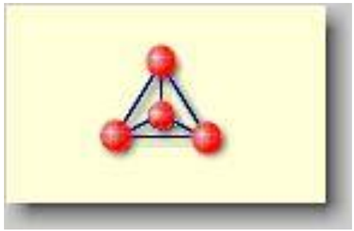


Single and double strand chain



Sheet structure

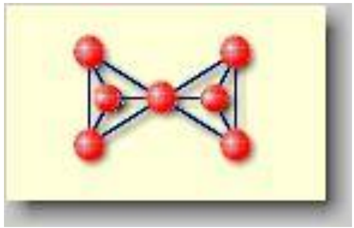
Classification of Silicate Structures I

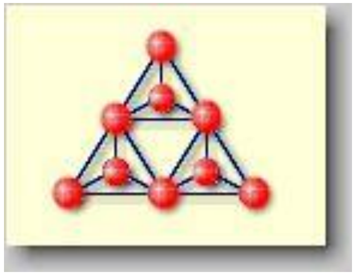


Nesosilicates [*neso* (*gr.*) = island] or independent tetrahedral silicates: The isolated $[SiO_4]^{4-}$-tetrahedrons exist as independent units which are linked together by cations (e.g. **zircon $Zr[SiO_4]$**).

‘Zircon’

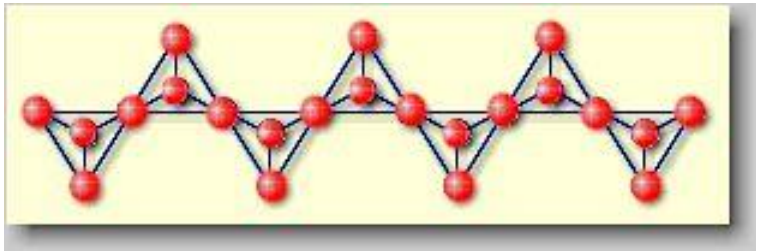
Sorosilicates [*soro* (*gr.*) = group] or double tetrahedral silicates: Two $[SiO_4]^{4-}$-tetrahedrons are linked together by sharing on oxygen atom forming a $[Si_2O_7]^{6-}$ ion.





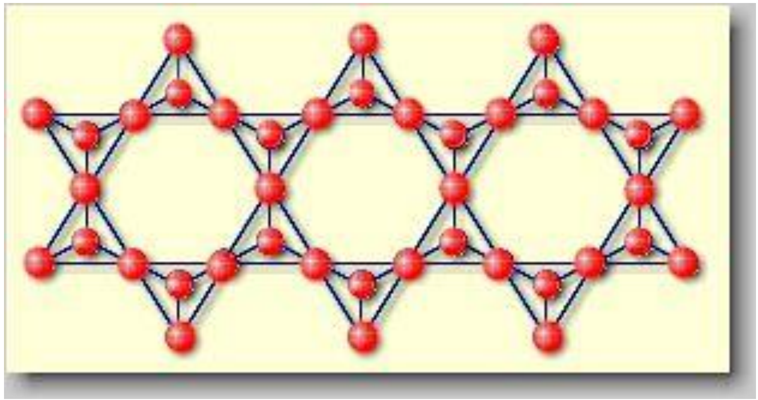
Cyclosilicates [*cyclo* (*gr.*) = ring] or ring silicates: Three $[SiO_4]^{4-}$-tetrahedrons are linked together forming a ring with the formula $[Si_3O_9]^{6-}$. A further variation is possible by forming a ring consisting of six $[SiO_4]^{4-}$-tetrahedrons as an $[Si_6O_{18}]^{12-}$ ion.

Classification of Silicate Structures II

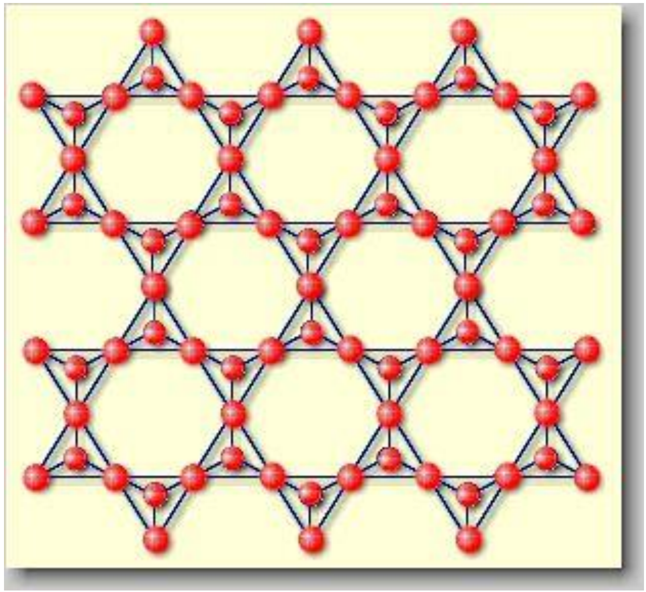


Chain silicates: Chain silicates are realized by linking $[SiO_4]^{4-}$-tetrahedrons in a way to form continuous chains. They may be represented by a composition of $[SiO_3]^{2-}$.

Double chain silicates: Two silicate chains of the inosilicates are linked by the corners forming double chains yielding $[Si_4O_{11}]^{6-}$ ions.

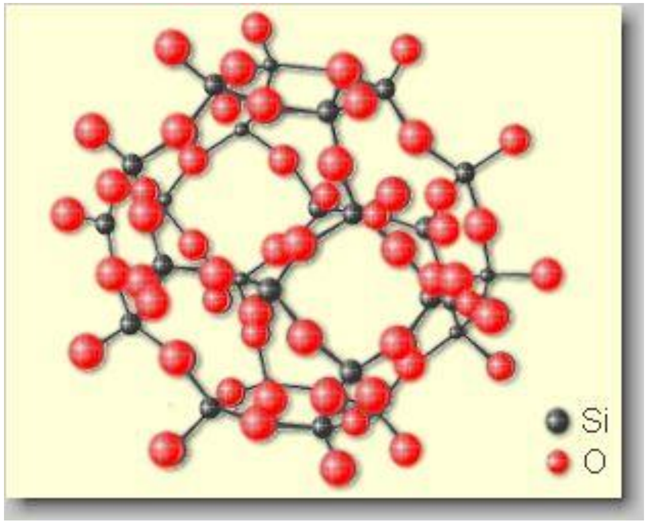


Classification of Silicate Structures III



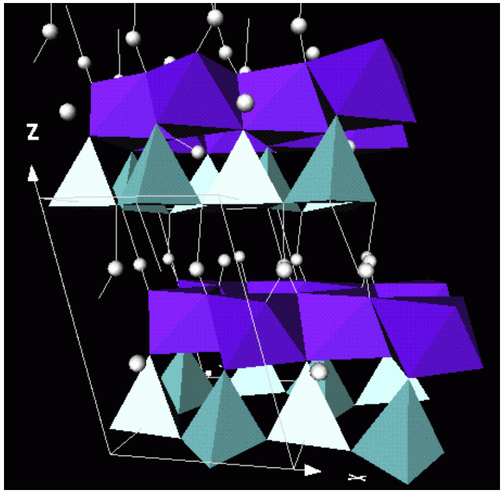
Sheet silicates: They are formed if the above described $[SiO_3]^2$-chains are linked together to form continuous sheets with the chemical formula $[Si_2O_5]^{2-}$.

Tectosilicates [*tecto* (*gr.*) = framework] or framework silicates: Tectosilicates are formed by a $[SiO_4]^{4-}$-tetrahedron, which is linked together with four tetrahedrons in a three-dimensional framework in such a way, that the tetrahedrons share one oxygen atom.

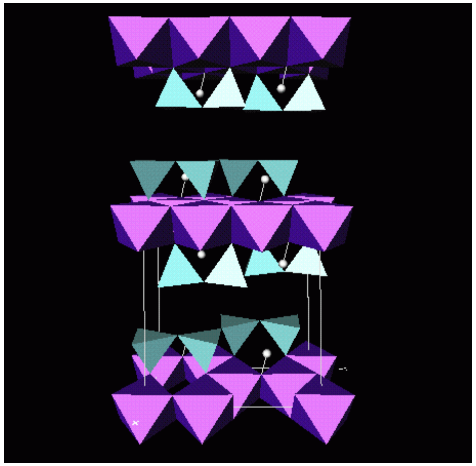


Clay Minerals

Clay minerals are sheet silicates in which the sheets of silica tetrahedra are held together by only weak interatomic forces between the layers, often hydrogen bonding from water. In **kaolinite**, one of the most important clay minerals, a single sheet of corner connected silica tetrahedra is connected by common apex oxygen atoms to a single sheet of edge-connected alumina octahedra. Kaolinite is widely used in papermaking and rubber production.



Structure of kaolinite
$Al_4(OH)_8[Si_4O_{10}]$



Structure of talc
$Mg_3(OH)_2[Si_4O_{10}]$

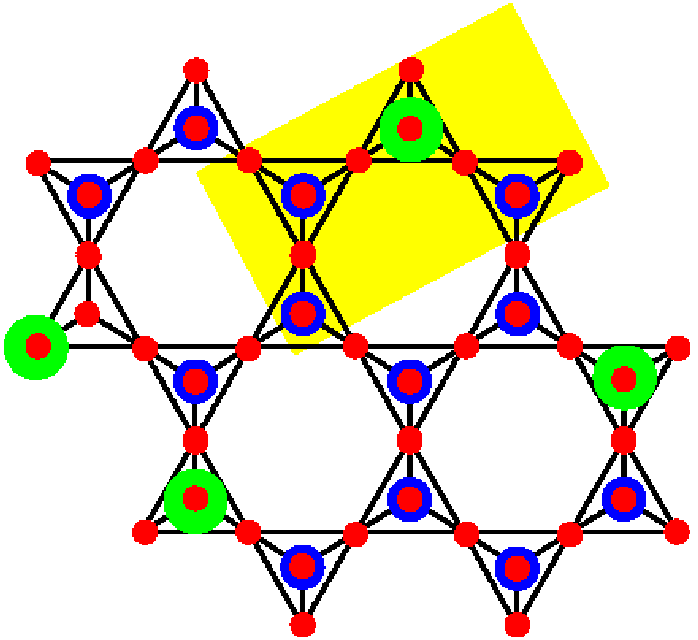
Common **talc** is another phyllosilicate usually found in the bathroom. It consists of double layers of silica tetrahedra sandwiching a single layer of MgO octahedra. The hydrogen atoms appear to play little or no role in binding these layers together, which explains why talcum powder is so slippery !

Aluminosilicates

- Al^{3+} replaces the formal Si^{4+} in silicates.

- The replacement can be statistically or in a regular fashion.

$$Si_2O_5^{2-} \equiv Si_4O_{10}^{4-} \rightarrow AlSi_3O_{10}^{5-}$$



Sheet structure in mica: $KAl_2[AlSi_3O_{10}][OH]_2$

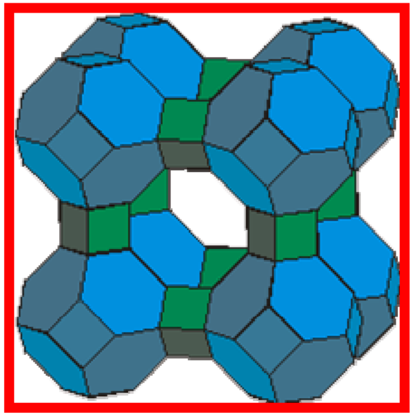
Zeolites ('Molecular Sieves')

- Natural or synthetic aluminosilicates that form 3-D structures with open pores or cavities.

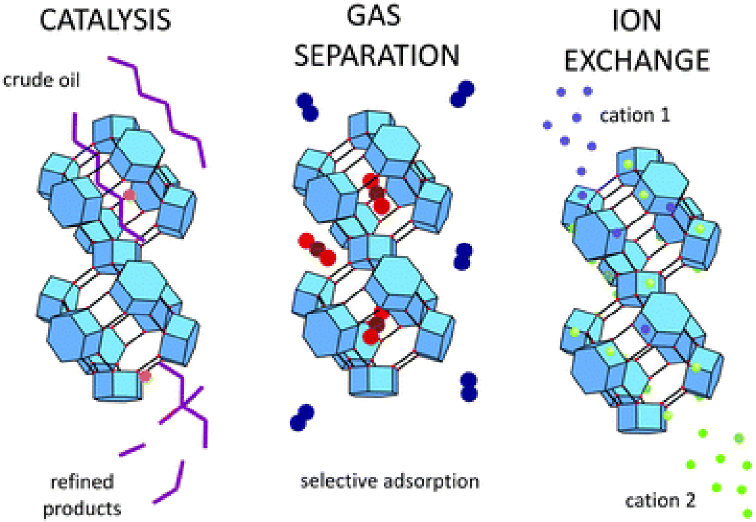
- They are produced on millions of tonne scale industrially.

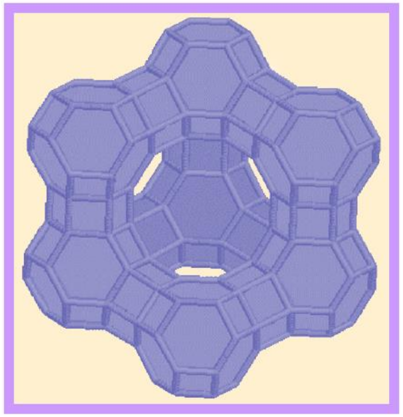
- Zeolites are often drawn to emphasize the cavity structure by connecting the non-oxygen atoms Si and Al. O-atoms are found at the midpoint of each edge and some vertices.

- Uses: ion exchanger; general absorbents, drying agents, gas separations; catalysts.



'Zeolite A'
4 Å molecular sieve





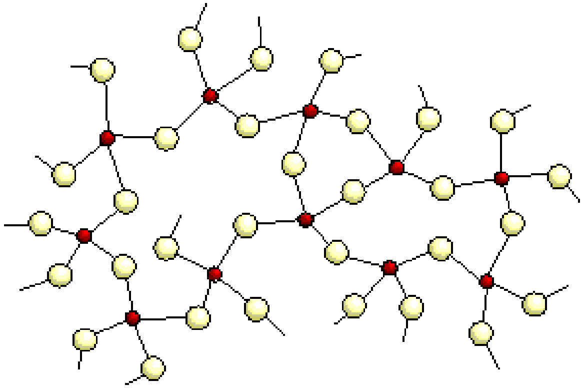
'Faujasite'
7 Å pore

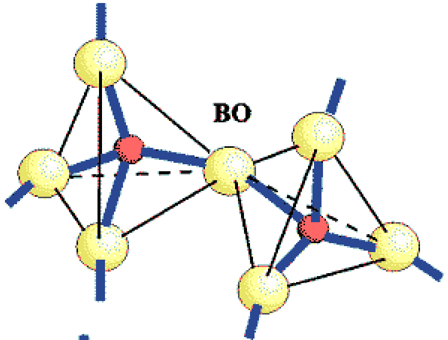
Glasses

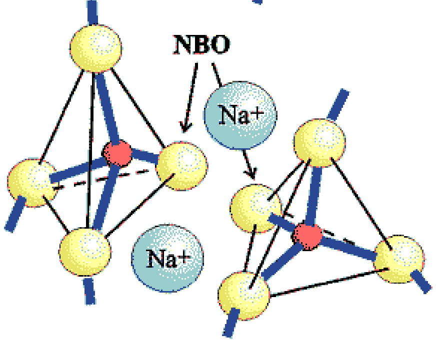
- If liquid SiO_2 is cooled rapidly, metastable quartz glass is formed. It crystallizes when tempered at T > 1000 °C.

- Classical glass consists of SiO_2 and basic oxides such as Na_2O, K_2O and CaO. The metal oxides act as network modifiers. Their charge is compensated by NBOs created by breaking bridges between adjacent SiO_4 tetrahedra.

- Other modifiers: PbO (high refraction index); B_2O_3 (increased chemical resistance), Al_2O_3 (stiffer).

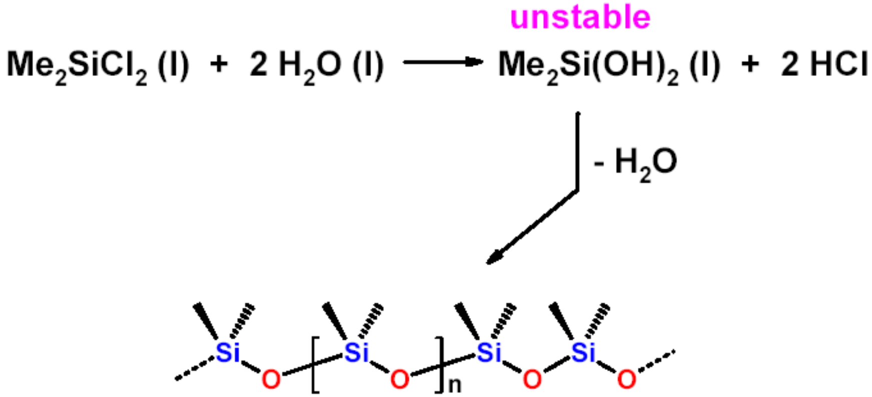






Silicones

- Are prepared by the hydrolysis of R_2SiCl_2 (R is usually CH_3).
- Higher thermal, chemical and O_2 stability than carbon-based organic polymers (Si-O > C-C by about 90 kJ/mol = 30 %).
- Used as oils, grease or solids, depending on the molecular weight.



$$Me_2SiCl_2\ (l) + 2\ H_2O\ (l) \longrightarrow \overset{\text{unstable}}{Me_2Si(OH)_2\ (l)} + 2\ HCl$$

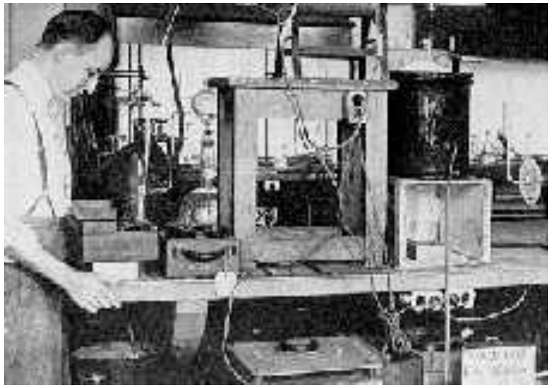
$(CH_3)_3SiCl$ = end groups

CH_3SiCl_3 = branching groups

The Müller-Rochow Process

- Silicones were developed at more or less simultaneously at General Electric by Eugene Rochow and at Wacker by Richard Müller. Their great contribution was to find a process that allows the inexpensive manufacturing of dimethyldichlorosilane. This process is still operated today with only minor modifications and is called « Müller-Rochow Process ».

- The essential copper catalyst was discovered by accident (Cu impurity in Si).



Rochow repeating his first effective synthesis (1940).

$$\mathrm{Si} + \mathrm{CH_3Cl} \xrightarrow{\substack{[\mathrm{Cu}] \\ 300\ ^\circ\mathrm{C}}} \mathrm{(CH_3)_2SiCl_2}\ \text{(main product)} + \mathrm{(CH_3)_3SiCl} + \mathrm{CH_3SiCl_3}$$

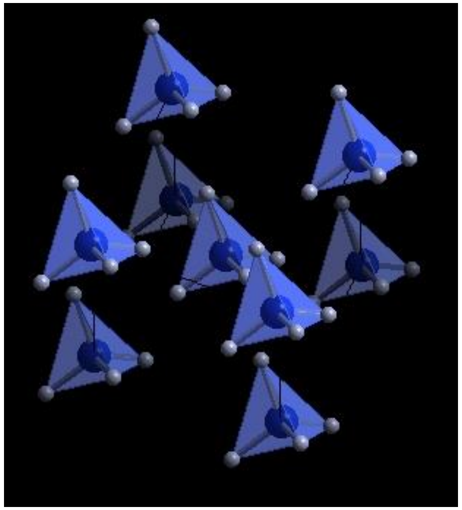
Distillation!

Si-F Compounds

- **SiF_4 (Silicon tetrafluoride)** is a highly reactive gas. It is obtained from a mixture of CaF_2, SiO_2 and conc. H_2SO_4:

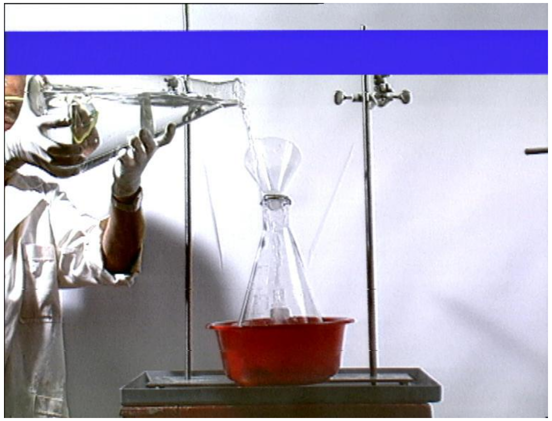
$$2\ CaF_2 + 2\ H_2SO_4 \longrightarrow 2\ CaSO_4 + 4\ HF$$

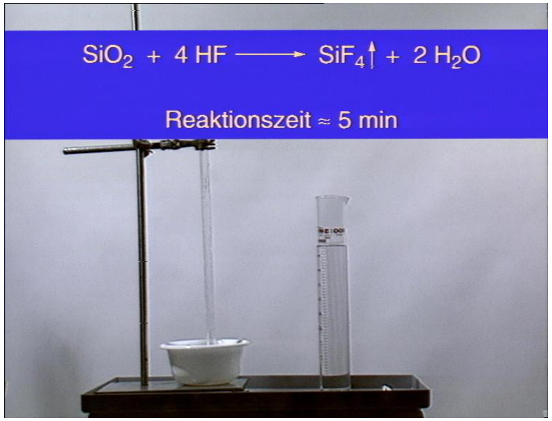
$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O$$



Structure of SiF_4

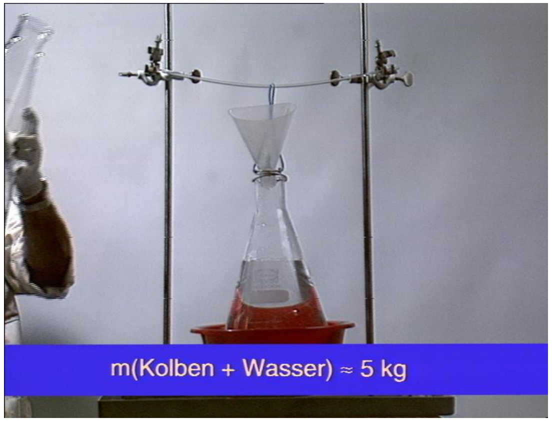
The Magic Glass Rod





$SiO_2 + 4\,HF \longrightarrow SiF_4\uparrow + 2\,H_2O$

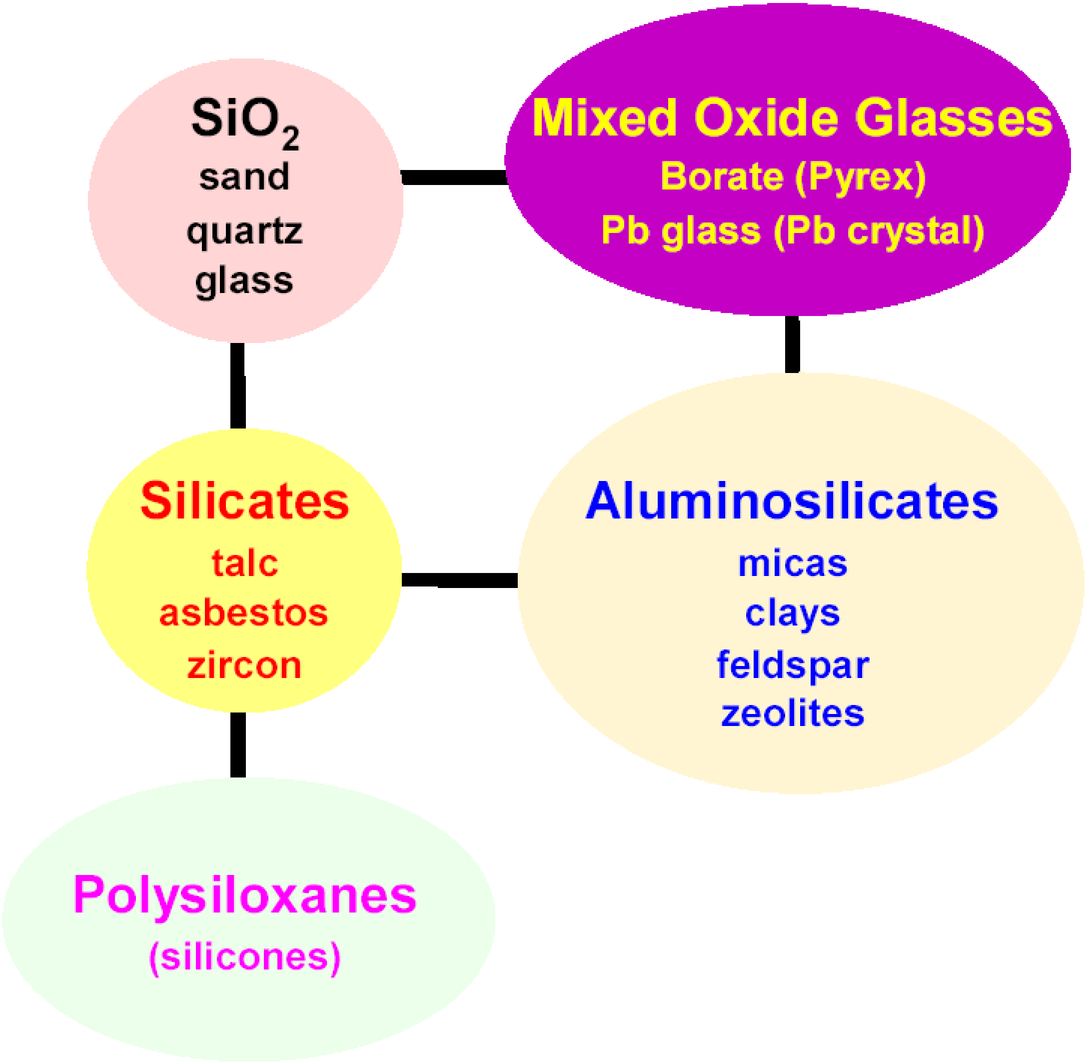
Reaktionszeit ≈ 5 min



m(Kolben + Wasser) ≈ 5 kg

The brittleness of glass is caused by microscopic fissures in its surface. Glass bursts along these fissures. The load is concentrated at the tip of such fissures when we try to bend the glass rod. The structure is unable to bear the large forces exerted on it, the fissure increases in size, and eventually the rod snaps. The surface of the glass reacts with hydrofluoric acid. This reaction leads to a "melting" of the surface fissures, or at the very least, the fissure tips are blunted. The stability of the glass rod is thereby substantially increased.

Si-O Compounds – Summary



SiO_2
sand
quartz
glass

Mixed Oxide Glasses
Borate (Pyrex)
Pb glass (Pb crystal)

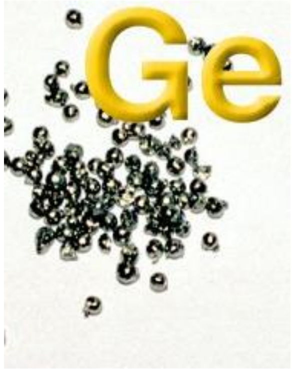
Silicates
talc
asbestos
zircon

Aluminosilicates
micas
clays
feldspar
zeolites

Polysiloxanes
(silicones)

Germanium

- First proposed to exist by Dmitri Mendeleyev based on gaps in his newly created Periodic Table .
- The element is recovered as a by-product of zinc and copper refining. Germanium can be separated from other metals by fractional distillation of its volatile tetrachloride. The techniques permit the production of germanium of ultra-high purity.
- When germanium is doped with arsenic, gallium, or other elements, it is used as a transistor element in electronic applications. The most common use of germanium is as a semiconductor.



Tin

- Archaeological evidence suggests that people have been using tin for at least 5500 years. Tin is primarily obtained from the mineral cassiterite (SnO_2) and is extracted by roasting cassiterite in a furnace with carbon.

- Two allotropes of tin occur near room temperature: non-metallic gray tin and metallic white tin.

- Tin resists corrosion and is used as a protective coating on other metals. A tin can is actually made from steel. A thin layer of tin is applied to the inside and outside of the can to keep the steel from rusting.

- Tin is obtained by reduction of tin oxide with coal:

$$SnO_2 + 2\,C \longrightarrow Sn + 2\,CO$$

Tin Pest

- White tin (stable allotrope of tin at room temperature) is thermodynamically less stable than grey tin below 13°C, and as grey tin is less dense than white tin, the structural integrity of the part is compromised as the 'blisters' form on the metal surface. These gradually increase in size and the metal slowly turns into a grey powder.

- Tin pest is rarely reported in practice and is normally only seen for parts that are kept at -20°C or lower for many months.

$$\alpha\text{-Sn} \overset{13\ ^\circ\text{C}}{\rightleftarrows} \beta\text{-Sn}$$

α-Sn	β-Sn
Grey	White
Non-metallic	Metallic
CN = 4	CN = 6
Density: 5.77 g/cm^3	Density: 7.28 g/cm^3

Appearance of Sn + 0.5 mass% Cu aged at 255 K.

Tin Pest

http://www.youtube.com/watch?v=FUoVEmHuykM&feature=watch_response

Sn(IV) Compounds

- Stannane, **SnH_4**, is a toxic gas which is stable at room temperature. Upon heating to 100 °C it decomposes:

$$SnH_4 \xrightarrow{100\ °C} Sn + 2\ H_2$$

- Tin tetrachloride, **$SnCl_4$**, is a fuming, colorless liquid, which is easily hydrolyzed :

$$SnCl_4 + 2\ H_2O \longrightarrow SnO_2 + 4\ HCl$$

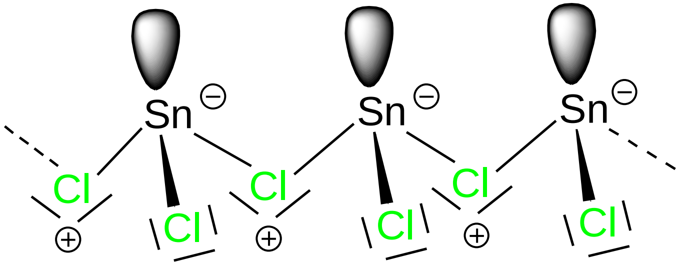
- Tin dioxide, **SnO_2**, occurs in nature as cassiterite. It is thermally and chemically very stable. Used in glass industry.

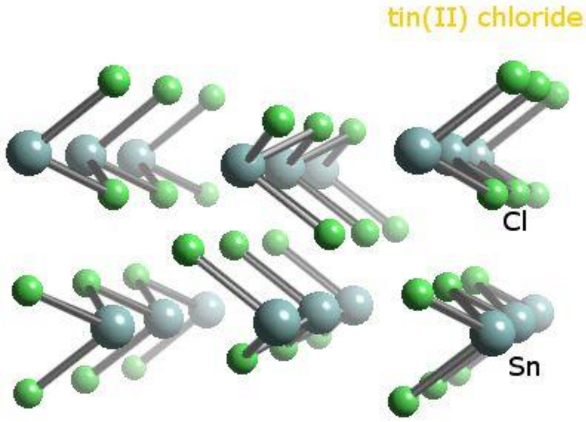
Cassiterite, SnO_2, is usually brown to black and is the most common source of tin. It has a hardness of 6 to 7.

Sn(II) Compounds

- Sn(II) compounds are reducing agents (**preferred oxidation state: +4**). The non-bonding $5s^2$ electron pair is stereochemically active.

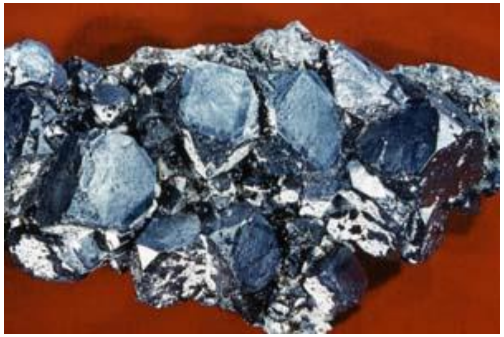
- **$SnCl_2$** is able to reduce Au, Ag and Hg-salts to the corresponding metal.





Lead

- Lead has been known since ancient times. It is sometimes found free in nature but is usually obtained from minerals (e.g. galena, PbS).
- Although lead makes up only about 0.0013% of the earth's crust, it is not considered to be a rare element since it is easily mined and refined.
- Lead is a soft, malleable and corrosion-resistant material
- The ancient Romans used lead to make water pipes, some of which are still in use today (unfortunately for the ancient Romans, lead is a cumulative poison).
- Most of the lead used today is used in the production of lead-acid storage batteries.



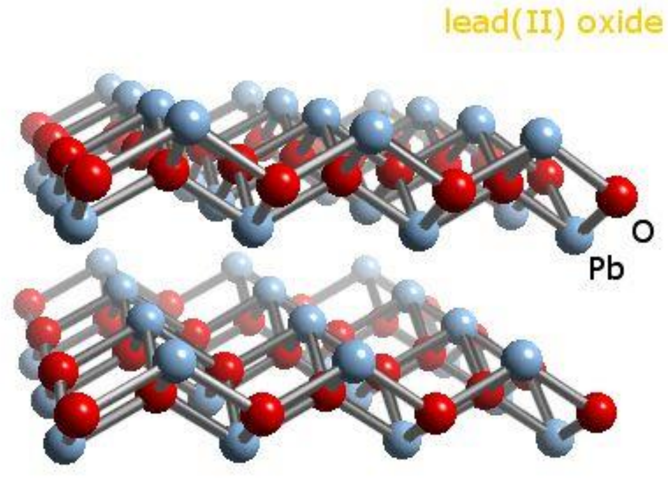
Galena, PbS, the principle ore of lead

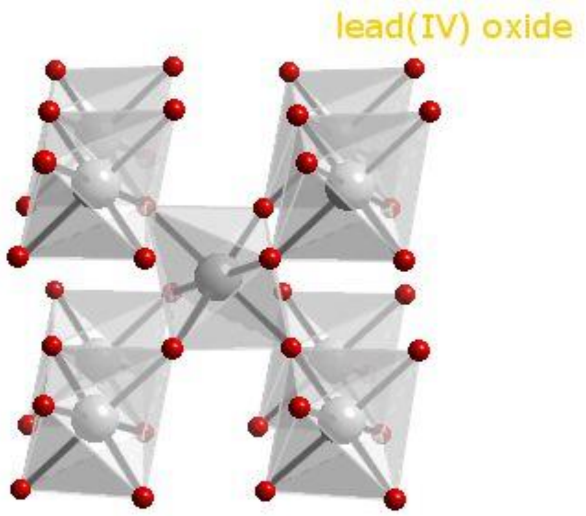
Lead Oxides

- Lead monoxide (**PbO**), is a yellow solid that is used to make some types of glass, such as lead crystal and flint glass, and as a paint pigment.

- Lead dioxide (**PbO_2**) is a brown material that is used in lead-acid storage batteries.

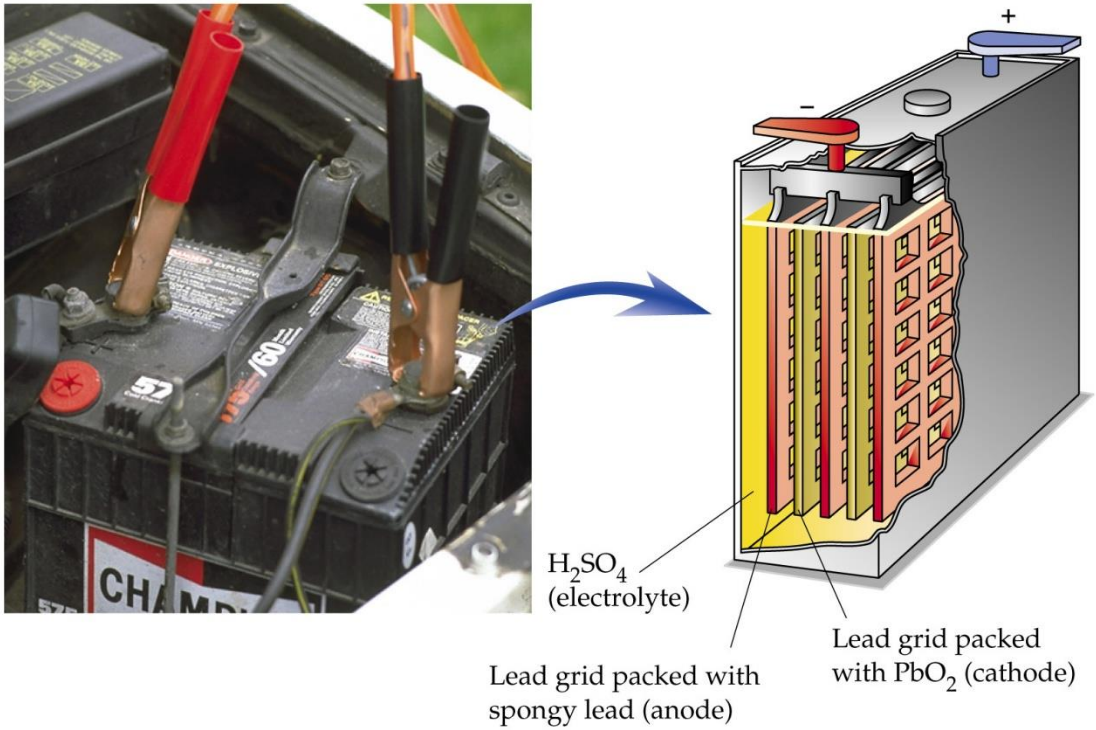
- Trilead tetraoxide (**Pb_3O_4**), also known as red lead, is used to make a reddish-brown paint that prevents rust on outdoor steel structures.





Lead Batteries

A lead storage battery and a cutaway view of one cell. Each electrode consists of several grids with a large surface area so that the battery can deliver the high currents required to start an automobile engine. The electrolyte is aqueous sulfuric acid.



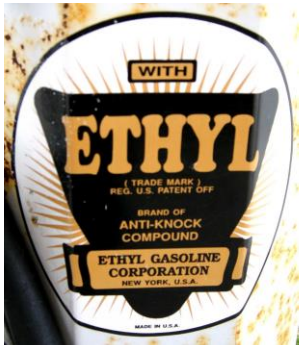
$$PbO_2\,(s) + 4H^+\,(aq) + SO_4^{2-}\,(aq) + 2e^- \longrightarrow PbSO_4\,(s) + 2\,H_2O\,(l)$$

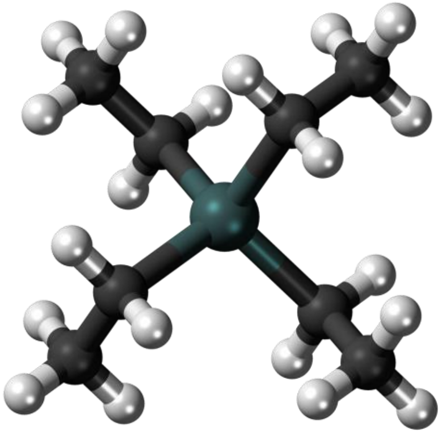
$$Pb(s) + SO_4^{2-}\,(aq) \longrightarrow PbSO_4\,(s) + 2e^-$$

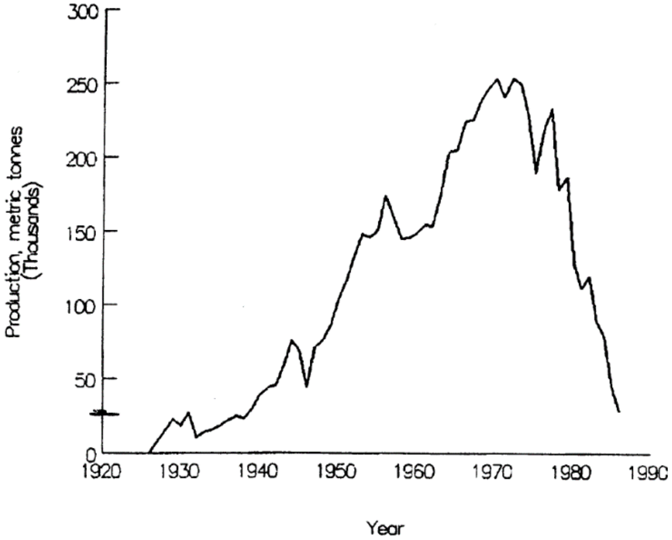
$$Pb(s) + PbO_2\,(s) + 2\,SO_4^{2-}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,PbSO_4\,(s) + 2\,H_2O\,(l)$$

Tetraethyl Lead ($PbEt_4$)

It is a "low percentage" antiknock agent.







Consumption of lead in gasoline in the USA.