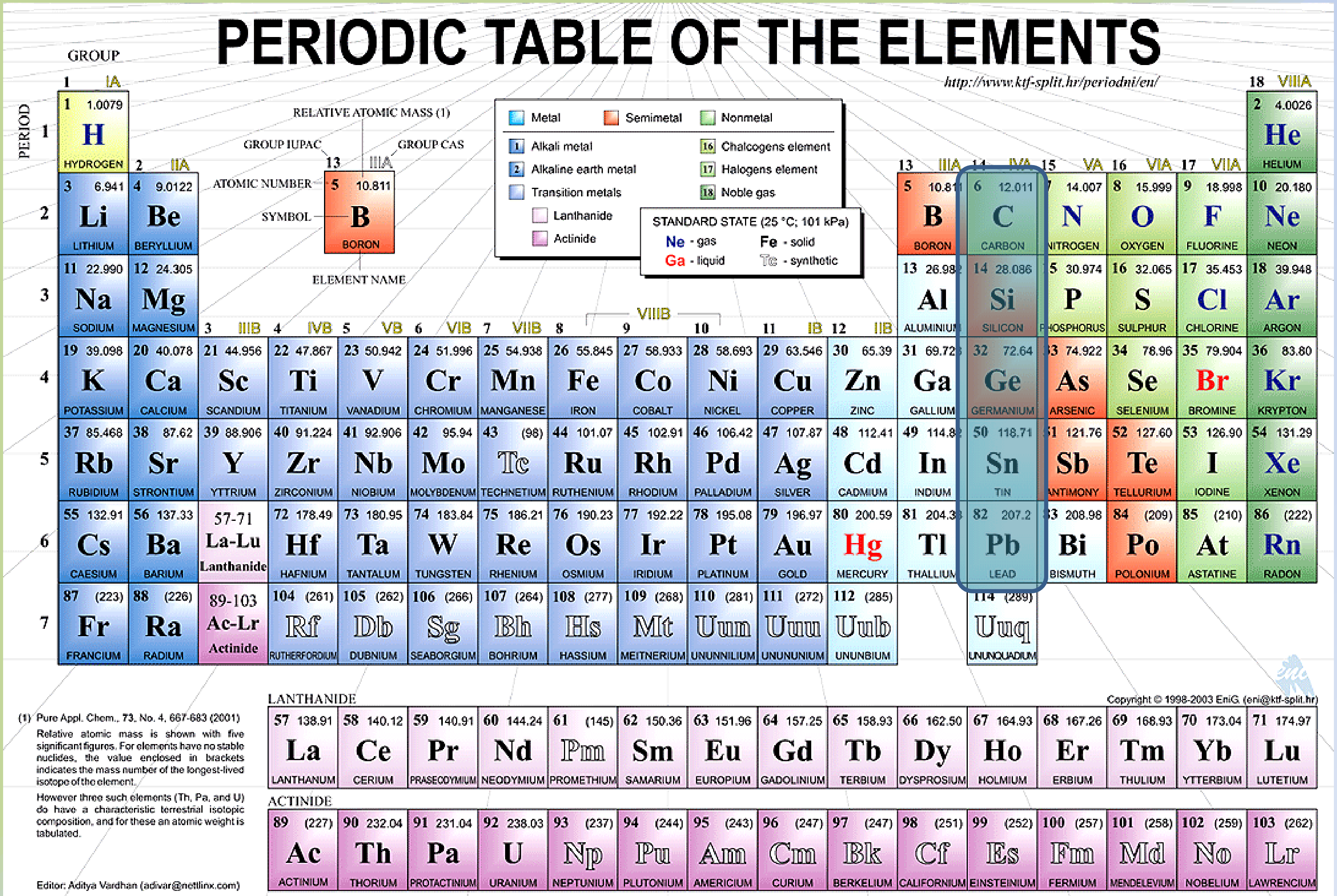
Elements from IV A group

Lecture 9

Main topics of the lecture

1. Overall characteristic of the elements from group IVA.
2. Carbon: natural resources, chemical properties, important compounds.
3. Silicon: natural resources, chemical properties, important compounds.
4. Metals from IVA subgroup: natural resources, chemical properties, important compounds.
5. The usage of compounds from IVA group in medicine.



PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9
10
VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
13 IIIA
5 10.811 B BORON
Metal
Semimetal
Nonmetal
1 Alkali metal
2 Alkaline earth metal
Transition metals
Lanthanide
Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.922 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
Editor: Aditya Vardhan (adivar@netlinx.com)
Copyright © 1998-2003 EniG. (eni@ktf-split.hr)

Overall characteristic of elements from IVA group

	Mass % in the Earth crust	Metallic properties	The type of crystal lattice	Electron configuration	Radius, nm	Elecronegativity	Oxidation states
C	0.48	Nonmetal	Atomic	…$2s^2 2p^2$	0.077	2.50	**+4**, +2, **−4**
Si	27.6	Nonmetal	Atomic	…$3s^2 3p^2 3d^0$	0.134	1.74	+4, +2, −4
Ge	$7.0 \cdot 10^{-4}$	Metalloid	Atomic	…$3d^{10}\underline{4s^2 4p^2 4d^0}$	0.139	2.02	**+4**, +2, −4
Sn	$8.0 \cdot 10^{-3}$	Metal	Metallic or atomic	….$4d^{10}\underline{5s^2 5p^2 5d^0}$	0.158	1.72	**+4**, +2
Pb	$1.6 \cdot 10^{-3}$	Metal	metallic	….$4f^{14}5d^{10}\underline{6s^2 6p^2 6d^0}$	0.175	1.55	+4, **+2**

Natural resources of carbon

CO_2;

Living organisms;

Oil, gas, and coal;

Minerals (carbonates):

limestone – $CaCO_3$,

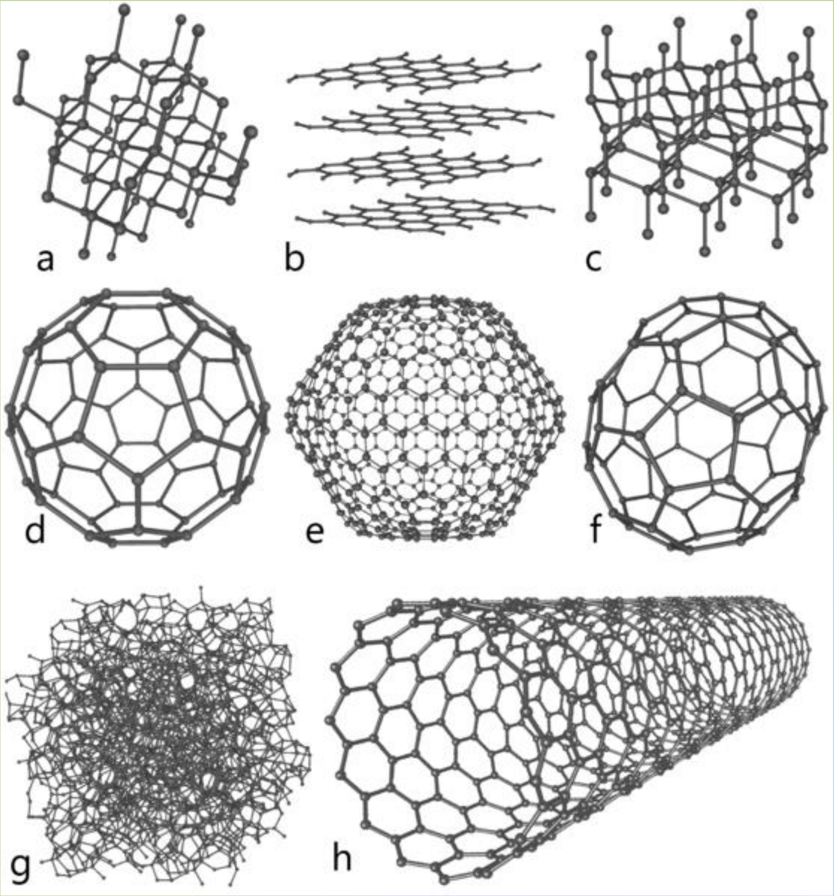
dolomite – $(CaMg)(CO_3)_2$;

As a pure chemical element:

diamond;

graphite.

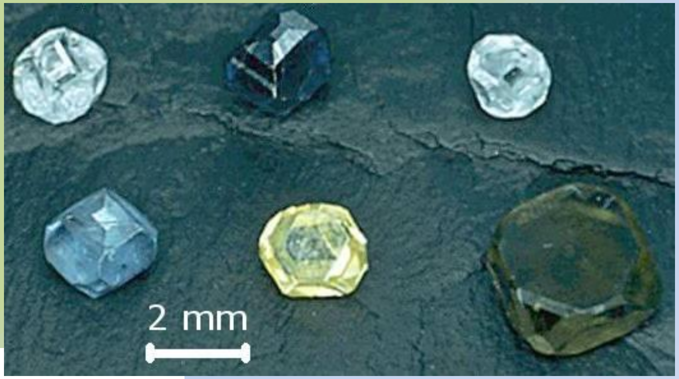
Crystal lattices of different allotropes of carbon

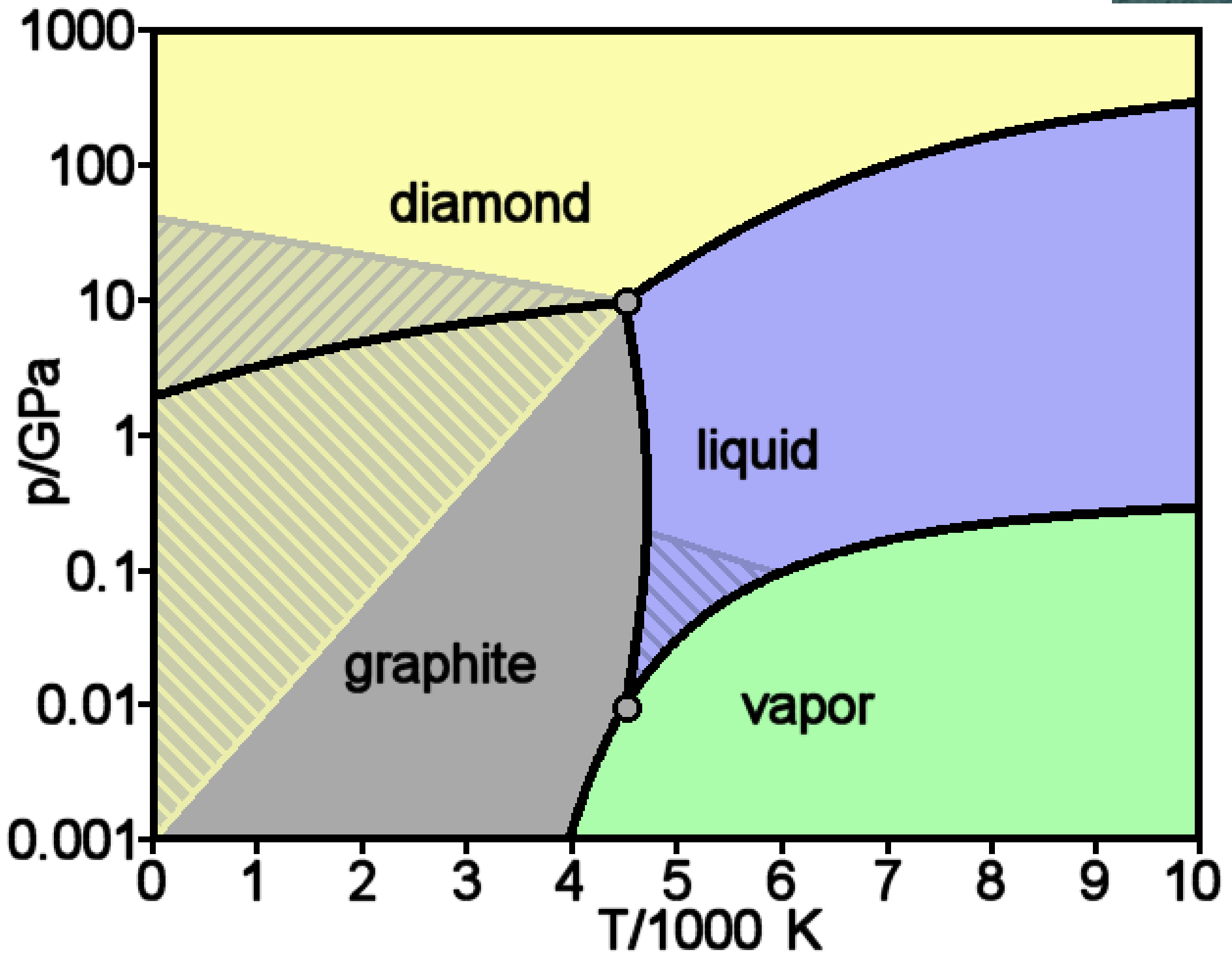


a. Diamond
b. Graphite
c. Lonsdeilite
d, e, f. Fullerens
g. Amorphous carbon
h. Nanotube

Amorphous carbon may be different:
soot, coal, burnt wood.

Phase diagram of carbon

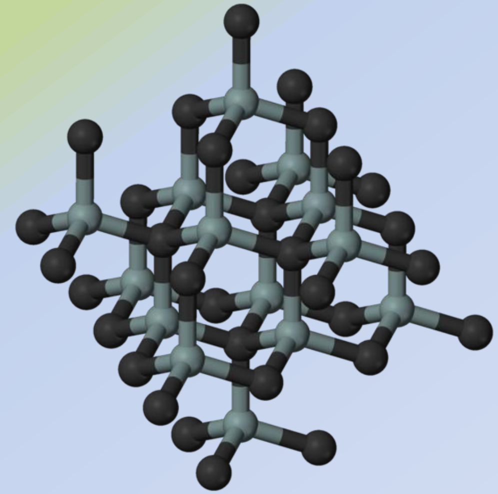




Chemical properties of carbon

In normal conditions all the allotropes of carbon are quite inert.

At high temperature the most active form of carbon is amorphous carbon



$C + 2H_2 \rightarrow CH_4$

$2C + H_2 \rightarrow C_2H_2$

$C + Si \rightarrow SiC$

$C + 4B \rightarrow B_4C$

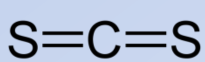
$2C + Ca \rightarrow CaC_2$

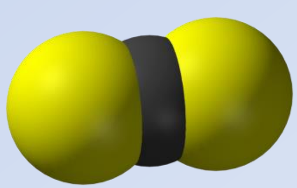
$3C + 4Al \rightarrow Al_4C_3$

$C + O_2 \rightarrow CO_2$

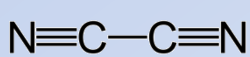
$2C + O_2 \rightarrow 2CO$

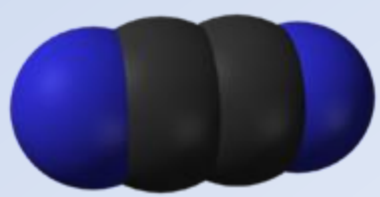
$C + 2S \rightarrow CS_2$





$2C + N_2 \rightarrow NCCN$





$C + 2F_2 \rightarrow CF_4$

Chemical properties of carbon

Amorphous carbon reacts with metal oxides, concentrated oxidizing acids, and even some salts

$C + CuO \rightarrow Cu + CO$

$C + Fe_2O_3 \rightarrow 2Fe + 3CO$

$3C + CaO \rightarrow CaC_2 + CO$

$C + H_2SO_4(conc.) \rightarrow CO_2 + SO_2 + H_2O$

$C + 4HNO_3(conc.) \rightarrow CO_2 + 4NO_2 + 2H_2O$

$5C + 4KNO_3 \rightarrow 2K_2CO_3 + 3CO_2 + 2N_2$

$2C + Na_2CO_3 \rightarrow 2Na + 3CO$

$4C + BaSO_4 \rightarrow BaS + 4CO$

$$C + 4HNO_3(\text{conc.}) \rightarrow CO_2 + 4NO_2 + 2H_2O$$

Binary compounds of carbon with less electronegative elements are known as:

Carbides

(according to the type of chemical bonds)

Ionic (salt-like)

Li_2C_2, Na_2C_2, K_2C_2, Cu_2C_2, Ag_2C_2, MgC_2, CaC_2, Al_4C_3 etc.

- Methanides $(C)^{4-}$
- Acetylides $(C_2)^{2-}$

Covalent

$B_{12}C_3$

SiC

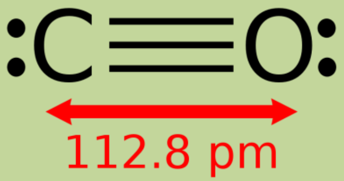
Metal-like

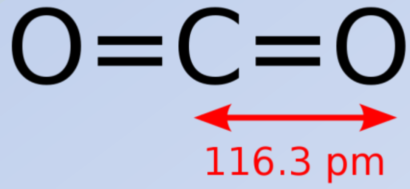
TiC, ZrC, VC, NbC, TaC, MoC, WC, V_2C, Nb_2C, Ta_2C, Mo_2C, Mn_3C, Fe_3C, Co_3C, Ni_3C

Nonstoichiometric

Carbon monoxide

$Hb \cdot O_2 + CO \leftrightarrow Hb \cdot CO + O_2$ stops the transport of O_2 by hemoglobin





- **CO is a stable molecule**
- **that can be a ligand in carbonyles**
- **and cannot form salts**
- **but can participate in redox reactions**
- **mostly as a reducer**

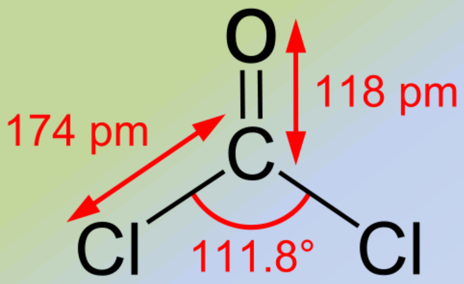
$$Ag_2O + CO \rightarrow Ag\downarrow + CO_2$$

CO as a reducer:

$$CO + O_2 \rightarrow CO_2$$

$$CO + CuO \rightarrow Cu + CO_2$$

$$CO + Cl_2 \rightarrow COCl_2$$



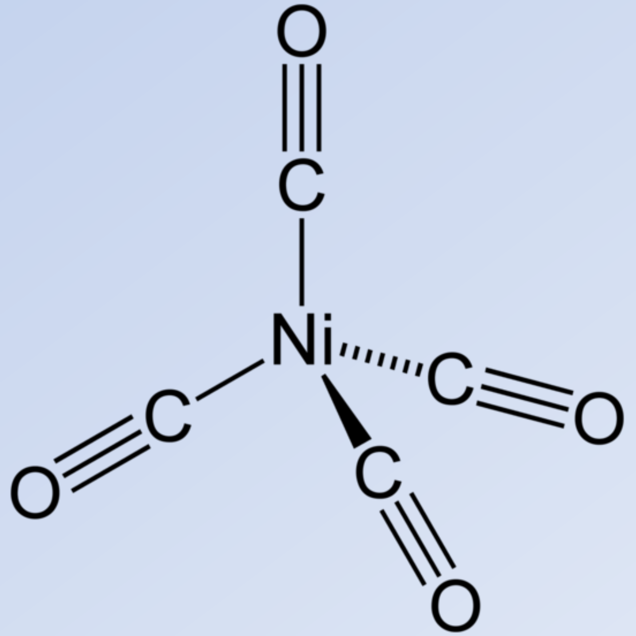
phosgene

Carbonyles of metals:

$$Ni + 4CO \rightarrow Ni(CO)_4$$

Carbonyles are instable:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$



Prussic acid = hydrogen cyanide

$NCCN + H_2\ (t°) \rightarrow 2HCN$

colorless volatile liquid ($t_{boiling}$ = 26.5 °C) with the flavor of almond. It is one of the most venomous poisons. A lethal dosage is just 50 mg.

In industry it is produced in the following way:

$$2CH_4 + 2NH_3 + 3O_2\ (t°) \rightarrow 2HCN + 6H_2O$$

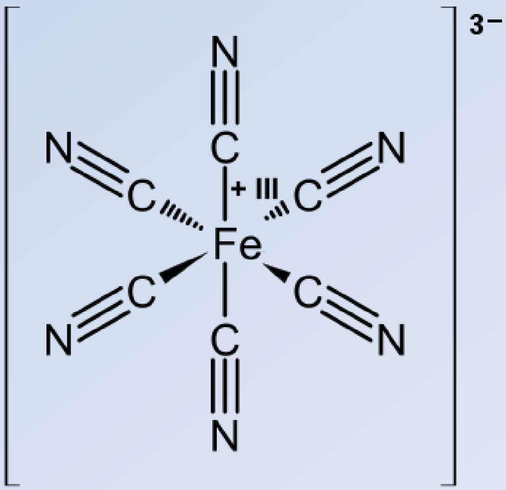
$$H\text{–}C{\equiv}N: \ \Leftrightarrow \ H\text{–}N{=}C:$$

Toxic isoform

Toxic isoform of hydrogen cyanide binds cytochrome C oxidase and breaks down the process of oxidative phosphorylation in mitochondria.

Water solution of HCN is known as prussic acid:

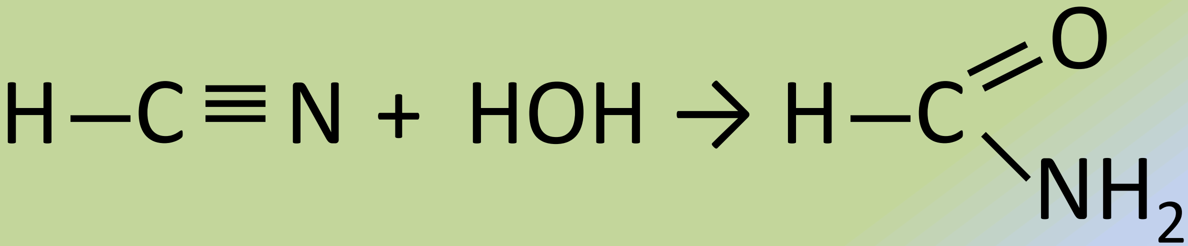
$$HCN \leftrightarrow H^+ + CN^- \qquad K_a \approx 10^{-10}$$



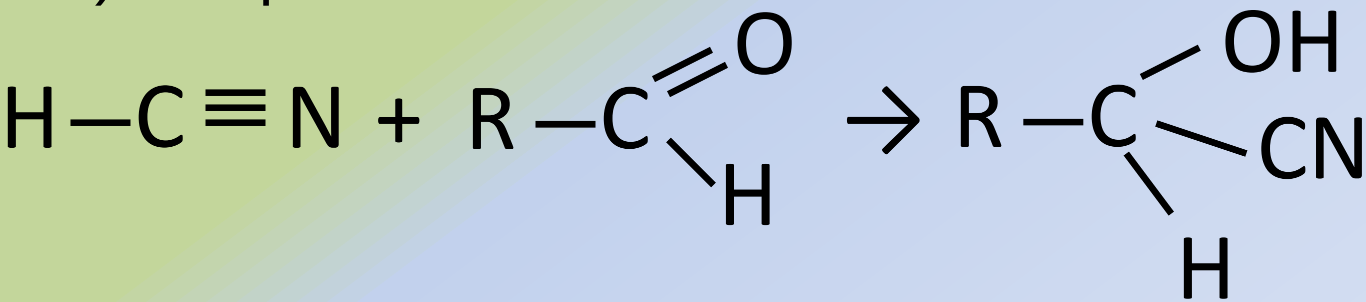
Salts of this acid are hydrolyzed

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

In water solution of hydrogen cyanide a reaction of electrophylic addition proceeds slowly. Amid of formic acid is formed as a product of that reaction:



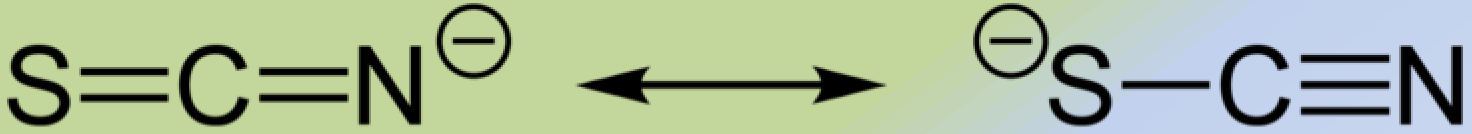
Cyanhydrates are formed in the reaction between aldehydes (or ketones) and prussic acid:



Since cyanhydrates are much less toxic (there is no more lone pair of electrons on carbon), glucose acts as an antidote for prussic acid.

Thiocyanates:

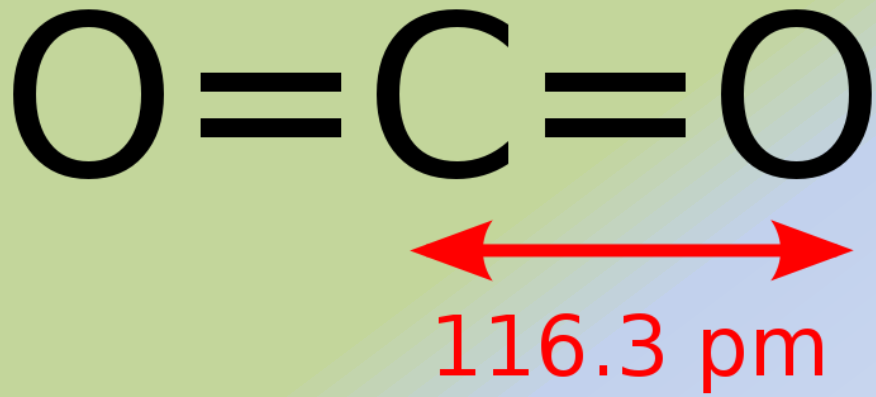
$8CN^{-} + S_8 \rightarrow 8SCN^{-}$



Sodium thiosulfate can be used as an antidote against cyanides :

$$KCN + Na_2S_2O_3 \rightarrow KSCN + Na_2SO_3$$

Carbon dioxide CO_2



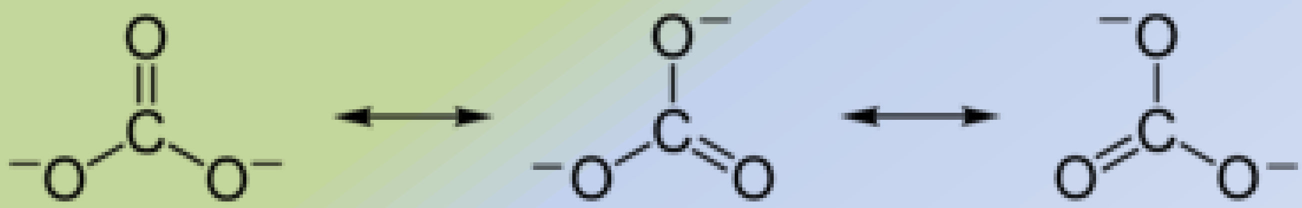
Molecules of CO_2 are nonpolar, and so their solubility in water is low. At 25°C its solubility in water is about 0.03 mol/L. The process of carbon dioxide dissolving in water has a chemical mechanism as well:

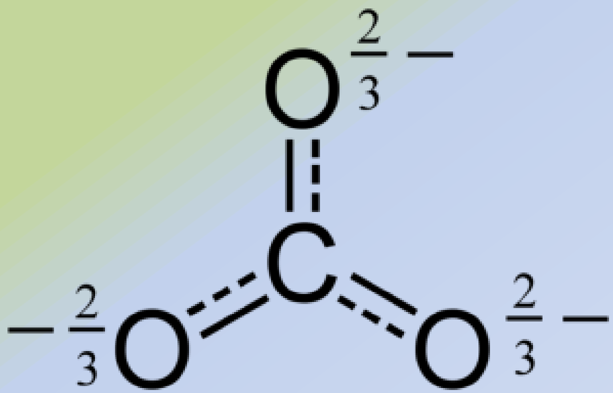
$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

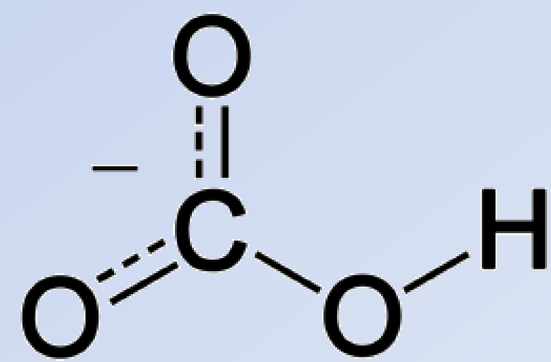
Carbonates. Bicarbonates.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

$$CaCO_3\downarrow + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$







Compounds of halogens and carbon (carbon halides)

$C + 2F_2 \rightarrow CF_4$ (carbon reacts directly just with F_2)

CF_4 is an inert gas ($t_{boiling}$ = –128°C). It cannot react neither with acids, nor with bases. This is one of the reasons why CF_4 and similar compounds (CF_2Cl_2 with $t_{melting}$ = –155°C, $t_{boiling}$ = –30°C) are used as freons in refrigerators.

Chloroform ($CHCl_3$) is used as a solvent and anesthetic, iodoform (CHI_3) is used as antiseptic.

Silicon

There are more than 400 minerals of silicon, while the basic motif in those minerals is silicon dioxide (SiO_2).

Quartz

Sand

Silicon (with concretions of iron and manganese oxides)

Production of silicon:

1. In the laboratory silicon can be produced by the way of silicon dioxide (SiO_2) reduction by magnesium:

$$SiO_2 + 2Mg = 2MgO + Si$$

2. In the industry silicon dioxide is reduced by carbon in the electric oven:

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

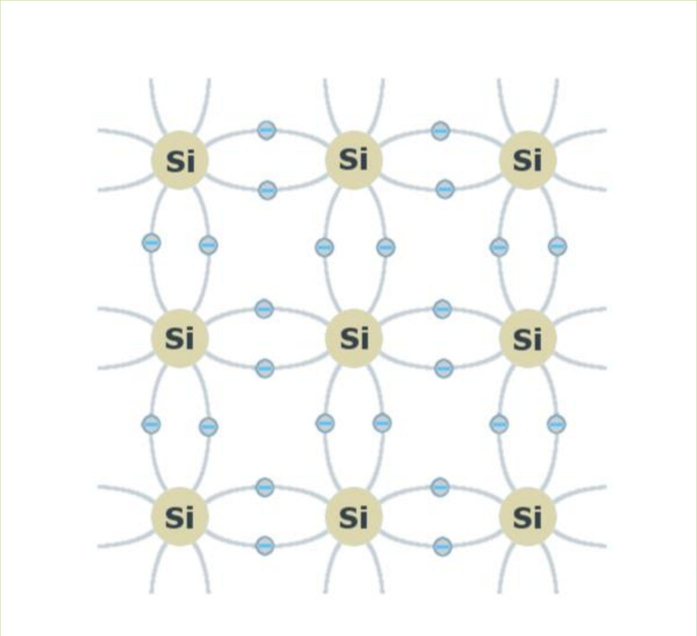
3. High purity silicon (semiconductor) is produced by the reduction of $SiCl_4$ and $SiHCl_3$ by hydrogen:

$$SiCl_4 + 2H_2 = Si + 4HCl,$$

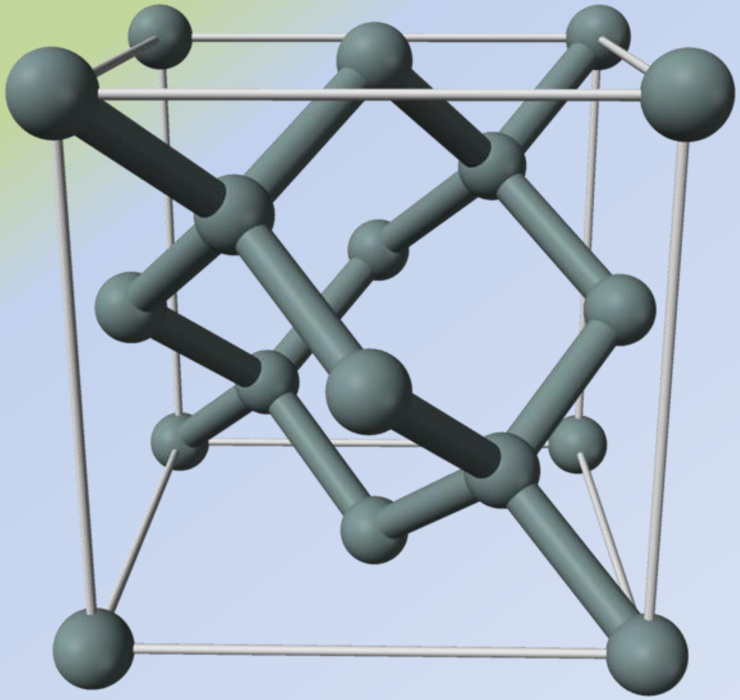
$$SiHCl_3 + H_2 = Si + 3HCl,$$

as well as by the thermal decomposition of silane:

$$SiH_4 \rightarrow Si + 2H_2.$$



- $t_{boiling}$ =1415°C
- hard
- fragile
- semiconductor



(diamond-like lattice)

Graphite-like lattice of silicon is very instable

Chemical properties of silicon

At normal temperature it reacts just with fluorine:

$Si + F_2 \rightarrow SiF_4$

At high temperature:

$Si + Cl_2 \rightarrow SiCl_4$

$Si + O_2 \rightarrow SiO_2$

$Si + C \rightarrow SiC$

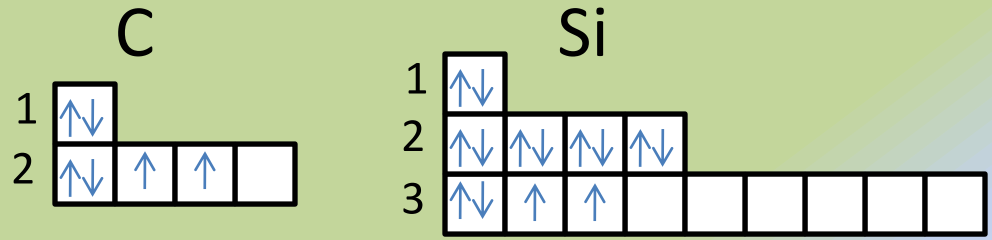
$Si + N_2 \rightarrow Si_3N_4$

$Si + Mg \rightarrow Mg_2Si$

$Si + H_2O \rightarrow SiO_2 + H_2$

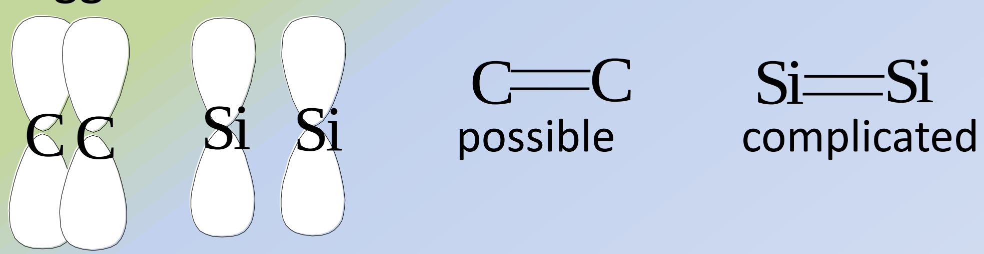
$Si + 4HF \rightarrow SiF_4 + 2H_2$

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow$$

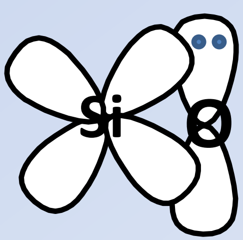


The differences between Si and C:

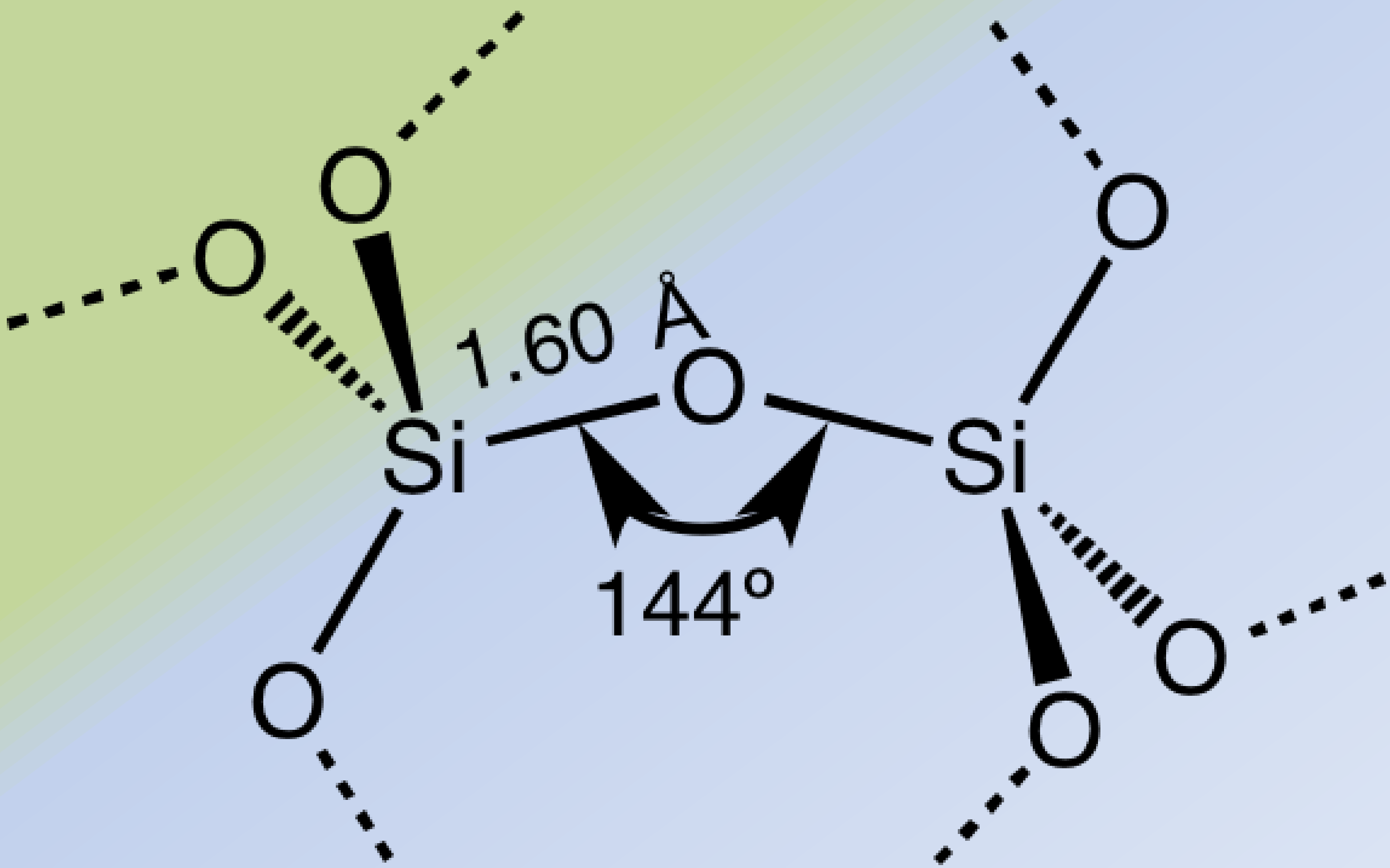
1. r (Si) > r (C) , the formation of π – bonds by p-electrons of in Si is complicated by the bigger radius of the atom



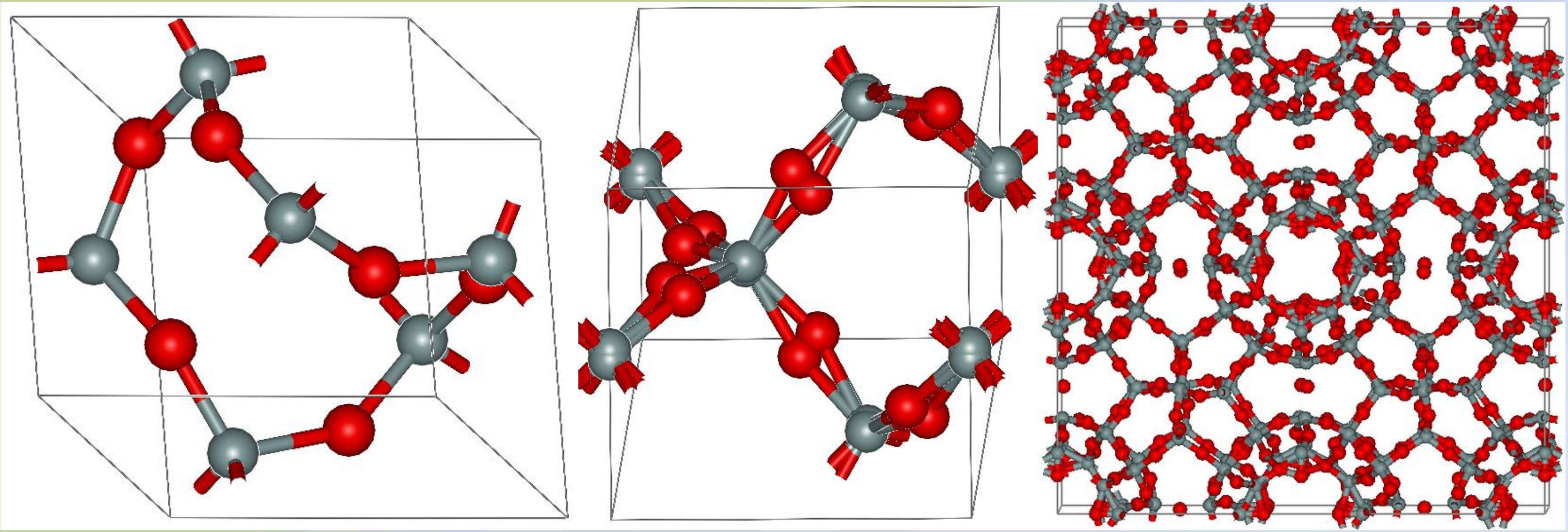
2. However, vacant d-orbitals may form of Si may form π – bonds with lone pairs of electrons on orbitals of O, N and Cl.



The bonds between silicon and oxygen in silicon dioxide are strong because of the stabilization by dative π – bonds



SiO_2 has many polymorphic variants



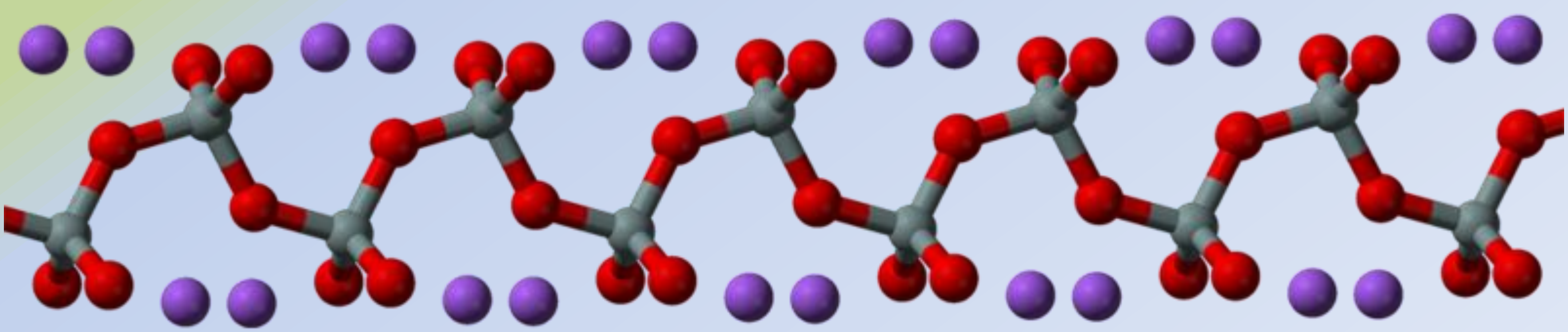
Oxygen containing compounds of silicon

- SiO;

- SiO_2 – is a compound with atomic crystal lattice $(SiO_2)_n$;

- H_2SiO_3 – is better described by $mSiO_2 \cdot nH_2O$;

- Silicates are salts of silicic acid

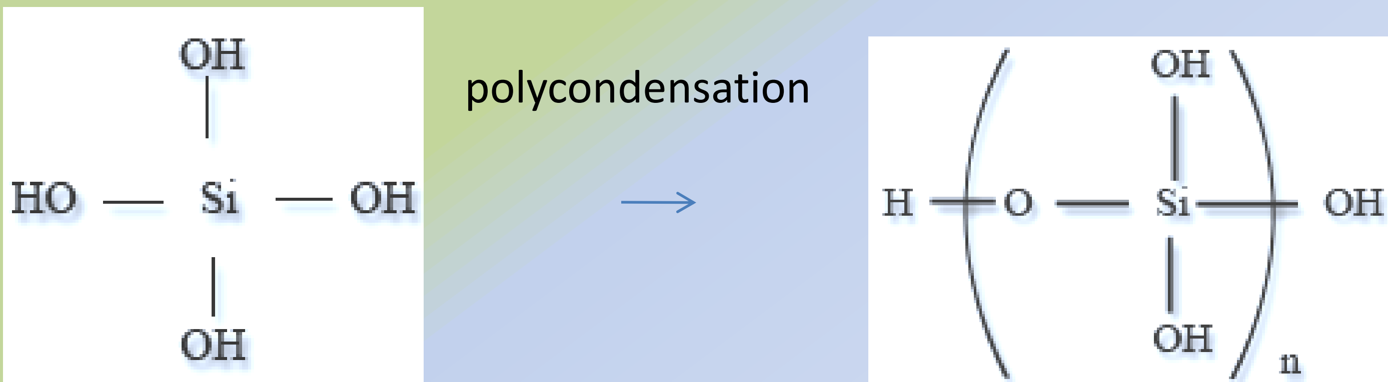


Silicic acid(s) - $\boldsymbol{m}\mathbf{SiO_2 \cdot}\boldsymbol{n}\mathbf{H_2O}$

$$Na_2SiO_3 + 2HCl + H_2O \rightarrow H_4SiO_4 + 2NaCl$$

$$H_4SiO_4 \rightarrow SiO_2 \cdot 2H_2O$$

gel



Silicic acid (silanol) exists in the water solution upon precipitate of silicagel

$$mSiO_2 \cdot n\, H_2O \xrightarrow{-H_2O} (SiO_2)_n$$

Silicagel is a well-known adsorbent

Production of silicic acid

Silanes

Si_nH_{2n+2}

Silicon hydrides are a family of compounds with formulas from SiH_4 until Si_8H_{18}. Higher silanes are less stable than SiH_4 and Si_2H_6.

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4 \text{ (and other silanes)}$$

All silanes are strong reducers and they are burning spontaneously in the open air immediately after their formation:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

Silanes are relatively stable in neutral and acidic solutions, while they are easily hydrolyzed in the basic medium:

$$SiH_4 + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 4H_2$$

Production of silanes

Silicon halides

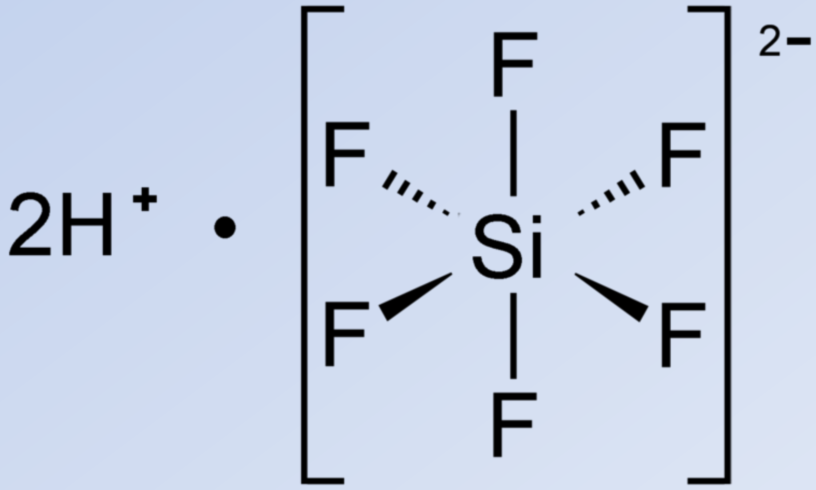
$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$$

Hydrolysis of SiF_4 has two steps:

$$SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 4HF$$

$$4HF + 2SiF_4 \rightarrow 2H_2[SiF_6]$$

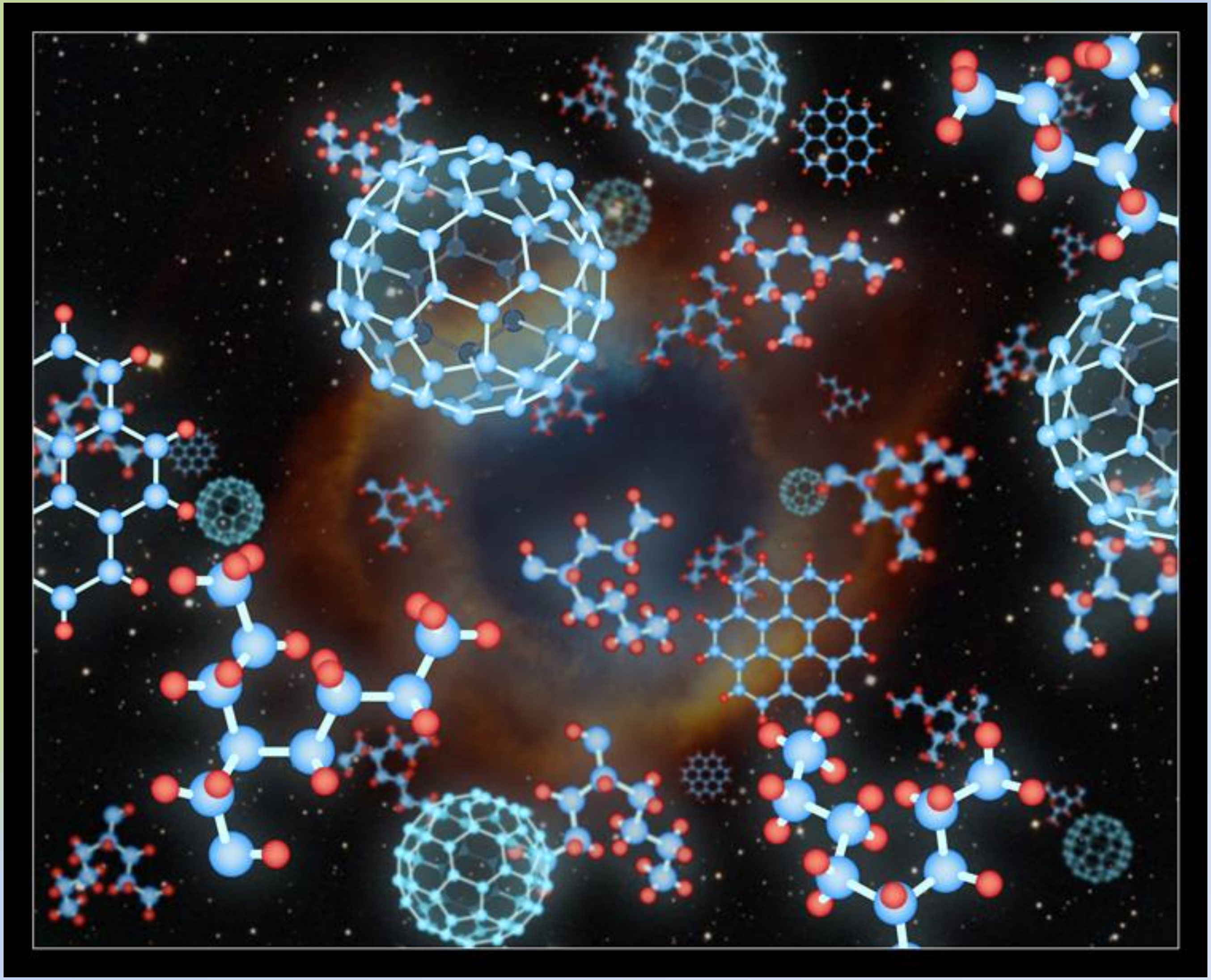
$$3SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 2H_2[SiF_6]$$



Why carbon ???

- The number of valence electrons is exactly the same as the number of valence orbitals in carbon (there are no empty orbitals and lone pairs of electrons)
- Carbon can form single, double, triple and aromatic bonds
- Partially negative charge exists on the carbon atom, and not on the hydrogen atom (electrons are “shielded” by protons of hydrogen atoms)
- Hydrocarbons have no acidic or basic properties

Fullerenes are found in the outer space



Elements from “germanium family”

1. At room temperature Ge and Sn are resistant to oxygen, while Pb is slowly covered by a thin oxide layer.

2. At high temperature they form corresponding oxides: GeO_2, SnO_2, and PbO.

3. They react with halogens: GeX_4, SnX_4, PbX_2

4. They form sulfides: GeS or GeS_2, SnS or SnS_2, and PbS.

5. Metals from germanium family cannot react with hydrogen, carbon and nitrogen.

Reactions with acids:

$Ge + 4HNO_{3\ conc.} \rightarrow H_2GeO_3 + 4NO_2 + H_2O$

$Sn + 4HNO_{3\ conc.} \rightarrow H_2SnO_3 + 4NO_2 + H_2O$

$Sn + 4HNO_{3\ dilute} \rightarrow Sn(NO_3)_2 + NO + H_2O$

$Pb + 4HNO_{3\ conc.} \rightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$ (at high t°)

$Pb + 4HNO_{3\ dilute} \rightarrow Pb(NO_3)_2 + NO + 2H_2O$

$Sn + HCl \rightarrow SnCl_2 + H_2$

$Pb + H_2SO_{4\ dilute} \rightarrow PbSO_4 + H_2$

$Ge + H_2SO_{4\ dilute} \neq$

Reactions with alkalis:

Ge can react with alkalis only in the presence of oxidizers

$$Sn + 2NaOH + 2H_2O \rightarrow Na_2[Sn(OH)_6] + H_2$$

$$Pb + 2NaOH + 2H_2O \rightarrow Na[Pb(OH)_3] + H_2$$

Compounds with halogens $E\mathit{Hal}_4$

Cannot form salts

GeF_4 - gas

$GeCl_4$ - liquid

$SnCl_4$- liquid

$PbCl_4$- liquid

$SnBr_4$- solid

GeI_4 - solid

1. These compounds are hydrolyzed:

$SnCl_4 + 6H_2O = 4HCl + H_2[Sn(OH)_6]$

2. They also participate in complexation reactions:

$GeCl_4 + 2HCl = H_2[GeCl_6]$

Both properties are the result of free orbitals existence

$PbCl_4$ is instable and decomposes in the presence of water by the mechanism of “intramolecular” redox reaction:

$$PbCl_4 \rightarrow PbCl_2 + Cl_2.$$

$SnCl_4 + 2HCl \rightarrow H_2[SnCl_6]$,

$H_2[SnCl_6] + 2KOH \rightarrow K_2[SnCl_6] + 2H_2O$.

Compounds of halogens with a formula like E*Hal*$_2$ are typical salts

They are hydrolyzed in water solutions.
Ge*Hal*$_2$ salts are hydrolyzed completely

$SnCl_2 + H_2O \leftrightarrow SnOHCl_2 + HCl$

$GeCl_2 + H_2O \rightarrow Ge(OH)_2 + 2HCl$

Oxides

Mixed

Pb_3O_4

monoxides

Reductive properties

GeO

SnO

PbO

Basic properties

dioxides

Oxidative properties

GeO_2

SnO_2

PbO_2

Acidic properties

GeO and SnO, in contrast to PbO, disproportionate at high temperature:

$$2GeO \rightarrow GeO_2 + Ge$$
$$2SnO \rightarrow SnO_2 + Sn$$

$$3PbO_2 \rightarrow Pb_3O_4 + O_2$$

Hydroxides of Ge, Sn and Pb in the oxidation state of +2 ($xMeO \cdot yH_2O$) are amphoteric.

$Ge(OH)_2 + 2KOH_{conc.} \rightarrow K_2[Ge(OH)_4]$

$Ge(OH)_2 + 2HCl \rightarrow GeCl_2 + 2H_2O$

$Sn(OH)_2 + NaOH \rightarrow Na[Sn(OH)_3]$

At high temperature:

$2Na[Sn(OH)_3] \leftrightarrow Sn\downarrow + Na_2[Sn(OH)_6]$,

$Sn(OH)_2 + 3HCl \rightarrow H[SnCl_3] + 2H_2O$.

$Pb(OH)_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + 2H_2O$

$Pb(OH)_2 + 2KOH \rightarrow K_2[Pb(OH)_4]$ (at pH≥13)

$Pb(OH)_2 + 4HCl_{conc.} \rightarrow H_2[PbCl_4]$.

Hydroxides of Ge and Sn in the oxidation state of +4 ($xMeO_2 \cdot yH_2O$) are also amphoteric.

($xPbO_2 \cdot yH_2O$ are unknown)

$$Sn(OH)_4 + OH^- \rightarrow [Sn(OH)_6]^{2-}$$

$$Ge(OH)_4 + 4H^+ \rightarrow Ge^{4+} + 4H_2O$$

Compounds with Pb^{+4} are strong oxidizers!

$$PbO_2 + 4HCl = PbCl_2\downarrow + Cl_2\uparrow + 2H_2O$$

The usage of compounds of elements from IVA group in medicine

Activated coal

Na_2CO_3, $CaCO_3$, $NaHCO_3$

Fullerenes

Isotopes of carbon

Silicon implants and silicon containing lenses.

Sielast is used in dentistry

$Pb(CH_3COO)_2$ – lead acetate (defrutum).

PbO - is a component of «diachilic oitment».

Thank you for listening!