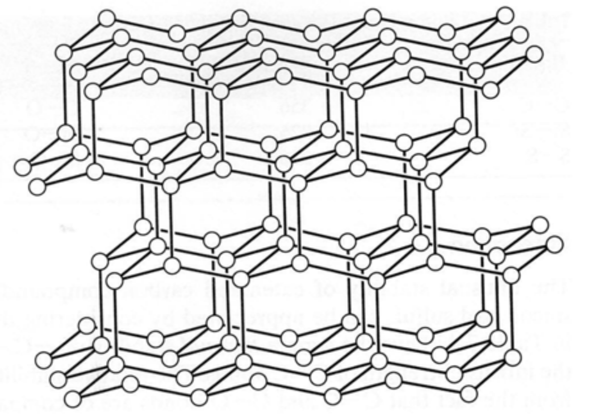
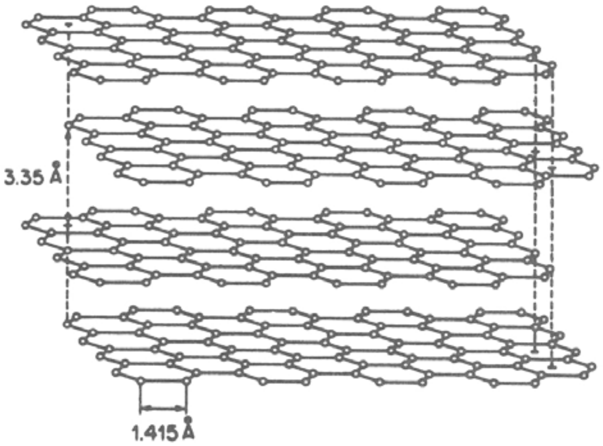
# Group 14 - The Elements
## Carbon

- Carbon's two naturally occurring allotropes are graphite and diamond, with graphite the more stable form.



Diamond



Graphite

| allotrope | bond order | $d_{\text{C-C}}$ (pm) | $\Delta H^{\circ}_{f}$ kJ/mol | $\Delta G^{\circ}_{f}$ kJ/mol | $S^{\circ}$ J/mol·K |
|---|---|---|---|---|---|
| diamond | 1 | 154 | 1.88 | 2.84 | 2.43 |
| graphite | 1⅓ | 141.5 | 0 | 0 | 5.69 |

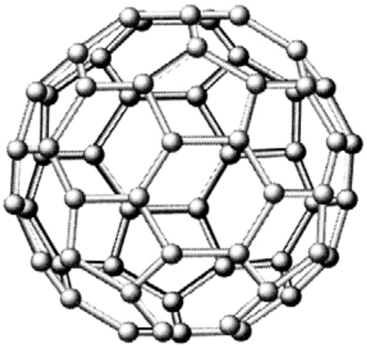
- Graphite is the stable form because it has shorter and stronger bonds, owing to π-delocalization in the hexagonal rings that comprise the sheets.

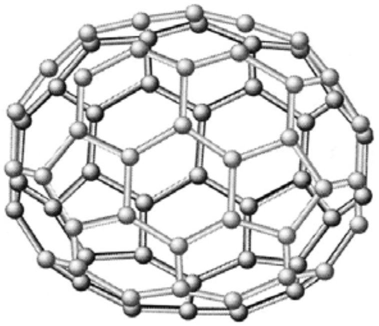
- Diamond, being a more ordered structure, has lower absolute entropy.

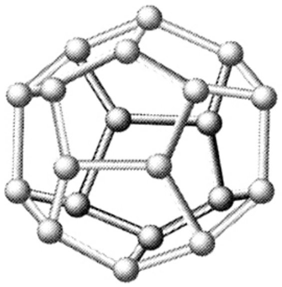
- Although conversion of diamond to graphite is thermodynamically favored, it is kinetically inhibited.

# Fullerenes

- Fullerenes are a family of allotropes with the formula $C_{2n}$ ($2n$ = 20, 60, 70, 76, 78, 82, 84, 96) made by passing a large electrical current through graphite rods in a helium atmosphere, thereby evaporating the rods and producing "fullerene soot."


$C_{60}$ ($I_h$)


$C_{70}$ ($D_{5h}$)


$C_{20}$ ($I_h$)

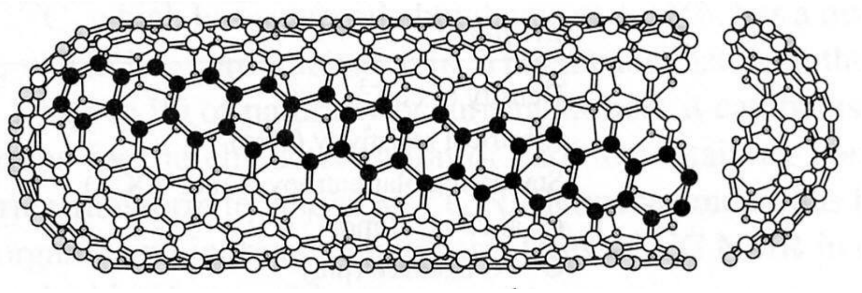
  - The soot is soluble in benzene and other organic solvents, allowing chromatographic isolation of gram quantities of $C_{60}$ and $C_{70}$, and smaller quantities of other fullerenes.

- All C atoms of $C_{60}$ are equivalent, but there are both single and double bonds with C–C distances of 145.3 pm and 138.3 pm.
  - $C_{60}$ has 20 hexagons and 12 pentagons, like a soccer ball.
  - $C_{60}$ is one of the most strained molecules known, but is kinetically stable.
  - $C_{60}$ decomposes at ~750 °C.

- Fullerenes are less stable than graphite or diamond.

  $C_{60}$ $\Delta H^\circ_f \approx 42.5$ kJ/mol  $C_{70}$ $\Delta H^\circ_f \approx 40.4$ kJ/mol

# Nanotubes



- Carbon nanotubes are prepared by arc-evaporating graphite.
- They are needle-like cylindrical tubes with graphite-structured walls, capped by fullerene-like hemispheres.
- Nanotubes are metallic, semiconducting, or insulating, depending on their preparation.
- Tube ends can be opened by nitric acid and then filled with various metal oxides.

# Silicon and Germanium

- Si and Ge are hard and brittle solids with the diamond structure ($d_{\text{Si-Si}}$ = 235 pm).

- Si is the second most abundant element by weight (after oxygen) on earth.
    - Si is found in many minerals and silica ($SiO_2$ - quartz, sand, etc.).

- Ge is recovered from flue dusts and coal ash.

- Both Si and Ge are important semiconductors.

# Tin and Lead

- Tin is found as the mineral cassiterite, $SnO_2$, in Indonesia, Bolivia, Zaire, Nigeria, Thailand, and China (largest producer).

- Tin has two well characterized allotropes, nonmetallic grey tin ($\alpha$-Sn) and metallic white tin ($\beta$-Sn).

$$\alpha\text{-Sn} \overset{18\ ^{o}\text{C}}{\rightleftharpoons} \beta\text{-Sn} \overset{232\ ^{o}\text{C}}{\rightleftharpoons} \text{Sn}(l)$$

  - Grey tin ("tin pest") has a diamond structure and is brittle, hard, and fragile.
  - White (metallic) tin has a distorted close-packed structure.

- Sn(*l*) is used in making plate glass.

- Lead only has a *ccp* metallic form.

- Lead is found as its ore galena, PbS, from which the metal can be won by roasting.

$$PbS + O_2 \xrightarrow[\Delta]{} Pb + SO_2$$

## Obtaining Si, Ge, Sn, Pb

- All can be obtained by reduction of their oxides with carbon.

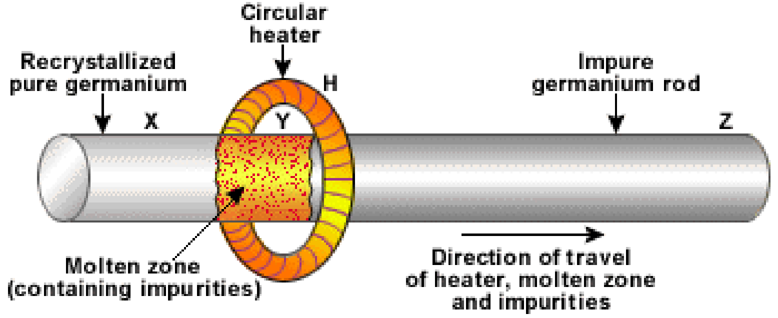
$$MO_2 + C \xrightarrow[\Delta]{} M + CO_2 \qquad M = \text{Si, Ge, Sn, Pb}$$

- Si and Ge can be obtained in high purity for semiconductor use by reduction of the chloride or thermal decomposition of the iodide over a hot Ta wire.

$$SiCl_4 + 2H_2 \xrightarrow{\text{hot Ta wire}} Si + 4HCl$$

$$SiI_4 \xrightarrow{\text{hot Ta wire}} Si + 2I_2$$

- Further purification is done by zone refining.[1]



Zone refining of germanium metal.

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[1] Image source: http://home.att.net/~cat6a/metals-XI.htm

# Catenation

- Carbon uniquely can form chains of M–M bonds (catenation) without limit, owing to the following factors.
  - Strength of M–M bond decreases with size.

M–M Bond Energy (kJ/mol)

| C–C | Si–Si | Ge–Ge | Sn–Sn |
|---|---|---|---|
| 356 | 210-250 | 190-210 | 105-145 |

  - Disparity between M–M and M–X bond strengths increases with size.

M–X Bond Energies (kJ/mol)

| | | | |
|---|---|---|---|
| C–O<br>336 | Si–O<br>368 | | |
| C–H<br>416 | Si–H<br>323 | Ge–H<br>290 | Sn–H<br>252 |
| C–Cl<br>327 | Si–Cl<br>391 | Ge–Cl<br>356 | Sn–Cl<br>344 |

  - As size increases, *p*π-*p*π bonding rapidly becomes less effective, being significant only for carbon.

# Group Oxidation States

- Although +4 is the group characteristic oxidation state, the +2 state becomes more stable down the group.

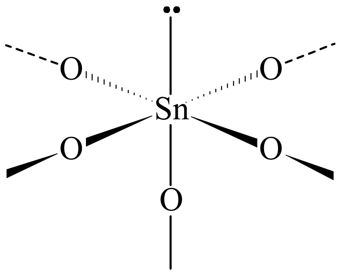
- Stable carbon and silicon compounds have +4 state.

- At Ge and Sn, both +2 and +4 states are stable.

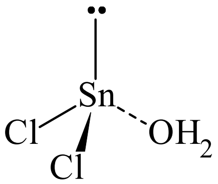
- At Pb, the bond strength is too low to compensate for the slightly higher ionization energy requirement of the Pb(IV) state in many cases. Hence, the +2 state is favored.

☛ The increasing stability of the +2 state is another example of the so-called "inert-pair effect."

- With $Sn^{2+}$ the unused pair appears to be stereochemically important in cases like SnO(*s*) and $SnCl_2 \cdot 2H_2O$(*s*).



SnO coordination in solid



$SnCl_2 \cdot 2H_2O$
(Other $H_2O$ in crystal lattice, lost at 80 °C)

- Similarly, $GeCl_3^-$ has trigonal pyramidal ($C_{3v}$) geometry.

# Carbon Chemistry - The Oxides

- There are three oxides:

| $C_3O_2$ | $CO$ | $CO_2$ |
|---|---|---|
| carbon suboxide | carbon monoxide | carbon dioxide |

- $C_3O_2$ is an evil smelling gas formed by dehydration of malonic acid.

$$3CH_2(CO_2H)_2 + P_4O_{10} \rightarrow 3C_3O_2 + 4H_3PO_4$$

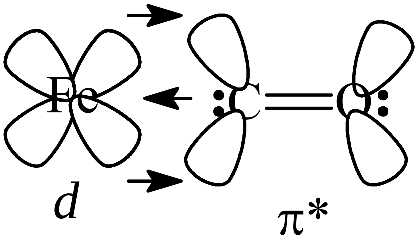
  - $C_3O_2$ is linear ($D_{\infty h}$).

$$\ddot{\underset{\cdot\cdot}{O}}=C=C=C=\ddot{\underset{\cdot\cdot}{O}}$$

- CO can be prepared by a similar dehydration with formic acid, using conc. $H_2SO_4$.

$$HCO_2H \xrightarrow{\text{conc } H_2SO_4} CO + H_2O$$

  - Toxicity is related to its ability to bind to $Fe^{2+}$ in hemoglobin through a back-bonding mechanism.



  - Donation of *d* electron density into the π* MO of CO weakens the bond, shifting the i.r. frequency lower.

# Carbon Chemistry - The Oxides

- $CO_2$ dissolves in water to function as carbonic acid, but the principal species in solution is $CO_2(aq)$, which is only loosely hydrated.
  - On this basis, acid hydrolysis equilibria should be written as

    $$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_1 = 4.3 \text{ x } 10^{-7}$$
    $$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad K_2 = 5.6 \text{ x } 10^{-11}$$

  - $H_2CO_3$ does exist, and using the "true" activity of $H_2CO_3$ has a $K_1 \approx 2 \text{ x } 10^{-4}$, in keeping with its structure as $(HO)_2CO$ ($C_{2v}$).[2]

- The rate of equilibrium between $CO_2$ and $H_2CO_3$ is measurably slow, which is physiologically, analytically, and industrially important.

- Neutralization at pH < 8 involves a two-step mechanism beginning with direct hydration of $CO_2$:

  $$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad \text{slow}$$
  $$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \qquad \text{fast}$$
  $$Rate = -d[CO_2]/dt = k_1[CO_2]$$

- Neutralization at pH > 10 involves direct attack on $CO_2$:

  $$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad \text{slow}$$
  $$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad \text{fast}$$
  $$Rate = -d[CO_2]/dt = k_2[CO_2][OH^-]$$

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[2] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, NY, 1999, p. 227.

## Carbides

- Carbon forms binary carbides with active metals, most important of which are methanides and acetylides.

- Methanides, which behave as if they contain $C^{4-}$ ions, are formed with high charge-density cations.
  - Methanides hydrolyze to give methane.

    $Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3$

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

- Acetylides, which contain $C_2^{2-}$ ions, are known with a number of metal cations:

  | | |
  |---|---|
  | $M_2C_2$ | $M^{I}$ = group 1, Cu, Ag, Au |
  | $MC_2$ | $M^{II}$ = group 2 |
  | $M_2(C_2)_3$ | $M^{III}$ = Al, La, Pr, Tb |

  - $C_2^{2-}$ is isoelectronic with $N_2$ and has a short bond length (119-124 pm), consistent with a triple bond.
  - Acetylides hydrolyze to give acetylene.

    $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

- A sesquicarbide, containing linear $C_3^{4-}$ ions, can be prepared by reacting Mg dust with *n*-pentane at ~680 °.[3]
  - In acid this hydrolyzes to give allene.

    $Mg_2C_3 + 4HCl \rightarrow C_3H_4 + 2MgCl_2$

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[3] Cotton *et al.*, *ibid.*, p. 220.

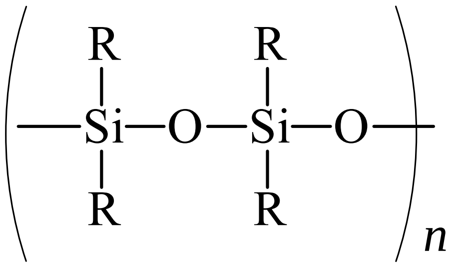
# Silicon and Germanium

- $SiO_2$ (silica) is the most important silicon compound.
  - $SiO_2$ melts at ~1700 ° to give quartz glass.
  - Other glasses contain silicates ($SiO_3^-$, $Si_2O_7^{6-}$, etc.), which are built up of linked $SiO_3$ and $SiO_4$ units, similar to borates. (n.b., diagonal relationship)

- A number of hydrides, called silanes, are known and are alkane analogues.

$$SiH_4, Si_2H_6, ..., Si_6H_{14} \quad ☛ \quad Si_nH_{2n+2}, n = 1\text{–}6$$

- Greater strength of the Si–O bond over the Si–Si bond favors formation of silicate structures.
  - Silicates include the well known silicone polymers.



$$\left( -\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O- \right)_n$$

- Ge chemistry is similar to Si chemistry, but less extensive.
  - The +2 state becomes more important, and the +4 state can sometime easily convert to the +2 state; e.g.,

$$GeCl_4 + Ge \rightarrow 2GeCl_2$$

# Tin and Lead Chemistry

- Tin(II) solutions readily hydrolyze in all but the most acidic media, producing trimeric $[Sn_3(OH)_4]^{2+}$.
  $3Sn^{2+}(aq) + 8H_2O \rightleftharpoons [Sn_3(OH)_4]^{2+} + 4H_3O^+ \qquad K = 1.7 \times 10^{-7}$
  - Hypothetical $[Sn(H_2O)_6]^{2+}$ is estimated to have $K_a \approx 10^{-2}$.

- Both SnO and $SnO_2$ are amphoteric.
  - In base $SnO_2$ hydrolyzes to give the stannate ion.
    $SnO_2 + 2OH^- + 2H_2O \rightleftharpoons Sn(OH)_6^{2-}$

- Lead(IV) is known only in covalent compounds, not as a free $Pb^{4+}$ ion.

- $PbO_2$ is a powerful oxidizing agent used in the lead storage battery.

| | | | | |
|---|---|---|---|---|
| Cathode: | $PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$ | $\rightleftharpoons$ | $PbSO_4 + 2H_2O$ | $E^o = 1.46$ V |
| Anode: | $SO_4^{2-} + Pb$ | $\rightleftharpoons$ | $PbSO_4 + 2e^-$ | $-E^o = 0.36$ V |
| Cell: | $PbO_2 + 4H^+ + 2SO_4^{2-} + Pb$ | $\rightleftharpoons$ | $2PbSO_4 + 2H_2O$ | $E^o_{cell} = 1.82$ V |

- Lead forms $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$, which were used as anti-knock ingredients in gasoline.
  - Their commercial synthesis involves a complicated reaction sequence that is not fully understood, but the overall reaction is
    $4NaPb + 4RCl \xrightarrow{80\text{-}100\ ^oC} R_4Pb + 3Pb + 4NaCl$
  - $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$ are nonpolar, highly toxic liquids.
  - $Pb(CH_3)_4$ decomposes at ~200 ° and $Pb(C_2H_5)_4$ decomposes at ~110 ° via a free radical mechanism.