Lecture 5

Group 4A
Carbon Family
Crystallogens

2nd year (Chem/Physics and Geology)

Carbon group elements

→ non-metal

→ metalloids

→ metals

Occurrence

Carbon occurs in nature in:

- **free state**
  as diamond, graphite and coal

- **in the combined state,**
  in many organic compounds such as hydrocarbons, carbohydrates, etc

- **in the atmosphere** as Carbon dioxide

Silicon

- It is present in sand, rocks, etc, in the form of silicates or silica
- Germanium is found in soil and plants
- Tin is present as its oxide ore, as Tin Stone, SnO_2
- Lead is present as its sulphide ore, Galena, PbS.

Electronic configuration

$_{6}C$	$1s^2\underline{2s^22p^2}$	$[He]2s^22p^2$
$_{14}Si$	$1s^22s^22p^6\underline{3s^23p^2}$	$[Ne]3s^23p^2$
$_{32}Ge$	$1s^22s^22p^63s^23p^63d^{10}\underline{4s^24p^2}$	$[Ar]\ 4s^24p^2$
$_{50}Sn$	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}\underline{5s^25p^2}$	$[Kr]\ 5s^25p^2$
$_{82}Pb$	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}\underline{6s^26p^2}$	$[Xe]6s^26p^2$

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The Group IV elements

➔ outermost shell electronic configuration of ns^2np^2

❖ Elements of this group also exhibit multiple oxidation states.

❖ ***Lower*** oxidation states become more prominent down the group…..**Why?**

❖ ***Carbon*** forms predominantly covalent bonds, but the larger members of the group form ionic bonds with increasing ionic character.

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Reactivity

- Carbon reacts with Hydrogen, Nitrogen, Oxygen, Phosphorus, and Sulfur.

- Silicon reacts with Nitrogen, Oxygen, Potassium, and Magnesium.

- Lead reacts with Oxygen, Tin, Fluorine, Bromine, Iodine, Nitrogen, Sulfur, and Phosphorus.

- Tin reacts with Copper, Iron, and Lead.

Carbon in Organic Chemistry

The large number and wide variety of ***organic*** compounds is due to the ability of C to bond to itself, and to form multiple bonds.

Catenation is the process whereby carbon bonds to itself to form stable chains, branches, and rings.

Since C is small, the C-C bond is short enough to allow effective side-to-side overlap of *p* orbitals. C readily forms double and triple bonds.

Carbon: $1s^2\ 2s^2\ 2p^2$

- Carbon forms sp, sp^2, and sp^3 hybridizations;
- In sp hybridization, each carbon forms 2 σ- and 2 π-bonds; example in H—C≡C—H
- In sp^2, each carbon forms 3 σ- and a π- bonds;
- In sp^3 hybridization each carbon forms 4 σ-bonds;

Inorganic Compounds of Carbon

Carbon bond with oxygen to form ***carbonates***. Metal carbonates such as $CaCO_3$ are abundant in minerals.

Carbon forms two common gaseous oxides, CO and CO_2, which are molecular. Other Group 4A(14) elements form network-covalent or ionic oxides.

Carbon halides have major uses as solvents and in structural plastics.

What do they have in Common?

- They all have 4 valence electrons
- Can form up to 4 bonds (More than all the other families)
- React in similar ways with oxygen and other elements

Silicon

- Larger atomic size than C which results in relatively few compounds that have Si=Si and Si=O bonds.
- Si compounds can act as **Lewis acids** where as C compounds typically cannot.
- Si compounds can expand its valence shell by using its *d*-electrons
- thereby allowing for the accommodation of lone pair electrons of an Lewis base.

Allotropy

Allotropes are different structures of the same element

Except Lead, Pb, all the other elements of group (IVA) show allotropy

The different allotropic forms of group(IV) elements are:

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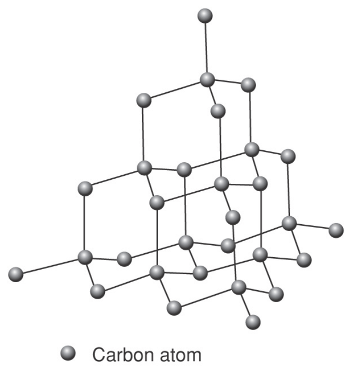
Forms of Carbon

Three common allotropes

- **Diamond**
- **Graphite**
- **Anthracite**
- **Fullerenes**
- **carbon nanotubes**

Diamond

- sp^3 Hybridized carbon (tetrahedral)
- Only C-C σ bonds
- ➔ each carbon atom is bonded to four other carbon atoms



Properties:
Rigid and hard
Transparent
Electrically insolating Solid (Inert)
Good conductor of heat

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Graphite

- sp^2 hybridized carbon in a hexagonal network
- Electrons are free to move from one carbon to another through π network formed by the overlap of unhybridized *p*-orbits on each of the carbon atoms

Uses In:
Electrical conductors in industry
Electrodes in electro-chemical cells
Lead in pencils

Properties:
Black
Lustrous
Electrically conductive
Slippery

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Structure of Graphite

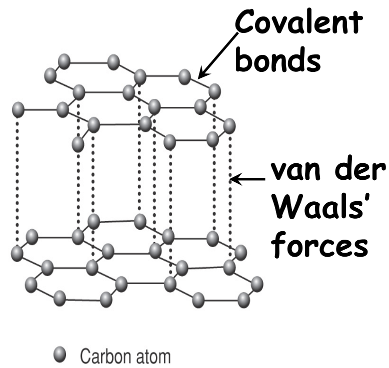
dull black

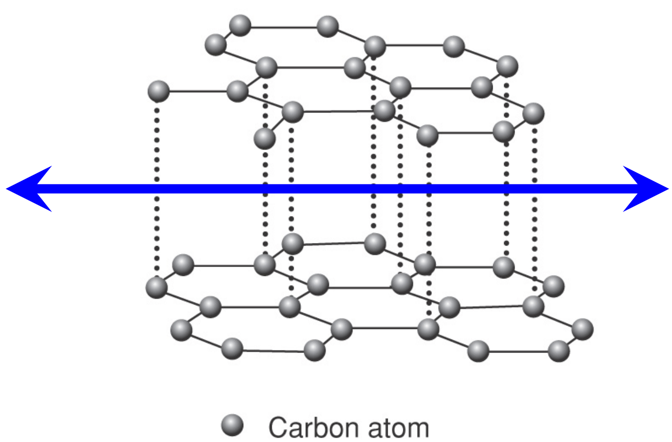
layered structure ➔

layers of covalently-bonded carbon atoms are held together by weak van der Waals' forces

➔ These layers slide over each other easily

➔brittle and soft





Electrons between layers are delocalized

⇒ conducts electricity along the layers

Activated Carbon (Activated Charcoal)

Made:

- Heating waste organic matter in the absence of air and then processing it to increase the porosity, producing a very high specific surface area.

Uses In:

- Air purifiers, gas masks, aquarium water filters, water purification plants

(remove organic compounds from drinking water)

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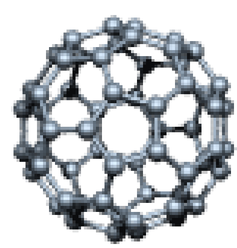
Fullerenes

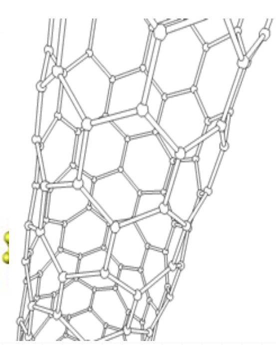
- Soccer ball shaped carbon molecules
- Different numbers of carbon atoms



C_{60}

Carbon Nanotubes

- These cylindrical carbon molecules have unusual properties.
- They are valuable for nanotechnology, electronics, optics and other fields of materials science and technology



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Silicon

$$SiO_2 + 2C_{(s)} \xrightarrow{\Delta} Si_{(s)} + 2CO_{2(g)}$$

(crude is exposed to $Cl_2(g)$)

$$SiCl_{4(l)} + 2H_2 \rightarrow Si_{(s)} + 4HCl_{(g)}$$

(purer form of elements)

Further purification is necessary before silicon can be used in the semiconductor industry

Germanium is mainly used in the semiconductor industry.

Germanium and Tin

- Tin is easily obtained from its ore (cassiterite (SnO_2)) by reduction with carbon.

$$SnO_2 + C(s) \xrightarrow{1200^oC} Sn(l) + CO_2(g)$$

- Tin is expensive and not very strong but it is resistant to corrosion. Its main use is in tin plating and used in alloys such as bronze.

Lead (Pb)

- Lead is also easily obtained from it ore (galena (PbS)) and converted to its oxide and then reduce with coke (form of carbon)

$$2PbS(s) + 3O_{2(g)} \xrightarrow{\Delta} PbO(s) + 2SO_{2(g)}$$

- Lead is durable and malleable which makes it useful in the construction industry
- In addition lead is very dense which makes it ideal as radiation shields from x-rays
- **Lead is also used as electrodes for rechargeable batteries**

Compounds of carbon

- CO – toxic gas (binds to hemoglobin); forms during combustion of carbon in limited oxygen supply; used in methanol production.
- CO_2 - end-product of combustion of carbon or carbon-containing compounds; greenhouse gas that keeps Earth temperature relatively warm;
- CO_2 is essential to life – used by plants in photosynthesis;
- Hydrocarbons
- $NaHCO_3$ – used as baking soda for cooking and as in fire-extinguishers;
- Na_2CO_3 – used in glass manufacture;
- $CaCO_3$ – used in steel production;

Oxides of Carbon

Carbon dioxide, CO_2

- Formed when organic matter burns in the a plentiful source of air and when animals exhale.
- CO_2 is always present in air but the burning of fossil fuels is increasing the amount of CO_2 in the air which is then in-turn leading to global warming
- **$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3(aq)$**
- Carbonated beverages have high partial pressures of CO_2 to drive the equilibrium to H_2CO_3 when the beverage is opened the equilibrium shifts to produce CO_2

Carbon monoxide, CO

- Formed when carbon burns in the a limited source of air

This happens in cigarettes

- CO can be produced in the laboratory by the dehydration of formic acid with hot, concentrated sulfuric acid

$$HCOOH \xrightarrow{150^oC,\ H_2SO_4} CO(s) + H_2O(l)$$

- CO is a reducing agent and is used in the production of a number of metals, most notably iron in blast furnaces

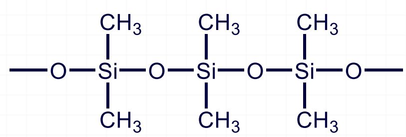
Properties:
Colorless
Odorless
Flammable
Almost Insoluble
Toxic Gas

Highlights of Silicon Chemistry

Silicon bonds to oxygen to form repeating –Si–O– units, which are found in ***silicates*** and ***silicones***.

The silicate building unit is the ***orthosilicate grouping***, $–SiO_4–$, which has a tetrahedral arrangement.
Silicate minerals are the dominant form of matter in the nonliving world. They include clay, sand, and semiprecious stones.

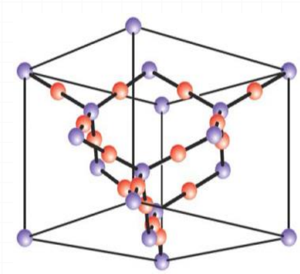
Silicone polymers are synthetic substances consisting of alternating Si and O atoms. They are used in a wide variety of applications.



Compounds of Silicon

SiO_2 (Silica)

- Occurs naturally in quartz,
- Sand is usually small fragments of quartz.
- The golden brown color is caused by iron oxide impurities
- Silica gets its strength from its covalent bonding network structure.



Red = Silicon
Purple = Oxygen

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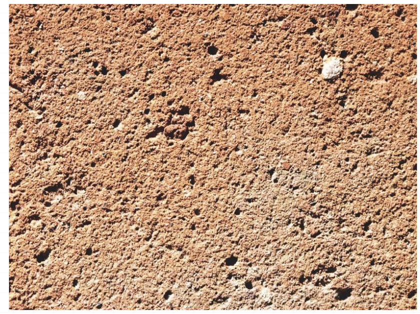
Sheet silicates

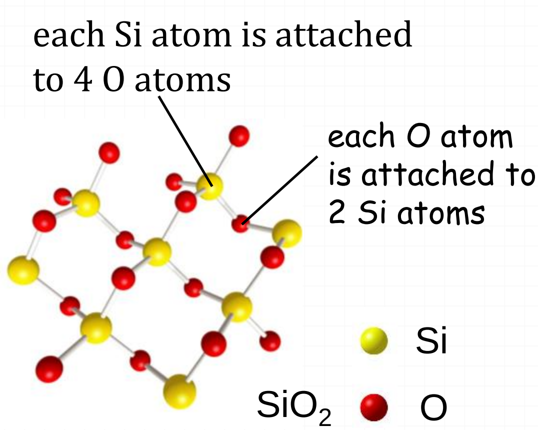
Mica



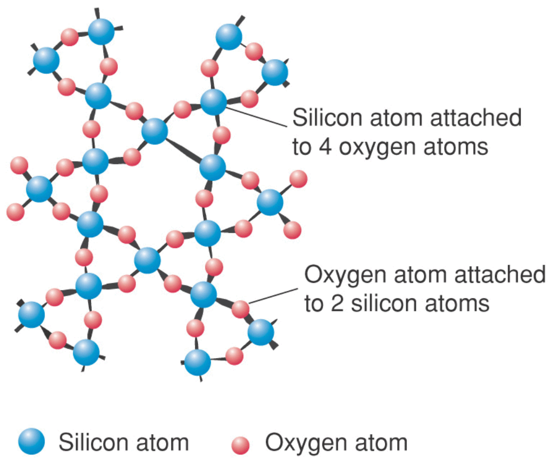
Clay

Mica is used as window glass and waveguide cover in microwave oven

Network silicates



- No plane of cleavage
- much harder than other types of silicates
- very high melting points



Structure of quartz (silicon(IV) oxide, SiO_2)

Network silicates

Feldspar

the most abundant group of minerals in the Earth's crust

- every oxygen atom is shared between SiO_4^{4-} tetrahedra
- some Si atoms are replaced by Al atoms

Formula of anions :

$[(AlO_2)_x(SiO_2)_y]^{x-}$ or $[Al_xSi_yO_{2(x+y)}]^{x-}$

when x=0 → SiO_2

Some Important Reactions of group IV Elements

Table 20.12 ▶ Selected Reactions of the Group 4A Elements

Reaction	Comment
$M + 2X_2 \longrightarrow MX_4$	X_2 = any halogen molecule; M = Ge or Sn; Pb gives PbX_2
$M + O_2 \longrightarrow MO_2$	M = Ge or Sn; high temperatures; Pb gives PbO or Pb_3O_4
$M + 2H^+ \longrightarrow M^{2+} + H_2$	M = Sn or Pb

Oxides

Two series of oxides formed by the Group IV elements

- ➔ the monoxides, MO(oxidation state of +2) (except Si)
- ➔ the dioxides (MO_2)(oxidation state of +4)

Going down the group ➔ a general increase in stability of the monoxides relative to the dioxides

The bond type and the relative stability of the monoxides and dioxides formed by the Group IV elements

Group IV element	Oxides formed	Bond type of the oxide	Relative stability
Carbon	CO	Covalent	Unstable (reducing)
	CO_2	Covalent	Stable
Silicon	(SiO)	–	Very unstable
	SiO_2	Covalent	Stable
Germanium	GeO	Predominantly ionic	Unstable in the presence of oxygen
	GeO_2	Partly ionic, partly covalent	Stable

The bond type and the relative stability of the monoxides and dioxides formed by the Group IV elements

Group IV element	Oxides formed	Bond type of the oxide	Relative stability
Tin	SnO	Predominantly ionic	Unstable (reducing)
	SnO_2	Partly ionic, partly covalent	Unstable (oxidizing)
Lead	PbO	Ionic	Stable
	PbO_2	Predominantly ionic	Unstable (oxidizing)

Oxides

CO_2
SiO_2
GeO_2
SnO_2
PbO_2

↓ Decreasing stability of dioxide

Tin (Sn)	Lead (Pb)
$[Kr]4d^{10}\,5s^2 5p^2$	$[Xe]\,4f^{14} 5d^{10}\,6s^2 6p^2$

The outermost ns^2 electrons are less shielded by the more diffused inner d and/or f electrons.

- ⇒ They are attracted more by the positive nucleus
- ⇒ Less available for forming bonds
- ⇒ Form only two bonds using np^2

Reaction with halides

- Carbon reacts with all halides to form a tetra halide - MX_4, This halide is thermally very stable.

$$M + X_2 \rightarrow MX_4$$

Two series of chlorides formed by the Group IV elements:

➔ the dichlorides (MCl_2)

➔ the tetrachlorides (MCl_4)

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Chlorides

All Group IV elements
➔ form tetrachlorides

➔ liquids at room temperature and pressure
➔ all are simple covalent molecules with a tetrahedral shape

CCl_4
$SiCl_4$
$GeCl_4$
$SnCl_4$
$PbCl_4$

Chlorides

↑ tendency to form dichlorides, MCl_2 down the group

➔ all possess covalent character though they exist as crystalline solids at room temperature and pressure

-
-
$GeCl_2$
$SnCl_2$
$PbCl_2$

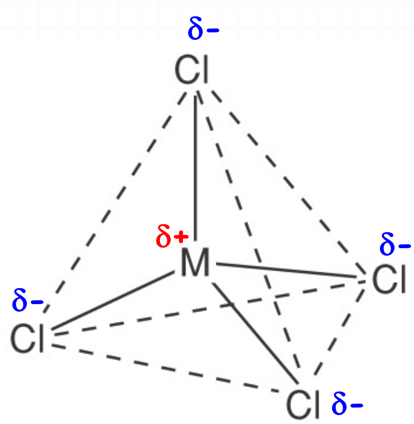
Chlorides

On moving down the group,
Metallic character of elements ↑
Ionic character of MCl_2 ↑

	-
	-
mainly covalent	$GeCl_2$
	$SnCl_2$
mainly ionic →	$PbCl_2$

Chlorides

On moving down the group,
➔ the relative stability of +4 oxidation state ↓
➔ the relative stability of +2 oxidation state ↑



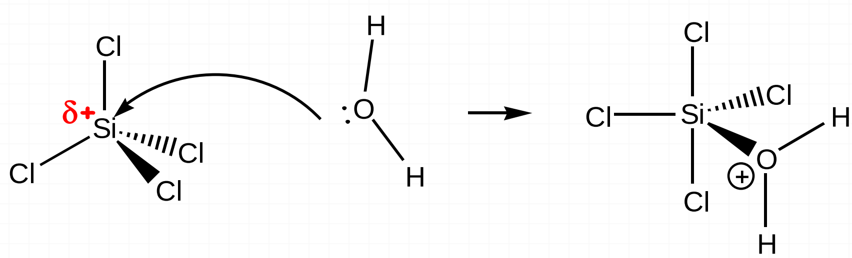
M – Cl bonds are polar with ionic character

Molecules as a whole are non-polar

Reactions with water

$CCl_4 + H_2O \rightarrow$ no reaction

$SiCl_4 + H_2O \rightarrow Si(OH)Cl_3 + HCl$



Important Compounds of Tin and Lead

- $SnCl_2$ – used as reducing agent, tin plating, catalyst;
- SnF_2 – additive in toothpaste to prevent cavity;
- PbO – used in ceramic glaze, and cement;
- PbO_2 – oxidizing agent and battery electrodes;
- $PbCrO_4$ – for making yellow pigment for paint;

Uses of groupIV elements

Carbon: Used in steel and filters.

Silicon: Used for semiconductors and it is the main ingredient for glass.

Germanium: Used as a material in semiconductors.

Tin: Used in the coating for steel cans.

Lead: Used for batteries, solder, shielding against radiation, and pluming.