

Chapter 8

“Back to Basics”

The Periodic Table and the Chemistry of the Elements

Q. How does one organize facts in the area we call inorganic chemistry?

A. Not as easy as for organic compounds. We are dealing with many more compounds and elements.

Best way is the Periodic Table.

Earlier in the course we discussed the theoretical basis for various periodic trends. Now let us turn to a chemical basis.

Part A

Types of Elements

Part B

Chemistry of the Elements in Relation to their position in the Periodic Table.

Part A

- Monoatomic Elements

He, Ne, Ar, Kr, Xe, Rn

Filled shell

- Diatomic elements

H₂, N₂, O₂, F₂, Cl₂, Br₂, I₂

ns² np⁵ elements can complete their octet by making bonds

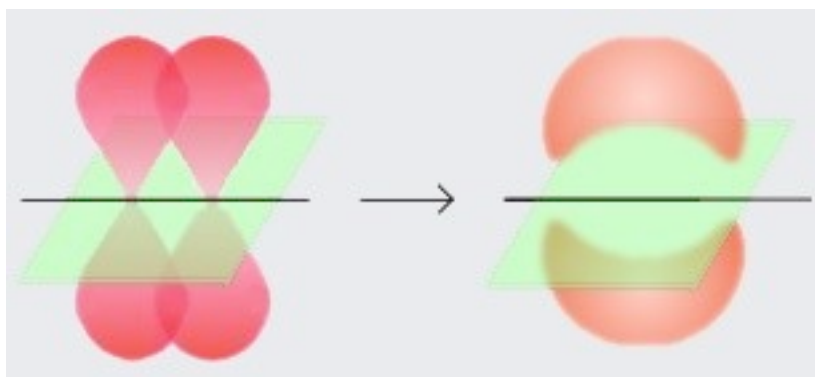
- Polyatomic Elements

P₄, S_n, Se₈, Fullerenes C₆₀, C₇₀ etc.,

After the first row elements the diatomics become unstable due to decreased pπ-pπ bonding (N≡N and O≡O for example have extensive π bonding)

The first thing to remember is the bonds between second-row elements (C, N, O) are shorter than those between third-row elements (Si, P, S), partly because third-row atoms are larger and partly because third-shell valence orbitals are larger than those in the second shell.

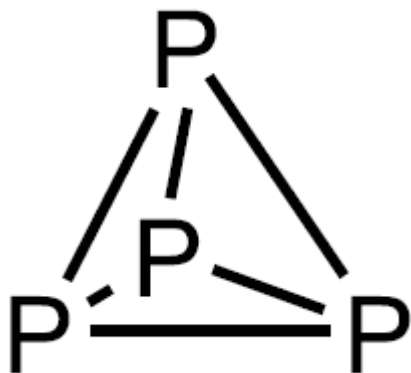
For a π - π bond to form you must have “sideways” overlap between the p - p orbitals on neighboring atoms.



2p orbitals are compact and concentrated. Furthermore, they are closer together because the bond between two second-row atoms (such as nitrogen) is intrinsically shorter, making the “sideways” overlap of their pp atomic orbitals that much better.

3p orbitals are more spread out and diffuse. Furthermore, they are further away from each other because the bond between two third-row atoms (such as phosphorus) is intrinsically longer, making the “sideways” overlap of their pp atomic orbitals that much poorer.

e.g.



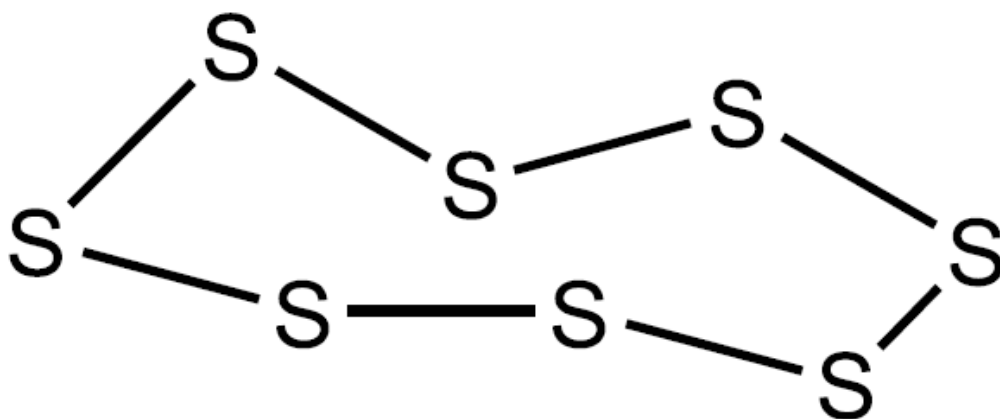
White Phosphorus is tetrahedral

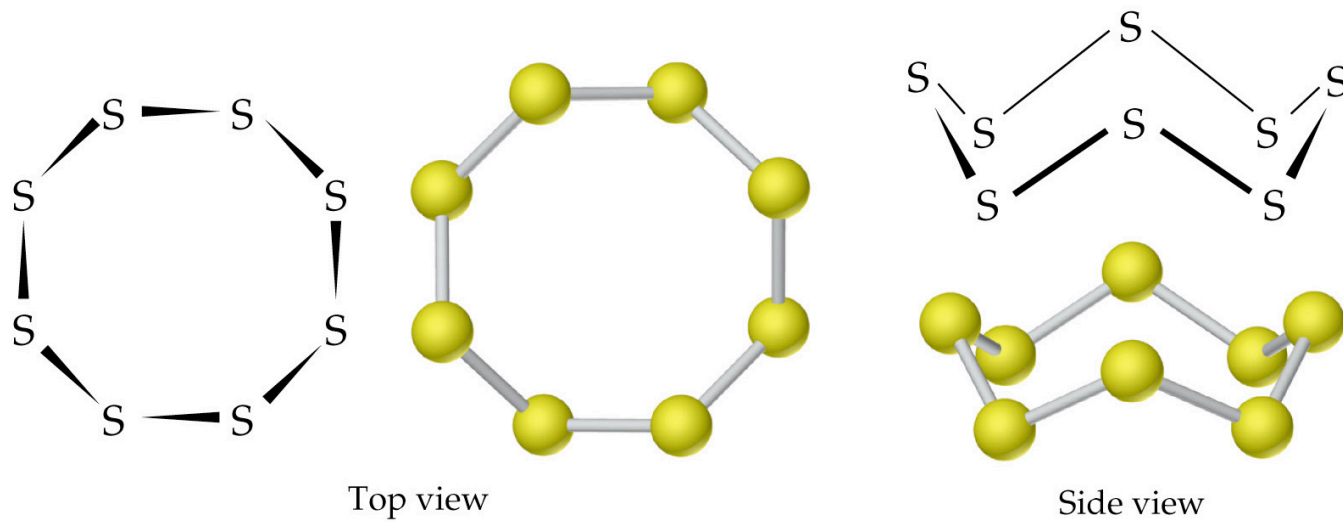
(makes six P-P bonds to be stable)

(P has three allotropes, white, black and red)

Sulfur has numerous allotropes that involve rings.

S_8 , ..., up to S_{20} .



S_8 – orthorhombic sulfur

Extended Structures for Elements

- Chains
- Two-dimensional layers
- Three – dimensional networks

Most
common
elements
that form
extended
phases

}

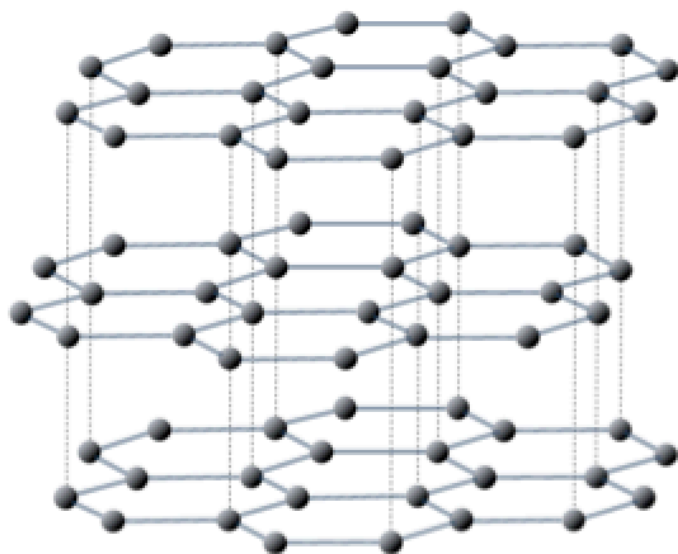
C	P	S
Si	As	Se
Ge	Sb	Te
Sn	Bi	

Carbon

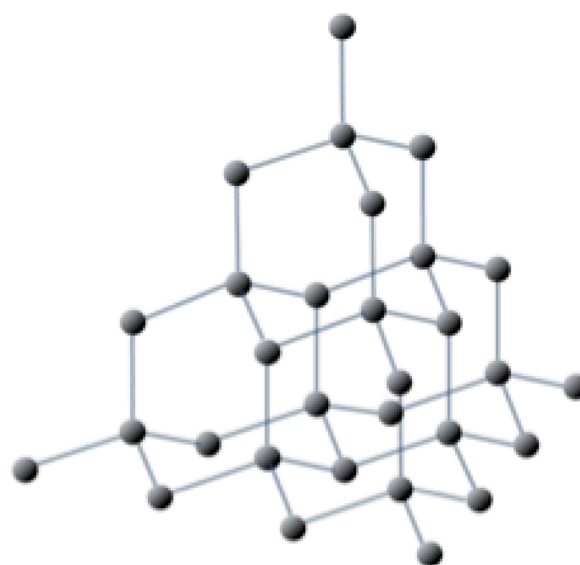
- graphite is two-dimensional
- diamond is three-dimensional
- fullerenes are molecular

Boron forms structures based on B₁₂ icosahedra

Carbon



Graphite (solid lines are strong covalent bonds, dotted lines are weak inter-layer bonds)



Diamond (all bonds are strong covalent bonds)

sp^2 hybridized carbon

Two-Dimensional Structure

delocalization within layers

Distance between the layers is 3.35 angstroms

sp^3 hybridization

Three-Dimensional Structure

The difference in the properties of diamond and graphite can be easily explained in terms their structures.

1. Diamond is very hard whereas graphite is soft:

In diamond there is a three dimensional network of strong covalent bonds. This makes diamond extremely hard. Because of hardness, diamond is used in making cutting and grinding tools.

On the other hand, in graphite there are flat layers of carbon atoms. These layers are held by weak van der Waal's forces and hence can easily slip one over the other. This makes graphite extremely soft and slippery.

Because of this soft and slippery nature graphite is used as a lubricant.

2. Density of diamond is more than that of graphite:

In graphite, there are large spaces between adjacent layers due to weak forces between them. On the other hand, in diamond, atoms are held by strong covalent bonds and relatively more closely packed. Hence, diamond has higher density than graphite. Density of diamond is 3510 kg/m^3 whereas that of graphite is 2250 kg/m^3 .

3. Diamond is poor conductor of electricity whereas graphite is a good conductor

In diamond, each carbon atom is directly linked to four other carbon atoms through covalent bonds. Thus, in diamond all the four valence electrons carbon are involved in covalent bonds and are not free to conduct electricity. This makes diamond a bad conductor of electricity.

On the other hand, in graphite, each carbon atom is directly bonded to only three other carbon atoms. Thus, each carbon atoms utilizes only three valence electrons for forming covalent bonds with other carbon atoms, the fourth valence electron is relatively free, can move from one carbon atom to the other in a layer, and hence is responsible for conducting electricity. Hence, graphite is a good conductor of electricity.

4. Melting points of graphite and diamond are very high:

In diamond as well as in graphite carbon atoms are held by strong network of covalent bonds. Therefore, both have very high melting points. The melting point of graphite is slightly higher than the melting point of diamond because in graphite C-C bonds have partial double bond character and hence are stronger and difficult to break. In fact, carbon as graphite has the highest melting point among all the elements.

5. Formation of Diamonds in Nature:

Diamonds are formed from the carbon present in the upper mantle at depths of over 92 miles under the effect of high pressure and high temperature. The temperature is $\sim 1500^{\circ}\text{C}$ and pressure ~ 70000 atmospheres. Diamonds formed in this way are brought to the surface of the earth by the igneous rock, kimberlite. However, for the diamonds to be intact when they reach the surface, the kimberlite rock must shoot up fast enough (at a speed of about 9 miles per hour) from the upper mantle towards the surface. This is because, although diamonds are quite stable at upper mantle depths and at the earth's surface, they are readily changed to graphite at intermediate depths.

6. Artificial Diamonds:

Graphite can be converted into diamonds by the action of high temperature ($\sim 20000\text{ C}$) and high pressure (100000 atmosphere) in the presence of transition metals (such as platinum). The artificial diamonds, however, are small in size and generally grey in color and hence cannot be used as gems. These are used for making cutting and grinding tools.

Uses of Diamond

Main uses of diamond are:

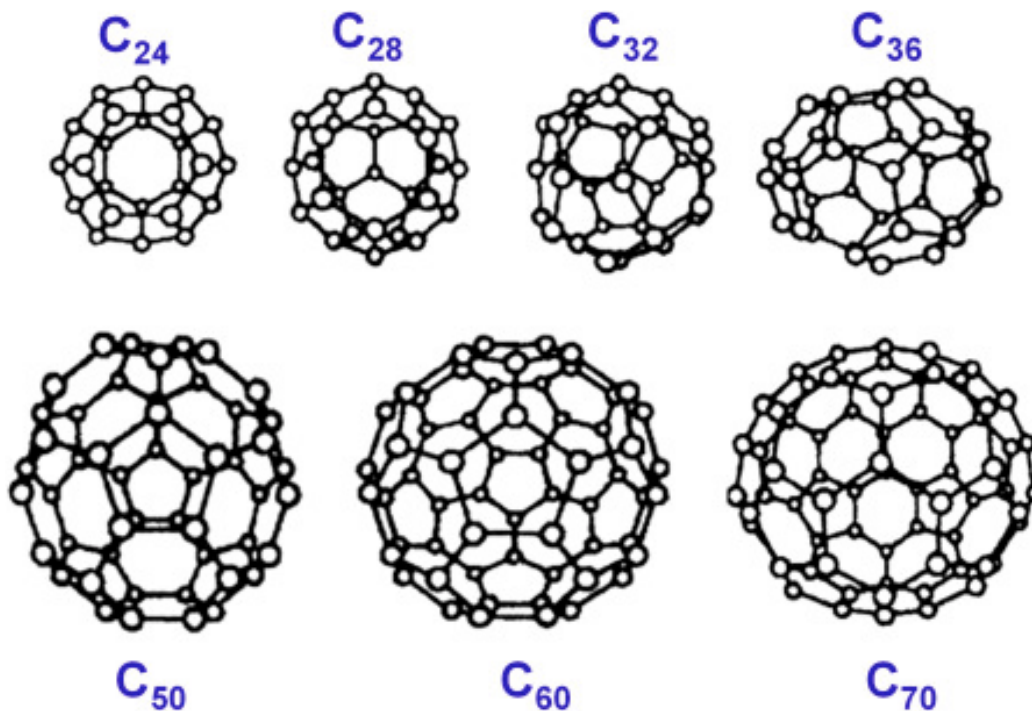
1. Diamond is the hardest naturally occurring substance. Due to this extreme hardness, it is used for making tools for cutting grinding other hard material and also in oil-well drills for drilling holes through the earth's rocky layers.
2. It is used in dies for the manufacture of tungsten filaments for electric light bulbs.
3. Diamond is transparent and has very high refractive index. Its extraordinary brilliance is why it is so valued.
4. Sharp-edged diamonds are used by eye surgeons to remove cataracts from eyes with high precision.
5. Because of its extraordinary sensitivity to heat rays, it is used in high precision thermometers.
6. It is used in protective windows for space probes as it keeps out harmful radiation.

Uses of Graphite

Main uses of graphite are:

1. as a lubricant either as a powder or as a dispersion in oil or water
2. Mixed with clay it is used in 'lead pencils'.
3. Since it is good conductor of electricity and is inert, it is used for making carbon electrodes in electrolytic cells and in dry cells.
4. Because of its high melting point, it is used for making graphite crucibles. Crucibles made of graphite are not affected by dilute acids or bases.
5. It is a component of printers' ink.
6. Graphite under the effect of high temperature and high pressure can be converted into diamonds.

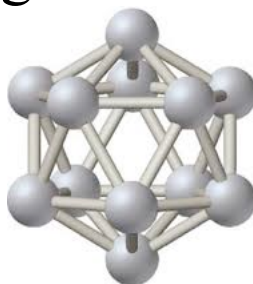
CARBON FULLERENES



“Buckminster Fullerenes” “Buckyballs”
 Named after F. Buckminster Fuller –
 Architect/Engineer of geodesic domes

Boron

Three allotropes based on the B₁₂ structural unit
 B₁₂ icosahedral building block



B₁₂ icosahedron in
 elemental boron

α – boron cubic-close-packed
 B_{12} spheres with weak links

β – boron complicated...

Tetragonal – boron B_{12} units with B-B bonds
most stable between them

Silicon and Germanium

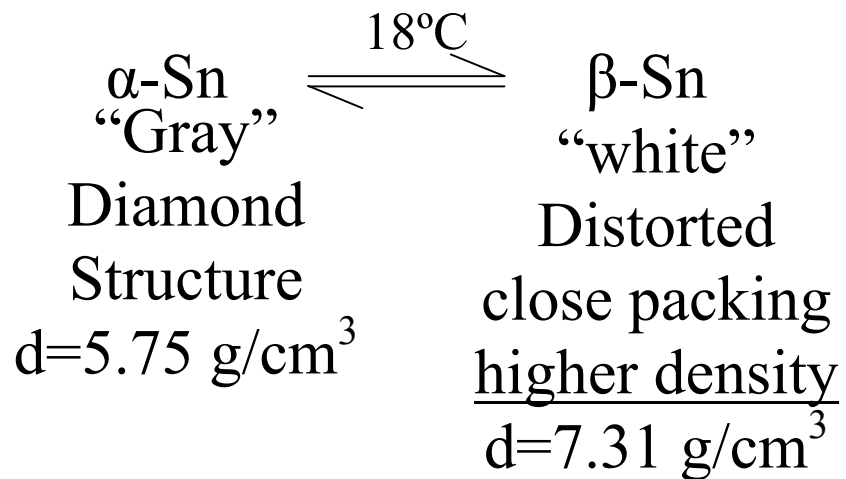
Si and Ge

diamond structure

Tin

Sn

Diamond structure but it displays an interesting equilibrium



Metals

Most of the elements in the periodic table are metals


Physical properties


- (1) High reflectivity
- (2) High electrical conductance
- (3) High thermal conductance
- (4) Mechanical Properties such as strength and ductility

Three main structural types for metals

1. Cubic Closest packed (ccp)
2. Hexagonal closet packed (hcp)
3. Body-centered cubic (bc)

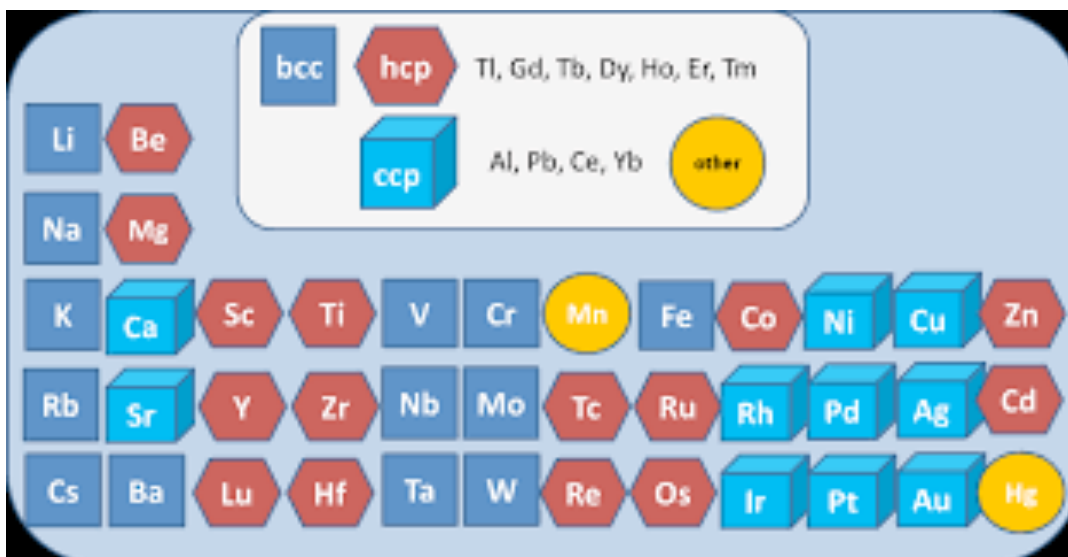
12 nearest neighbors





Distribution of ccp, hcp, bc, 8 nearest neighbors
in the periodic table:

Most deviate from the ideal structure



Bonding in Metals

- Coordination number is high, 8 or 12
 - Properties are very distinctive from other elements
- These two points hint that bonding in metals cannot be similar to that found in normal molecules:
- No ionic contribution is possible
 - Two-electron covalent bonds between all nearest neighbors is impossible

Q. What is going on?

A. To answer this, imagine bringing an array of atoms from an infinite distance apart to close interactions.
 → Atoms touch & orbitals overlap so many atoms are involved, such that the “*M.O. Diagram*” of such a growing array becomes essentially continuous.

A continuum of energy bands spreads over the entire metal \rightarrow the electrons are delocalized. The overlapping atomic orbitals form closely spaced orbitals in the metal called **bands**.

Bands can be filled or empty.

The **filled ones** are equiv. to HOMO's

(Highest Occupied Molecular Orbitals)

The **empty ones** are equiv to LUMO's

(Lowest Unoccupied Molecular Orbitals)

