

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

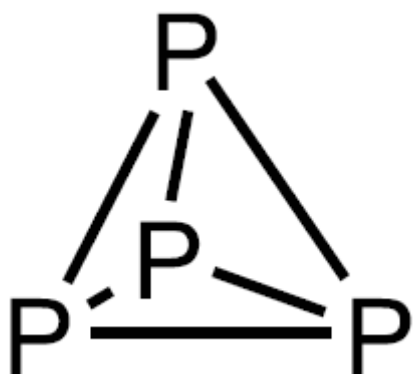
ns² np⁵ elements can complete their octet by making bonds

- 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)

e.g.



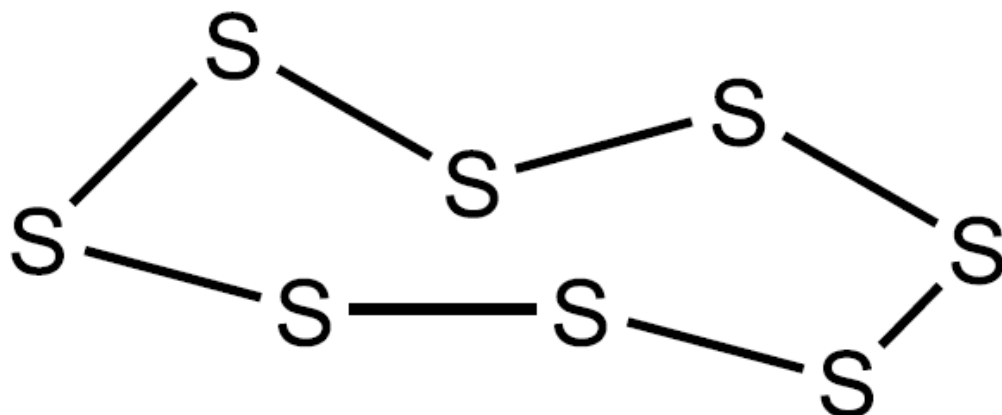
White Phosphorus is tetrahedral

(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

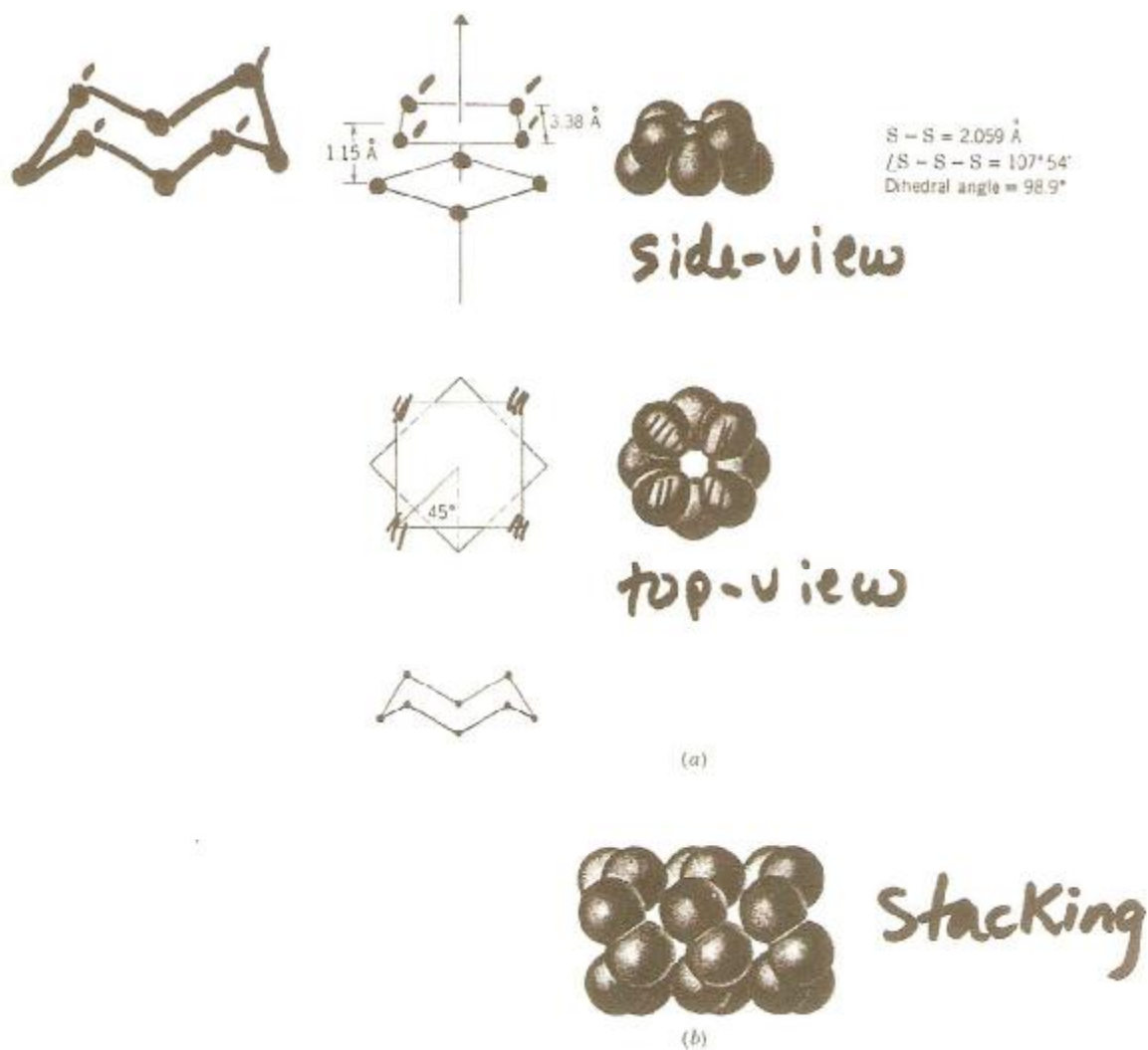


Figure 8-1 The structure of orthorhombic sulfur. (a) The cyclic S_8 molecule. (b) Stacking of S_8 molecules in the solid.

Extended Structures for Elements

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

Most
common
elements
that form
extended
phases

}

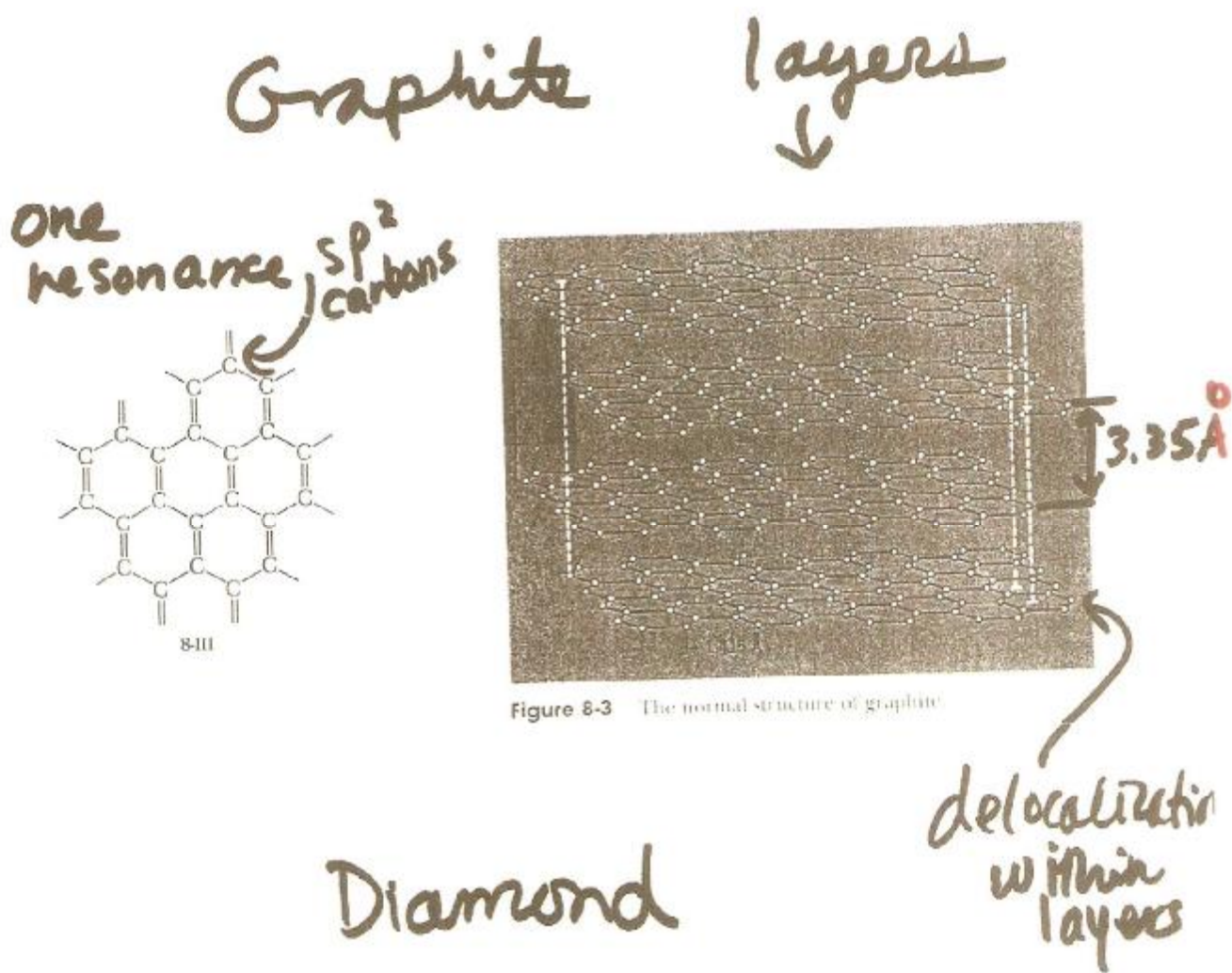
C	P	S
Si	As	Se
Ge	Sb	Te
Sn	Bi	

Carbon

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

Boron forms structures based on B₁₂ icosahedra

Carbon



Diamond

sp^3 carbons

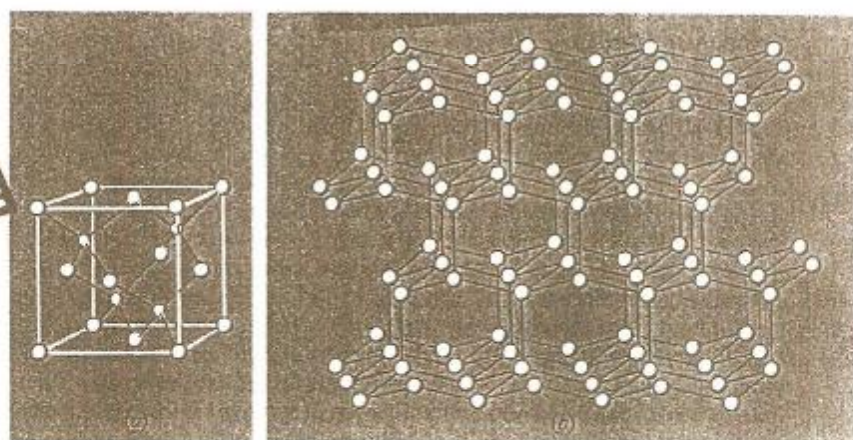


Figure 8-2 The diamond structure seen from two points of view. (a) The conventional unit cell. (b) A view showing how layers are stacked; these layers run perpendicular to the body diagonals of the cube. Remember, however, that this is not a layer structure; its properties are the same in all directions.

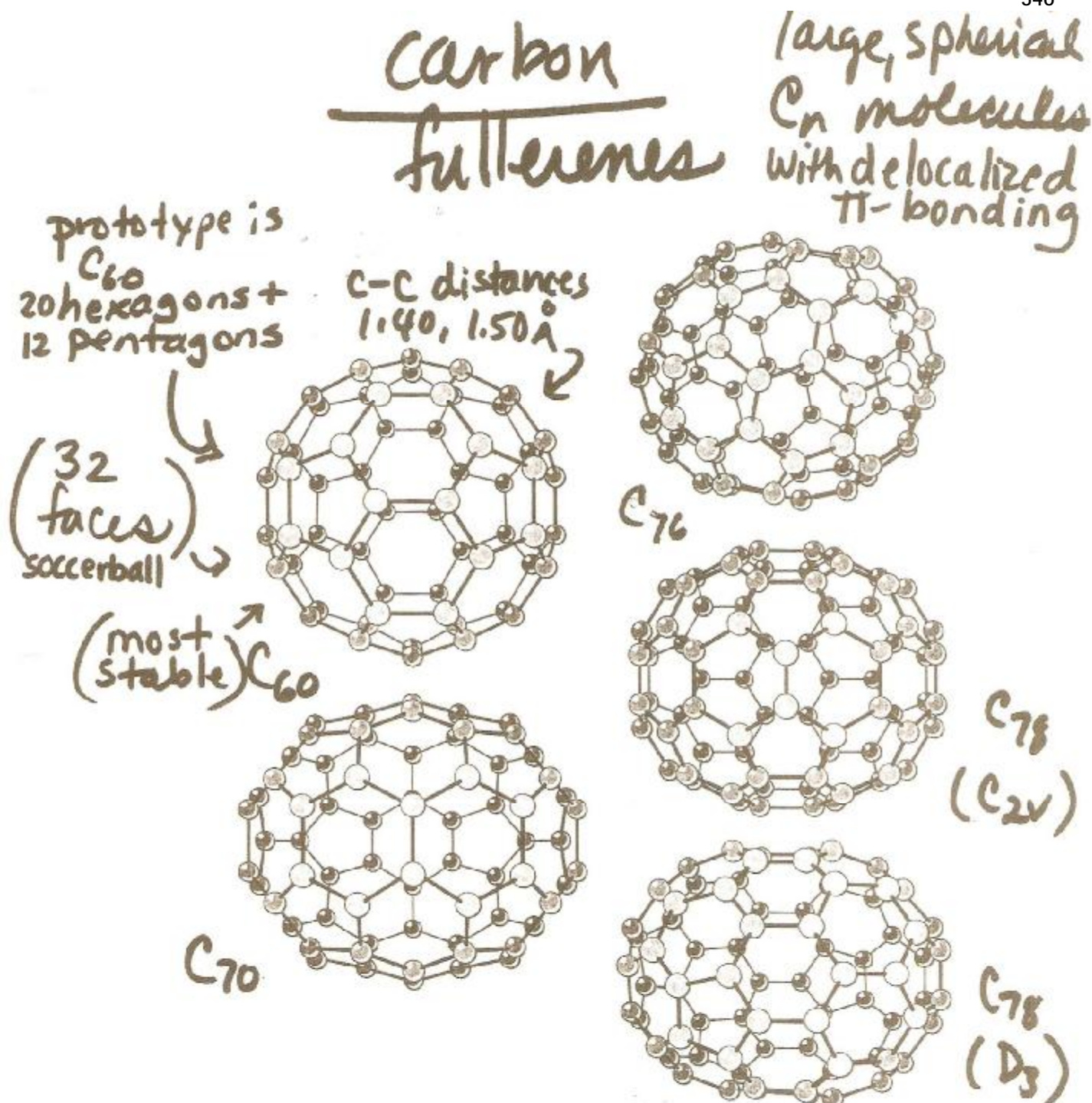


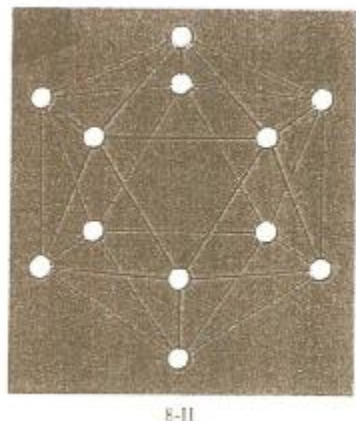
Figure 8-4. The structures of some of the smaller fullerenes, C_{60} , C_{70} , C_{76} , and two isomers of C_{78} . [Reprinted with permission from F. Diederich and R. L. Whetten, "Beyond C_{60} : The Higher Fullerenes," *Acc. Chem. Res.*, 25, 119–126 (1992). Copyright © (1992) American Chemical Society.]

“Buckminster Fullerenes” Bucky balls”

Named after F. Buckminster Fuller –
Architect/Engineer of geodesic domes

Boron

Three allotropes all of which are based on the B_{12} structural unit



B_{12} icosahedral
building block

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

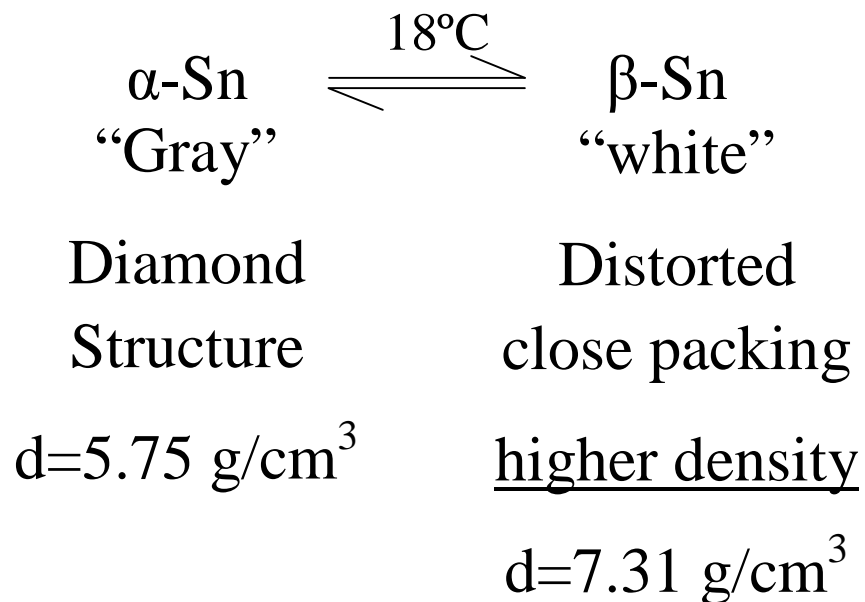
Tin

(Sn)

diamond structure

but it displays an interesting equilibrium

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

Most deviate from the ideal structure

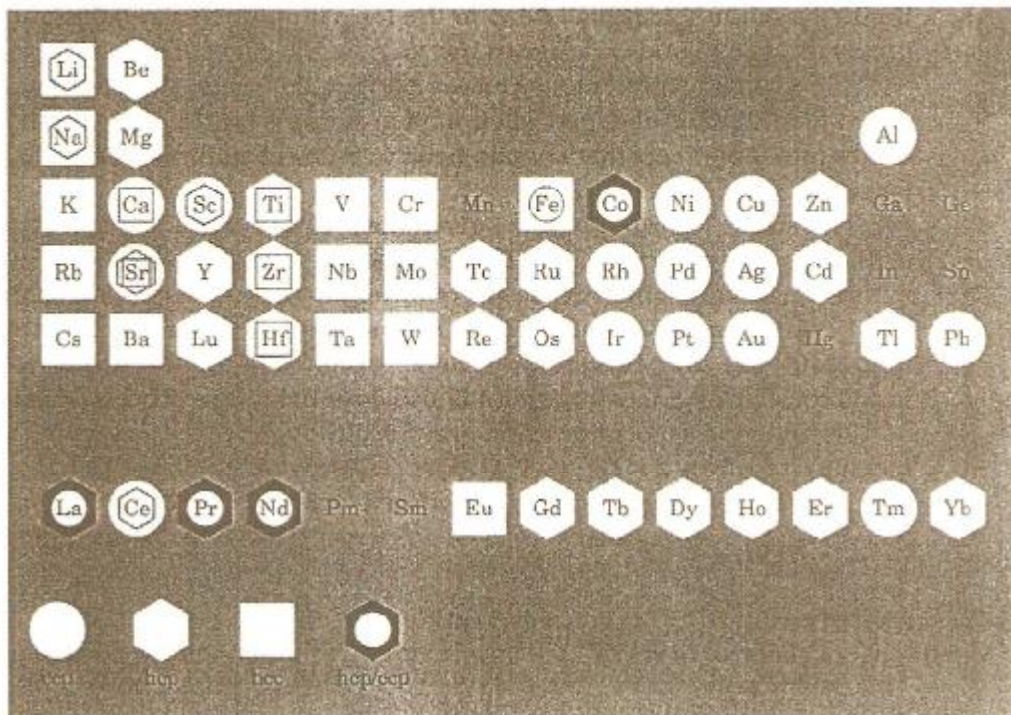


Figure 8-7 The occurrence of hexagonal close-packed (hcp), cubic close-packed (ccp), and body-centered cubic (bcc) structures among the elements. Where two or more symbols are used, the largest represents the stable form at 25 °C. The symbol labeled hcp/ccp signifies a mixed ... ABCABABCAB ... type of close packing, with overall hexagonal symmetry. [Adapted with permission from H. Krebs, *Grundzüge der Anorganischen Kristallchemie*, F. Enke Verlag, 1968.]

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.

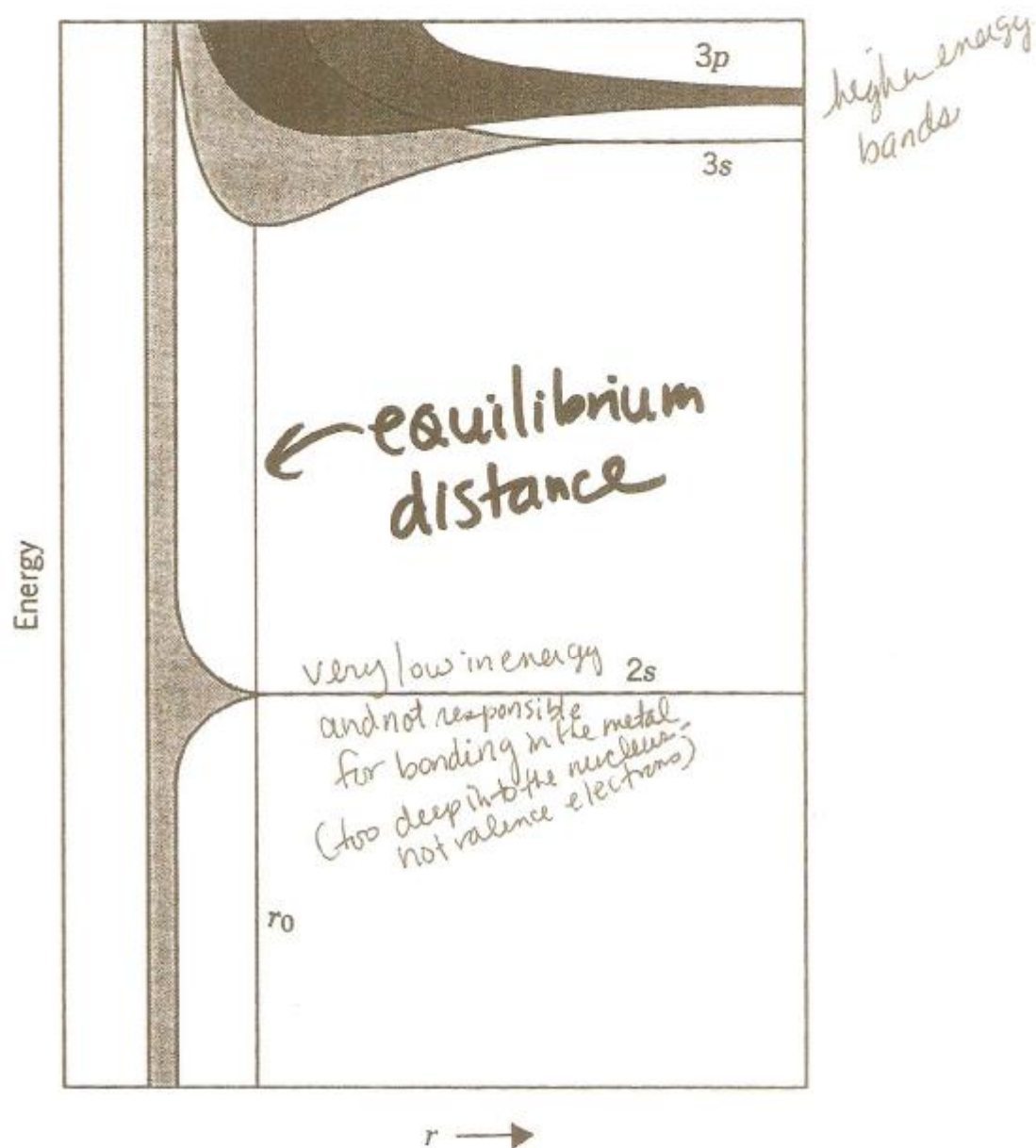


Figure 8-8 Energy bands of sodium as a function of internuclear distance. The actual equilibrium distance is represented by r_0 .

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)

