Inorganic Chemistry with Doc M.

Day 12. Ionic Thrills Part 3.

Topics:

1. Bravis fundamental lattice types
2. Silicates
3. MO of conjugated enes
4. Network covalents

5. Band theory
6. Semiconductors
7. Diodes
8. Photosensitive switches and LEDs

1. Fundamental lattice types.
Bravis determined that almost all natural crystals belong to one of 14 fundamental lattice types. Here we will study these lattices and learn their names.

(a) Cubic unit cells.
Cubic unit cells exhibit three equal dimensions along the x, y, and z-axes and three 90° angles. These are the three familiar unit cells, simple cubic, body-centered cubic and face-centered cubic.
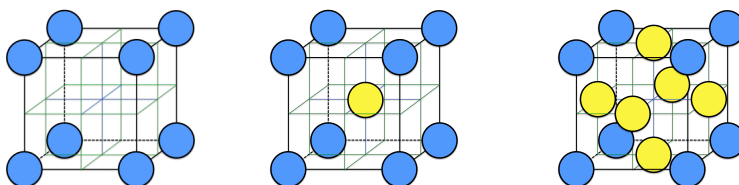

The three cell dimensions are referred to by the symbols *a*, *b*, and *c.* The angles are those measured between the a and b axes, the a and c axes and between the b and c axes. The angles are referred to by the symbols α, β, and γ. In the case of the cube, we can summarize the relationship of the three axes and three angles to each other as follows: All three, the simple cube, body-centered and face-centered cubes all feature a = b = c and $\alpha = \beta = \gamma = 90^O$

(b) Tetragonal and Orthorhombic Lattices.
Two simple variations on the cubic lattice are obtained by allowing the cell dimensions to vary from one another but continuing to require three 90° angles. In the simple cube, all three cell dimensions are identical. If we keep two cell dimensions identical and allow the third to be unique, we have produced a *tetragonal* unit cell. If all three cell dimensions are unique, we have an *orthorhombic* unit cell. There are three unit cells in which all angles are 90°:
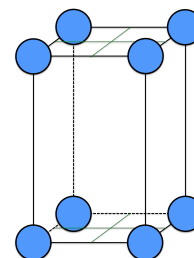
Name	Length of Cell Edge	Angles
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^O$
Tetragonal	a = b; c is unique	$\alpha = \beta = \gamma = 90^O$
Orthorhombic	all three unique	$\alpha = \beta = \gamma = 90^O$

In the Bravis system, the orthorhombic lattice can be modified to form face-centered orthorhombic and body-centered orthorhombic units cells. A fourth important variation exists for orthorhombic unit cell types. Two opposite faces of these unit cells can host a face-centered sphere, while the other four faces are clear. This variation is called the **base-centered orthorhombic** unit cell.
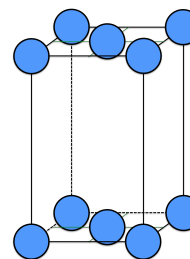
Summary of possible unit cells in which all angles are 90°:

Cubic	Tetragonal	Orthorhombic
1. Simple cubic	4. Simple tetragonal	6. Simple orthorhombic
2. Face-centered cubic	5. Body-centered tetragonal	7. Face-centered orthorhombic
3. Body-centered cubic		8. Body-centered orthorhombic
		9. Base-centered orthorhombic

(c) Monoclinic and triclinic lattices. Monoclinic and triclinic unit cells are frequently encountered in nature and chemistry. Each has three unique cell dimensions. Monoclinic unit cells have two 90° angles and one cell angle that is not 90°. Triclinic cells have all three angles unique and not equal to 90°. These parameters are summarized here.

Monoclinic and Triclinic Unit Cell Parameters.

Name	Length of Cell Edge	Angles
Monoclinic	all three unique	$\alpha = \gamma = 90^O \ \beta < 90^O$
Triclinic	all three unique	3 unique angles

Although it would be acceptable to describe monoclinic cells with the angle that is greater than 90°, by convention, most chemists assign the angle to a value less than 90°. So instead of listing the angles for a monoclinic unit cell as 90°, 90°, and 113°, for example, one would customarily list them as 90°, 90°, and 67°.

In the triclinic model, suppose that a chemist measured the three angles to be $\alpha = 102^O$; $\beta = 77^O$; and $\gamma = 94^O$. Convert these angles to standard format.

How many of the eight balls in the triclinic model, actually exhibit all three cell angles to be less than 90°?

Is it possible to have a monoclinic or triclinic unit cell with two cell dimensions exactly the same length?

In the Bravis system of 14 lattices, the monoclinic unit cell can exhibit a base-centered variation. Thus, we add three more lattices to the list:

Triclinic
  10. Simple triclinic

Monoclinic
  11. Simple monoclinic
  12. Base-centered monoclinic

(d) Hexagonal lattice (includes hcp!) Hexagonal lattice types are typical in chemistry. Many elements including beryllium, magnesium, cobalt, zinc, cadmium, carbon (graphite) and the elements of the triads of scandium and titanium all exhibit hexagonal close-packed lattices. Cell parameters include two cell angles that are 90° and one that is 60° (120°) as shown below. Hexagonal cell dimensions feature two equal lengths (a = b). Label the cell dimensions and angles in the figure.
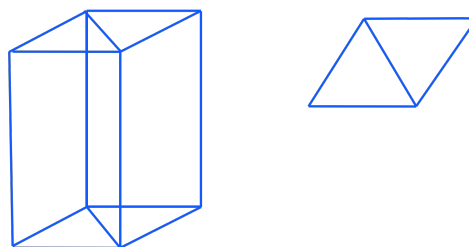
(e) Rhombohedral (trigonal) lattices. The rhombohedral unit cell is similar to the simple cubic unit cell in that all three cell dimensions are equal and that all three cell angles are equal. What distinguishes the rhombohedral from the simple cube is that the common angle cannot equal 90°. The rhombohedral lattice is often called the trigonal lattice.

The entire set of Bravis cell types is summarized here.

Summary of Fundamental Unit Cell Types.

Name	Length of Cell Edge	Angles
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^O$
Tetragonal	a = b; c is unique	$\alpha = \beta = \gamma = 90^O$
Orthorhombic	all three unique	$\alpha = \beta = \gamma = 90^O$
Monoclinic	all three unique	$\alpha = \gamma = 90^O; \beta < 90^O$
Triclinic	all three unique	3 unique angles; all < 90°
Hexagonal	a = b; c is unique	$\alpha = \beta = 90^O; \gamma = 60^O$ (120°)
Rhombohedral (trigonal)	a = b = c	$\alpha = \beta = \gamma < 90^O$

2. Silicates.

Silicates are tetrahedral anions in which the silicon atom is bound to four oxygen atoms. Silicates represent a major component of the earth's crust (26% by mass); over 90% of the rocks, minerals, and soils are classified as silicates. Feldspar, which makes up 60% of the crust is a silicate or silicon-oxygen anion. Quartz, mica, talc, basalt, garnet, topaz, zircon, kaolin (clay used to make glossy paper), zeolites and dozens of other less well-known minerals are also all silicates. Silicates can be categorized by structure. Some orthosilicate minerals include:

phenakite, Be_2SiO_4	willemite (Zn_2SiO_4)	olivine, (Mg, Fe)$_2SiO_4$
pyrope, $Mg_3Al_2(SiO_4)_3$	almandine (garnet) ($Fe_3Al_2(SiO_4)_3$)	grossular, $Ca_3Al_2(SiO_4)_3$
uvarovite (garnet) ($Ca_3Cr_2(SiO_4)_3$)	andradite, $Ca_3Fe_2(SiO_4)_3$	zircon ($ZrSiO_4$)

The simplest silicate is the orthosilicate anion, SiO_4^{4-} shown here:

tetrahedral silicate

top view
(down O-Si bond)

representation
of SiO_4^{4-}
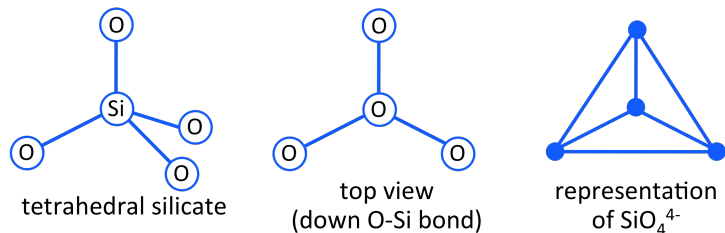
The ball and stick model does not show the fourth oxygen, which occurs directly above or below the silicon, which is centered in a tetrahedron. The line diagram at left gives a shorthand method for representing silicates. The four oxygen atoms that define the tetrahedron are shown. The silicon is located in the center of this tetrahedron and is not shown. You should associate this shape with SiO_4^{4-}.

Silicates can become more complex by condensing and sharing an oxygen atom at a corner. This is shown in the figure at left. Here two SiO_4^{4-} units have condensed by sharing an oxide. This amounts to adding two SiO_4^{4-} units and subtracting an O^{2-} unit to give the disilicate anion, $Si_2O_7^{6-}$. Bookkeeping is done by assigning oxidation states of +4 to silicon and -2 to oxygen.
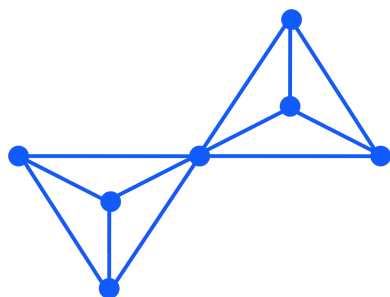
Dental crowns are made from milled lithium disilicate (the whiter molars)

Polysilicates involving infinite chains of condensed tetrahedra are quite common. A portion of such a polymeric anionic silicate is shown at right. In order to determine the empirical formula for this polysilicate, we first isolate a "repeating unit" and then use the same bookkeeping as before. One repeating unit has been identified with red the dashed lines in the figure. As a possible strategy, avoid cutting through atoms while identifying a repeating unit – see the green dashed lines. The box isolates three oxygen atoms (remember that the center is a Si and an O) and one silicon atom. Each empirical formula unit carries a -2 charge.
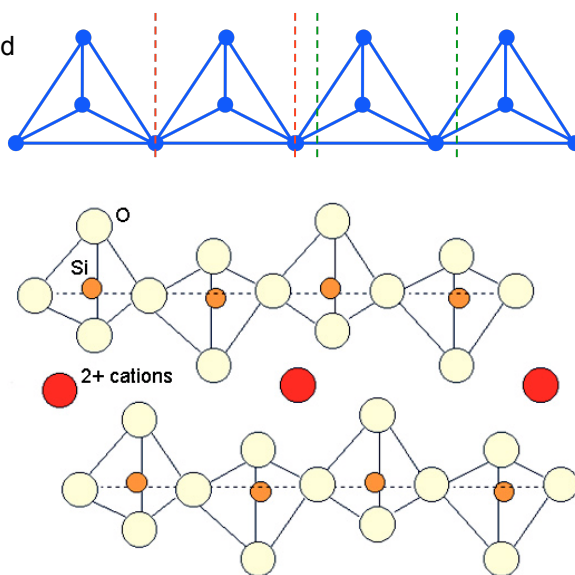
What is the empirical formula for the silicate anion shown above?

Another common silicate anion is the six-silicon ring, $Si_6O_{18}^{-12}$, shown here, along with an example, the gemstone beryl. Green forms of beryl are called emerald.
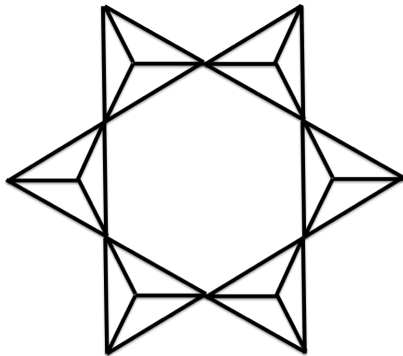
Beryl, $(Be_3Al_2(Si_6O_{18}))$

Polysilicates such as these are called chain structure polysilicates. They combined with Ca^{+2}, Mg^{+2}, Fe^{+2} and other cations found in nature. When the cations are Ca^{+2}, Mg^{+2}, Fe^{+2} the material is called pyroxenes, a common constituent of basalt. What is the empirical formula of a silicate with two Ca^{+2} for every one of each Mg^{+2} and Fe^{+2}?

Basalt forming hexangonal shaped columns along the shore of Lake Superior at Grand Marais, MN

Chain silicates can further condense to form double chain structures such as that shown at right. Keep in mind that only a small segment of a linear polymeric chain is shown here — and the cations are not shown. This complicated structure is the result of condensing a pyroxene anion chain with its mirror image.
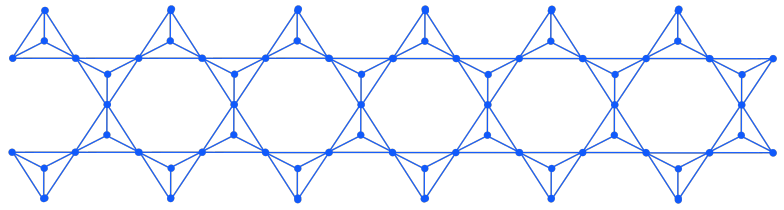
What is the empirical formula (Hint: $Si_4O_?^{-?}$) and charge for this silicate?

The double chain polysilicate shown above is called an amphibole. These can form fibrous materials providing that the polymeric chains crystallize in a parallel fashion. A familiar example of a fibrous amphibole is asbestos in which case the cations are magnesium and calcium.

Asbestos (left) and pyroxene (right) both feature double chain silicate anions.

Polysilicates can also form 2 dimensional sheets of condensed tetrahedra. A portion of such a sheet is shown at right. What is its empirical formula for this silicate anion?
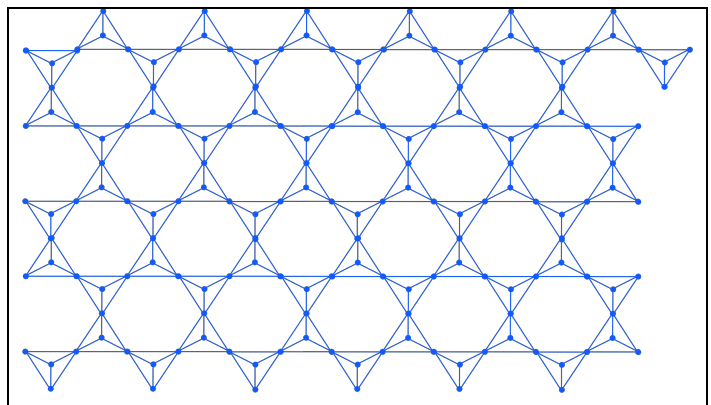
As you might imagine, there is considerable bond strength in the 2-dimensional sheet of silicate tetrahedral, typical of network covalent materials. Cations hold these sheets together. In some cases, the cations are all located between alternate sheets — they do not occur between every sheet; alternate sheets are held together only by dispersion forces. For this reason, sheets are easily cleaved from one another. The extremely soft mineral talc (talcum powder) is an example of this sheet-type polysilicate.

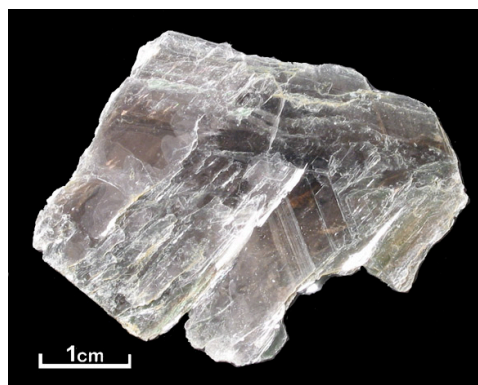*Mica (H^+, K^+, Al^{+3}, Li^+, Mg^{+2}, and Fe^{+2})($Si_4O_{10}^{-4}$)*

Talc has the empirical formula $Mg_3(OH)_2Si_4O_{10}$. Micas also utilize the sheet polysilicate structure, however in the case of micas, the cations exist between all sheets. There is a wide variety of minerals that belong to the mica group. The list of mica cations include H^+, K^+, Al^{+3}, Li^+, Mg^{+2}, and Fe^{+2}.

There is one final degree of polysilicate condensation that is possible. This joins the 2-dimensional sheets into a three dimensional structure with formula SiO_2. The mineral quartz has this structure. In quartz, the silicon atoms have a tetrahedral geometry as usual. Each oxygen joins two silicon atoms.

Like all examples of network covalent molecules, SiO_2 has an extremely high melting point. The various forms of SiO_2 have different melting points, however all are in the range of 1600 - 1700 $^\circ$C. The melting point of quartz, one of the more common forms of SiO_2 is 1610 $^\circ$C. SiO_2 in all forms is insoluble in water.

Semiconductors

A. Conjugated ene systems.

1. The p-orbitals for ethene or any ene look something like the picture shown below. The σ-interactions are not shown. The left one is [Circle: bonding/antibonding] and the right one is [Circle: bonding/antibonding.] Count the nodes *between* the two atoms in each MO. Sketch an energy diagram to the right of the figure.
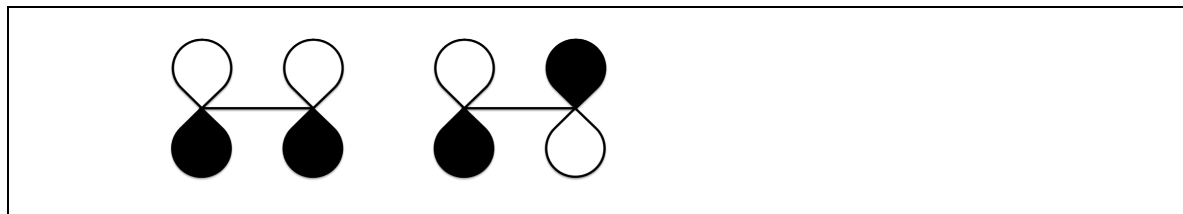
2. The π-manifold molecular orbitals for the allyl radical, $C_3H_7\cdot$, (or $C_3H_7^-$ or $C_3H_7^+$, for that matter) looks something like the picture shown below. The σ-interactions are still not shown. Recall that three AOs yield three MOs and that the top one (highest energy) is as antibonding as possible with two nodes between atoms. The lowest energy MO is as bonding as possible with no nodes between atoms. That suggests that the middle MO must have one node between atoms.

   (a) Sketch an energy diagram for these MOs and label each one as π, π(n) (non-bonding) and π*.
   (b) Make a 3 x 3 table with the columns labeled AO#1, AO#2 and AO#3 and the rows labeled MO#1(π), MO#2(p(π)) and MO#3(π*). Complete the table showing how each AO is distributed to the MOs in order to achieve the situation where each column and row add to 1.
   (c) Why must the columns and rows add to 1?
   (d) Populate the MO diagram with the three p-bonding electrons available for the allyl radical.
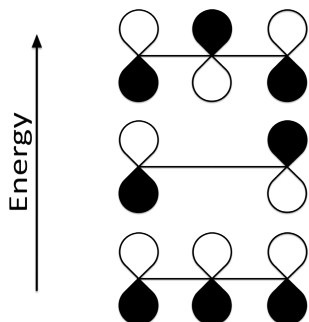
(e) As a reactive species, the allyl radical will abstract atoms from other molecules. Why do the abstracted atoms always end up on a terminal carbon and never on C2?

3. Extend the discussion for allyl radical to butadiene. (a) Sketch the MOs and the energy diagram. (b) count the nodes present in each MO. (c) Populate the diagram for butadiene (4 π-manifold electrons).

B. Extended conjugated ene systems.

1. The pattern that is emerging for the energy level diagrams of conjugated ene systems continues as expected. (a) Starting on the left, sketch the two lines you drew for the energy levels for the π-manifold of ethene. Next, add in the energy levels for the π-manifold of allyl, then butadiene and so on. Extend the energy level pattern that you see emerging to a conjugated system with a very large number of contributing conjugated orbitals (e.g. Avogadro's number). (b) Indicate which orbitals are populated and which are empty.

Energy

C_2 C_3 C_4 C_5 C_6 C_7 C_8 $C_{infinity}$

C. Network covalents.

1. What is a network covalent solid? Be able to describe this if necessary (check your gen chem book).

2. Classify each of the following substances as network covalent, molecular covalent, ionic, metallic or semi-metal.

(a) diamond	(b) tin	(c) calcium carbide
(d) silicon carbide	(e) silicon	(f) silicon tetrachloride
(g) sodium silicide	(h) graphite	(g) copper

3. The conjugated ene systems we started out with were used as an one-dimensional example of what could happen in either two or three dimensions for network covalents. (a) Sketch a small segment of the network covalent substance graphite using a slightly side-on view so that the p-orbitals involved in π-bonding show. (b) Does graphite exhibit a 2-dimensional or 3-dimensional p-manifold?
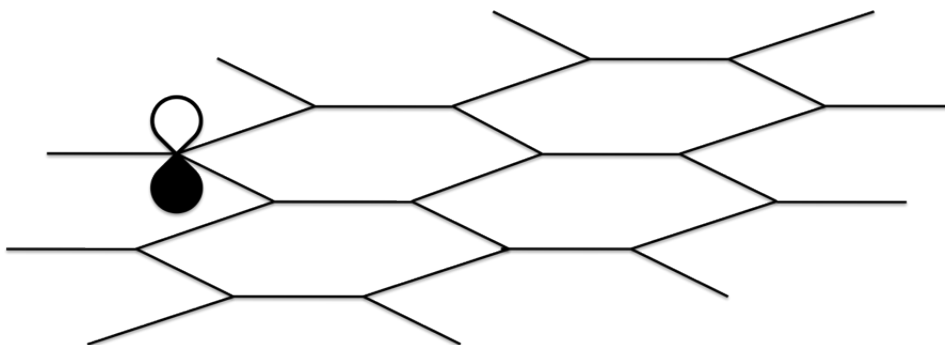
4. Do the valence d- orbitals on metals such as copper overlap in 2-dimensions or three dimensions? Sketch the d_{yz}-orbitals around the copper atoms assuming that the plane of the paper is the yz-plane. The sketch should show how the d-orbitals can overlap with each other in two dimensions. Of course, there are other d-orbitals such as the d_{xz} and d_{xy} that connect copper atoms in the third dimension. This should show you that metals overlap their valence d-orbitals in 3-dimensions.

Cu	Cu	Cu	Cu
Cu	Cu	Cu	Cu

D. Band theory.

1. The block of filled orbitals in the energy diagram you drew above (in "B") is called the **valence band** and can be represented as shown in the lower half of the leftmost figure below. The "code" is to draw the energy level as a blue line if it has electrons occupying it and as a light tan line if the orbital is empty. This is extended to the three blue and white MO diagrams. The filled MOs are represented by blue and the empty MOs as them empty boxes. The empty portion of each MO diagram is called the **conduction band**. The space between them (if there is one) is called the **band gap**.
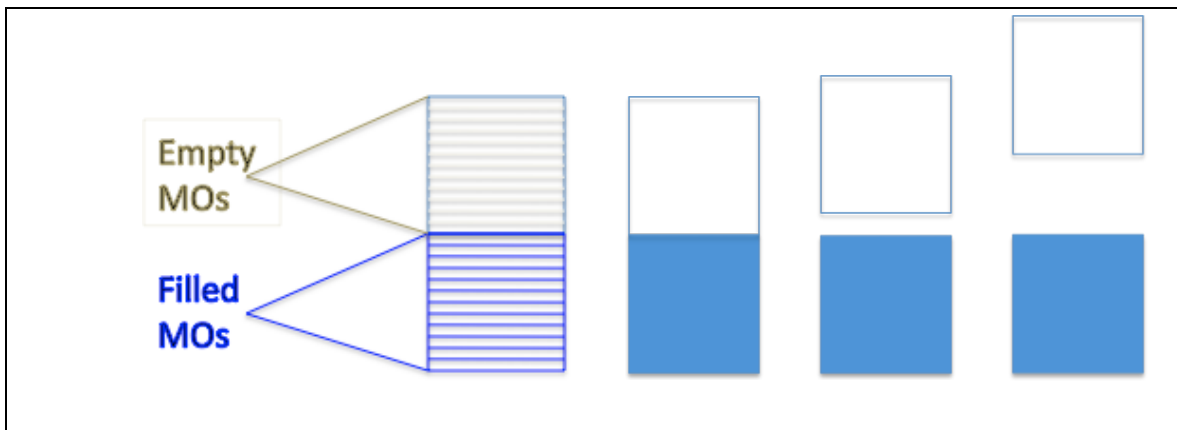
2. When the band gap is small or non-existent as is the case with conjugated enes, the electrons in the bonding orbitals can move to the empty orbitals and can travel through those unpopulated orbitals (jumping up and down as necessary to avoid nodes!). Materials that exhibit this scenario with little or no band gap are called **conductors**. When the gap is large, the substance is a **non-conductor** (insulator) and when the gap is small, it is a **semi-conductor**. Label the three scenarios above.

3. Transition metals use the s and d orbitals as their valence orbitals for MO formation. Thus, there are six orbitals from each atom used to form the MO diagram. Metals are all conductors because they (usually) have only partially filled d-orbitals as shown in the four MO diagrams below. With early transition metals, the lower half is less filled (left figure) and with later transition metals, they are more filled (right figure). The band gap may be small but usually non-existent. These MO diagrams are 25%, 50%, 75% and 100% filled. (a) What element from the first row transition metals does each represent? (b) Add the estimated bond order for each metal to its neighbors (use the familiar formula).
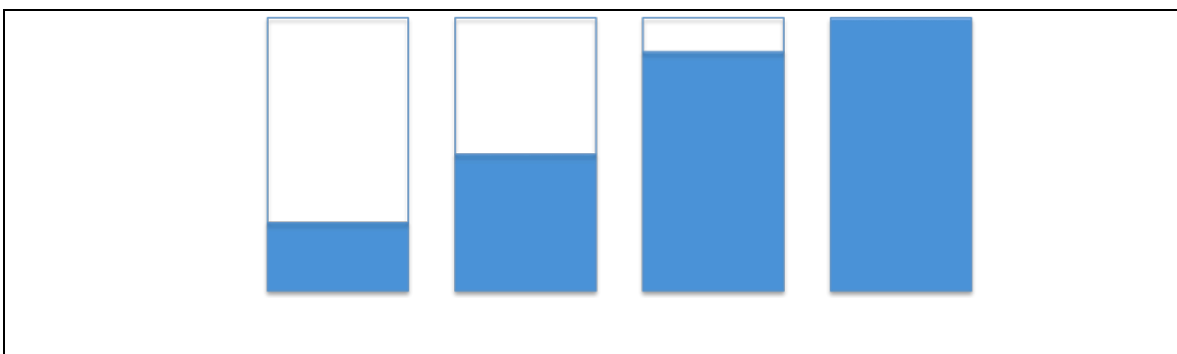
Bond order is a measure of how well each metal is bonded to its neighbors. Bond order should affect melting point. Look up the melting point of each metal. Is there a correlation?

Which element would you predict to be the strongest?

The last element in your previous answer should have been zinc. Note that cadmium and mercury are also in this triad and that mercury does indeed have a very low bond order and melting point. However zinc, cadmium and mercury must have some bond order and do indeed conduct electricity. The explanation is that the p-orbitals enter into the fray for MO construction. Modify the MO diagram above for zinc so that the three p-orbitals are included along with the s and d orbitals.

3. Back to semi-conductors, those species with small band gaps. Silicon, for example has a band gap of 1.1 eV or 106 kJ/mol. The figure at left is a semiconductor at 0 K and the figure at right is the same substance at room temperature. Again, the picture is stylized but what is indicated is that at room temperature there is enough energy (kT) to populate a few excited states with electrons from the valence band. These are not necessarily from the highest of the occupied block; it is possible that one low energy electron becomes excited to the conduction band instead of two higher energy electrons. (a) Would silicon be a conductor, semi-conductor or non-conductor at 0 K? (b) Sketch a Boltzmann distribution that shows how the population of electrons with suitable energy to be in the conduction band increases as the temperature increases. Sketch a vertical line on this diagram that represents the band gap and accounts for the electrons in anti-bonding MOs. Label it "band gap."
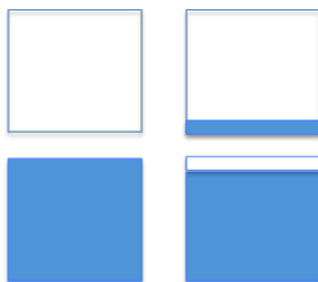
(a)	(b)

E. Semi-conductors.

1. Silicon can be prepared with trace levels of other
elements such as aluminum, gallium, phosphorus or
arsenic. This is called **doping**. The levels of non-silicon
atoms are so low that when the silicon crystallizes from
the liquid state, the added atoms behave as though they
are also silicon atoms (like a duck being raised in a
family of geese.) If aluminum is used the result is a
system that has a partially filled valence band because
aluminum has only three valence electrons, one less
than silicon's four as shown here.
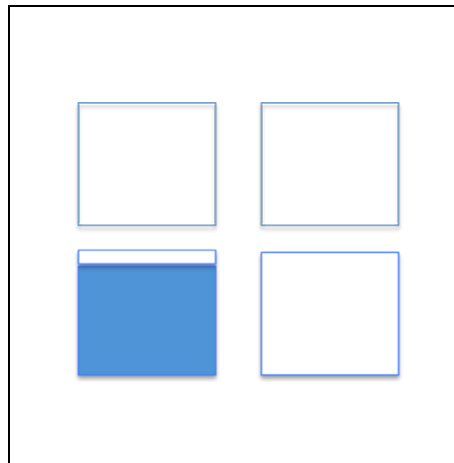
(a) Sketch (using the template given above, right) what results when P or As is used instead.
Both phosphorus and arsenic have five valence electrons.

(b) Both of the sketches above are semi-conductors. The one doped with Al or Ga is called a **p-type semiconductor** because it amount to silicon with fewer electrons that pure silicon (the "p" stands for "positive" — a misnomer as the substance is neutral — it just looks like silicon with electrons missing. The one you sketched is an **n-type semiconductor**.

F. Diodes: p-n junctions.

1. When p- and n-type semiconductors are joined
as shown at right, the result can be represented
schematically as shown below. In this scheme,
the MO energy diagram for the p- and n-type
semiconductors are joined with the diagonal
lines. This p-n junction is called a **diode** and is
extensively used to convert alternating current to direct current.
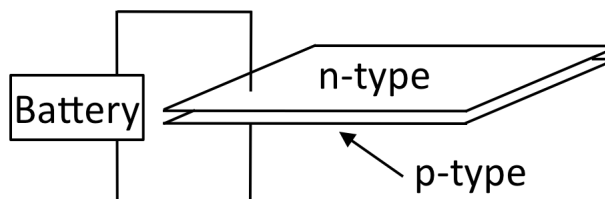
2. Label the p-type half and the n-type half. The
crooked lines join the two conduction and valence
bands. Because the p- and n-type are joined,
electrons can flow freely in the conduction band.
Some electrons from the higher energy orbitals on
the n-type (the conduction band) will drop into the
lower energy valence band of the p-type where
there are empty orbitals available at low energy.
This creates a charge on both halves.
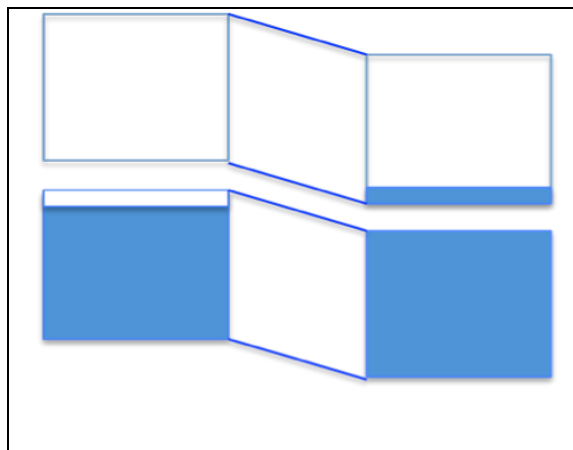
(a) The p-type semiconductor, originally neutral, is now slightly [**Circle either: positive or negative**] and the n-type, also originally neutral is now slightly [**positive or negative**]. (b) Show on this diagram what has been just described (using δ^+ and δ^-). This charge is limited and balanced by counteracting electrostatic forces, which prevent the charges from building up too much. An equilibrium is established that balances these two opposing forces.

3. At this point, the slightly skewed energy levels can be explained. The energies of the orbitals on any atom change when the atom becomes a cation. We have discussed this before: The energies of orbitals on cations are [**Circle: higher or lower**] than on their neutral or negative counterparts.

4. When a voltage is applied as shown at the bottom of the figure (+ on the p-side and – on the n-side), the *equilibrium* will shift and electrons will again shift (**Circle: left or right**) in the conduction band from (p-/n-) type to (p-/n-) type — LeChatelier would have said, "Hmmm, yes, of course I would have predicted that, hmmm, umm…, interesting." (a) Sketch this electron flow described when the voltage is applied.
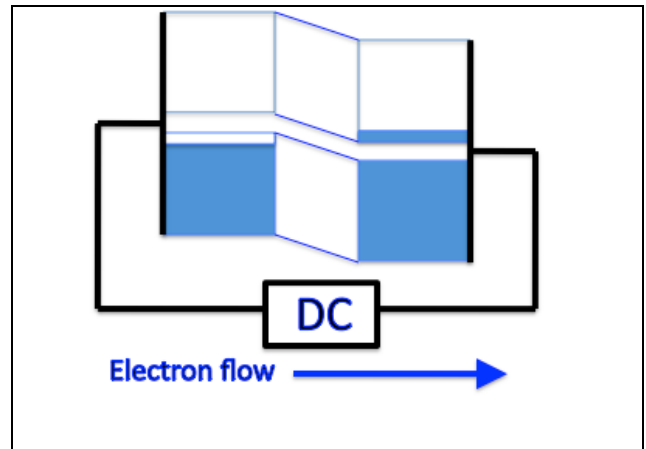
(b) Sketch electron flow through the diode MOs when it is part of an external circuit shown above. When the applied voltage is hooked up this way, it is called a ***forward bias***.

5. Here the applied voltage is the other way around — a ***reverse bias*** arrangement. (a) Try to repeat the electron flow sequence described above and describe the problems encountered.

When the applied voltage occurs as shown, does current flow?
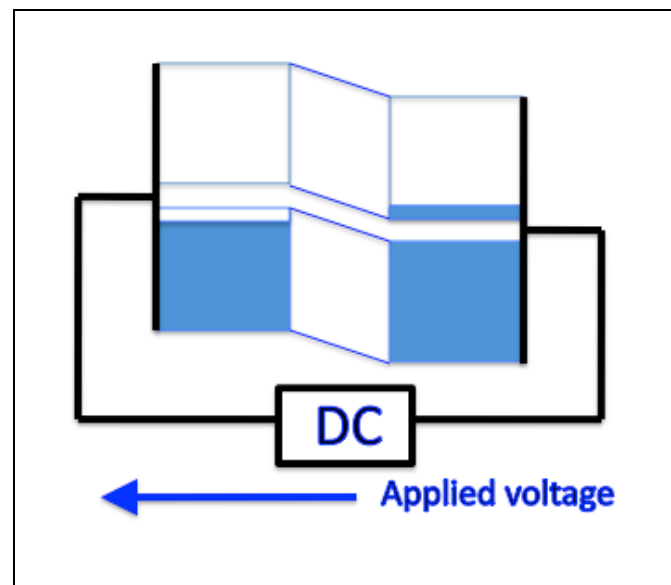
What we have just worked through is called a ***diode*** — a device that allows current to readily flow in one direction but offers high resistance to electron flow in the opposite direction.

G. Photosensitive switches.

1. Here we start with a reverse bias. (a) Label the p-type and n-type and the potentials (+ and -) for reverse bias. In photosensitive switches, the junction is designed so that when light falls on the switch, some electrons can move from the valence band to the conduction band. The band gap must have a small enough ΔE so that visible light (or infrared/uv — whatever is desired to flip the switch) has enough energy to exceed ΔE. (a) Sketch electrons moving from valence to conduction bands due to absorbing light. Then (b) complete the sequence to show how electrons can flow as long as light is applied. (c) Indicate ΔE on the figure and use an arrow and the word "photon" to indicate the role of the photons.
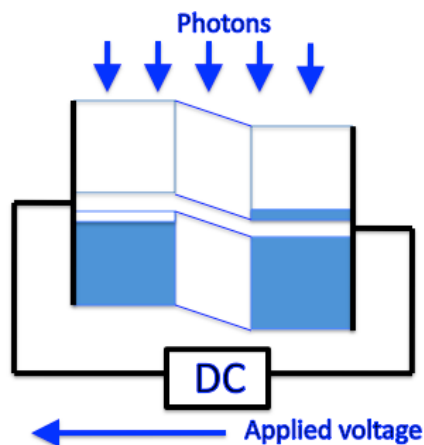
H. Photovoltaic cells (photocells).

1. Here we start with no applied voltage. (a) Label the p-type and n-type and the initial charges each half carries at equilibrium. In photovoltaic cells, when light falls on the cell, some electrons can move from the valence band of the p-type half to the conduction band of the n-type half. (b) Sketch this a two step process. An external wire connected to each of the two halves (represented by the heavy lines) can carry the electrons back through the circuit. This effectively turns light energy into a voltage (c) Complete the sequence to show how electrons and photons flow as long as light is applied.
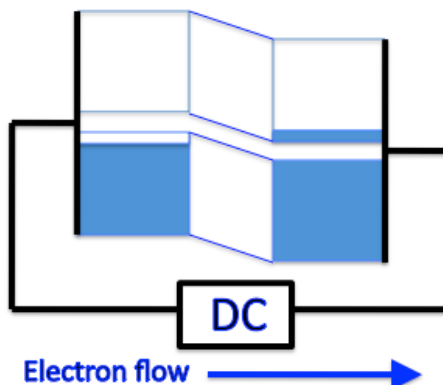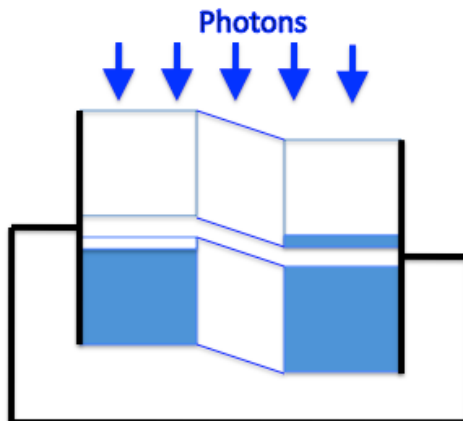
I. Light-emitting diodes.

LEDs work like photocells, except backwards: they emit light and consume electrical energy. Indicate ΔE on the figure and use an arrow and the word "photon" to indicate the role of the photons.

Diodes are constructed by depositing very thin films of p-type and n-type semiconductors in layers onto a substrate using chemical vapor deposition. The size of each LED diode can vary depending on the intended use. Large LEDs are used for brake lights (each circular light in the multi-light pattern of about 10 lights in a brake light cluster is a LED), while flat screen TVs use hundreds of thousands of them.

Related to diodes are transistors; they use p-n-p and n-p-n junctions. Millions of transistors can be gathered together on a silicon wafer making the familiar silicon chips used in computer processors.

Review for ACS Final Exam: Lattices and Semiconductors

1. Which of the following is an example of lattice energy?

(a) $M^{+n}(g) + n\ X^-(g) \longrightarrow MX_n(g)$

(b) $M^{+n}(g) + n\ X^-(g) \longrightarrow MX_n(s)$

(c) $MX_n(s) \longrightarrow M^{+n}(g) + n\ X^-(g)$

(d) $MX_n(g) \longrightarrow M^{+n}(g) + n\ X^-(g)$

(e) $M(s) + n/2\ X_2(g) \longrightarrow MX_n(s)$

2. Which of the following would exhibit the largest lattice energy?

(a) $CaCl_2$

(b) CaO

(c) KCl

(d) K_2O

(e) $BaCl_2$

3. A p-type semiconductor might consist of a lattice of silicon with a trace of

(a) gallium.

(b) Na^+.

(c) phosphorus

(d) potassium metal

(e) copper, silver or gold

4. Which of these materials is matched with its correct ability to conduct electron flow?

(a) phosphorus, conductor

(b) silicon, semiconductor

(c) germanium, conductor

(d) bismuth, insulator

(e) gallium, insulator

Answers: B, B, A, B

Answers for Day 11:

3. The hexagonal close packed lattice (hcp) (a) Each hcp unit cell contains 2 octahedral holes; (b) 1 B atom; (c) 1 A atom (these are on the corners); (d) The ratio of 1 A atom : 1 B atom : to 2 octahedral holes (e) area = $2 \times 3^{0.5} \times r^2$; (f) $4 \times 2^{0.5} \times r/3^{0.5}$; (g) $8 \times 2^{0.5} \times r^3$.

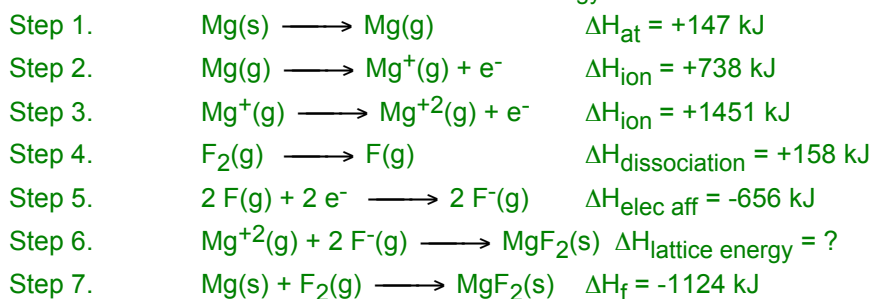Tetrahedral holes and the hcp. (a) four; (b) 1:1:2; (c) density = 1.74 g/ cm^3,

4. The cubic close packed lattice (b) No; (c) the density calculated for either close-packed lattice, hcp or ccp, would be the same

5. Radius ratio. (a) $e = 4r/2^{0.5}$; (b) the diameter of the octahedral hole is dia$_{oct\ hole}$ = $(2 \times 2^{0.5} - 2)r$, so the radius of the octahedral hole is $r_{oct\ hole}$ = $(2^{0.5} - 1)r$; (c) $(2^{0.5} - 1)r/r = 0.414$; (d) the zinc ions occupy tetrahedral holes in zinc blende. The radius of zinc(II) is 74 pm and sulfide is 170 pm, giving a radius ratio = 0.43; (e) if the small ions are a bit too big, they help to separate the large ions from each other; (f) Li$^+$, Be^{+2}, B^{+3}, etc.; (g) the radius of a tetrahedral hole is 0.225 r; (h) CsCl; (i) The radius ratio for NaCl is 116 pm/167 pm = 0.695;

6. Cubeoctahedron. (a) The coordination number for the filled in ion in the drawing is 12; (b) The coordination number for tetrahedral holes is 4 and for octahedral holes is 6, and for cubic holes is 8.

7. Occupying octahedral and tetrahedral holes. (a) half; (b) Perovskite is CaTiO$_3$; (c) NbO; (d) ReO$_3$;
   (e) 3/8; (f) (i) all of the octahedral holes are occupied (ii) $e = 2r_{cation} + 2r_{anion}$.

8. Lattice energy and the Born-Haber cycle. (a) $\Delta H_{lattice\ energy}$ = -2962 kJ

Step 1.	Mg(s) $\longrightarrow$ Mg(g)	ΔH_{at} = +147 kJ	
Step 2.	Mg(g) $\longrightarrow$ Mg$^+$(g) + e$^-$	ΔH_{ion} = +738 kJ	
Step 3.	Mg$^+$(g) $\longrightarrow$ Mg^{+2}(g) + e$^-$	ΔH_{ion} = +1451 kJ	
Step 4.	F$_2$(g) $\longrightarrow$ F(g)	$\Delta H_{dissociation}$ = +158 kJ	
Step 5.	2 F(g) + 2 e$^-$ $\longrightarrow$ 2 F$^-$(g)	$\Delta H_{elec\ aff}$ = -656 kJ	
Step 6.	Mg^{+2}(g) + 2 F$^-$(g) $\longrightarrow$ MgF$_2$(s)	$\Delta H_{lattice\ energy}$ = ?	
Step 7.	Mg(s) + F$_2$(g) $\longrightarrow$ MgF$_2$(s)	ΔH_f = -1124 kJ	

(b) $\Delta H_{lattice\ energy}$ = -787 kJ

4. Lattice energies in general. (b) Lattice energies are smallest for +1 and -1 salts. They tend to fall in the range 700 – 1000 kJ. Salts of +2 cations with -2 anions fall in the range 2000 – 4000 kJ/mol. 1:2 and 2:1 salts are intermediate; (c) solubility is greatest for salts with small lattice energies; (d) Phosphates are generally insoluble except for those of Group 1 and ammonium cations; (e) Generally, +1/-1 salts are (soluble), and +2/-2 salts are (insoluble). Sulfates are an exceptions to the generalization, as is AgCl; Among just the +1 and -1 salts, the lattice energy of LiF is the largest due to hard acid-hard base considerations.