Inorganic Chemistry with Doc M.

Fall Semester, 2009

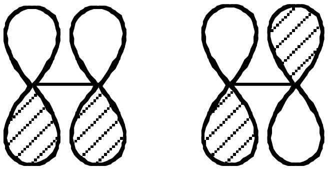
Day 14. Band Theory

Element team name:

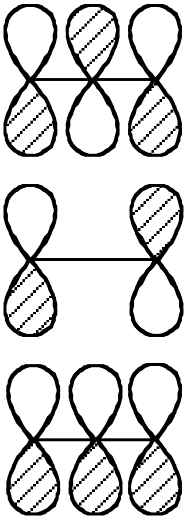
☐ My isotope partner and I worked together.
☐ I worked alone on this assignment.
Your Name(s):

A. Conjugated ene systems.

1. The π-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 upper 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(π(n)) 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 π-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.

E
n
e
r
g
y

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

C. Network covalents.

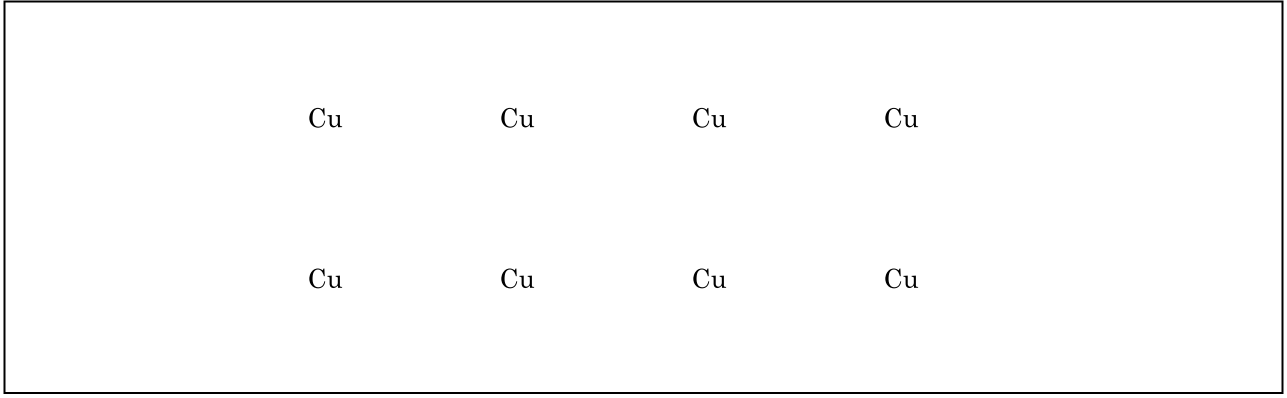
1. What is a network covalent solid? Be able to describe this if necessary (check your gen chem book).

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

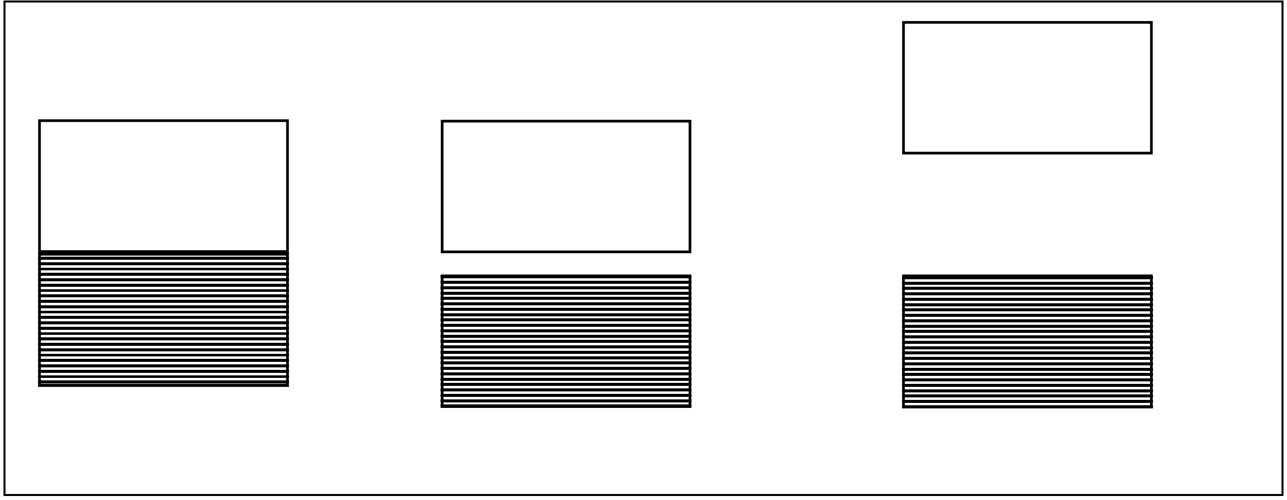
3. The conjugated ene systems we started out with were used as an one-dimensional example of what could happen in either two or three dimensions for network covalents. (a) Sketch a small segment of the network covalent substance graphite using a slightly side-on view so that the p-orbitals involved in π-bonding show. (b) Does graphite exhibit a 2-dimensional or 3-dimensional π-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.



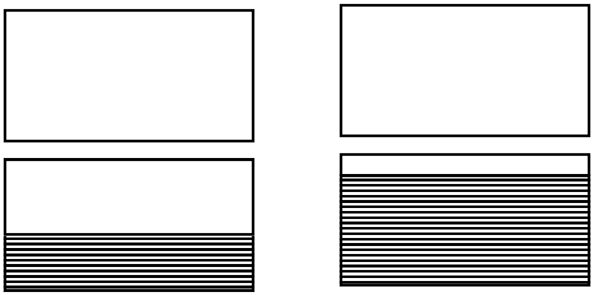
D. Band theory.

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 each figure below. The "code" is to draw the energy level as a line if it has electrons occupying it and to not draw the energy level line if the orbital is empty. The empty half is called the ***conduction band***. The space between them (if there is one) is called the ***band gap***.

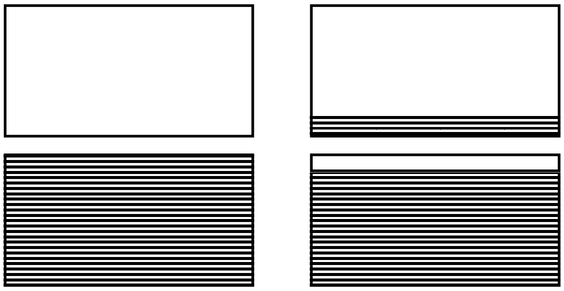


2. When the band gap is small or non-existent as is the case with conjugated enes, the electrons in the bonding orbitals can move to the empty orbitals and can travel through those unpopulated orbitals (jumping up and down as necessary to avoid nodes!). Materials that exhibit this scenario with little 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. Metals are all conductors but have only partially filled d-orbitals as shown below where the lower half is only partially filled. 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 frequently non-existent. What orbitals on copper form these overlapping molecular orbitals for copper?

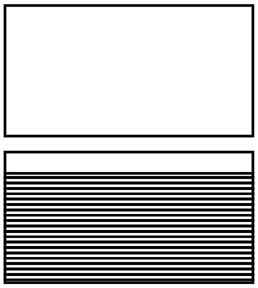


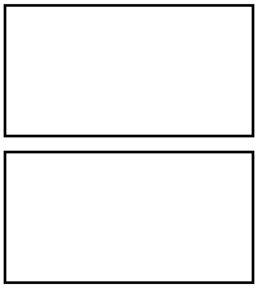
3. Back to semi-conductors, those species with small band gaps. Silicon, for example has a band gap of 1.1 eV or 106 kJ/mol. The figure at left is a semiconductor at 0 K and the figure at right is the same substance at room temperature. Again, the picture is stylized but what is indicated is that at 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.

	(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. This is represented as shown in the left figure:



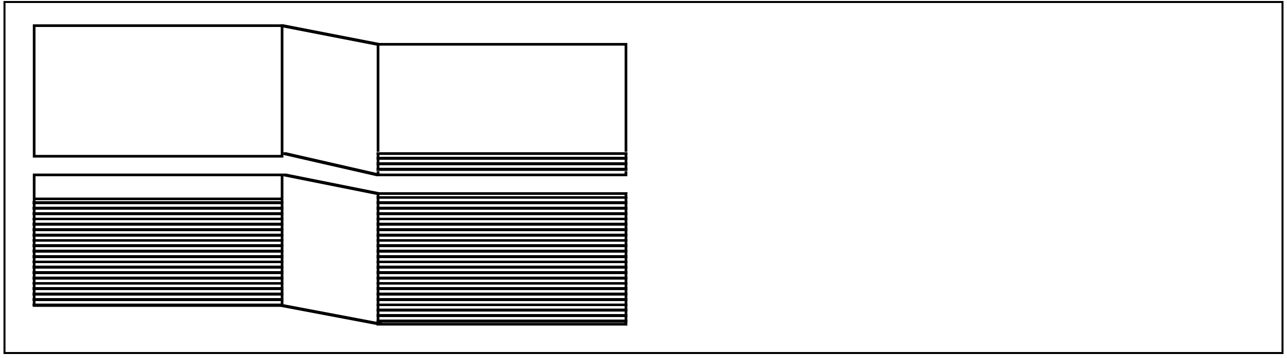


(a) Sketch (using the template given above, right) what results when P or As is used instead. Both P and As have five valence electrons.

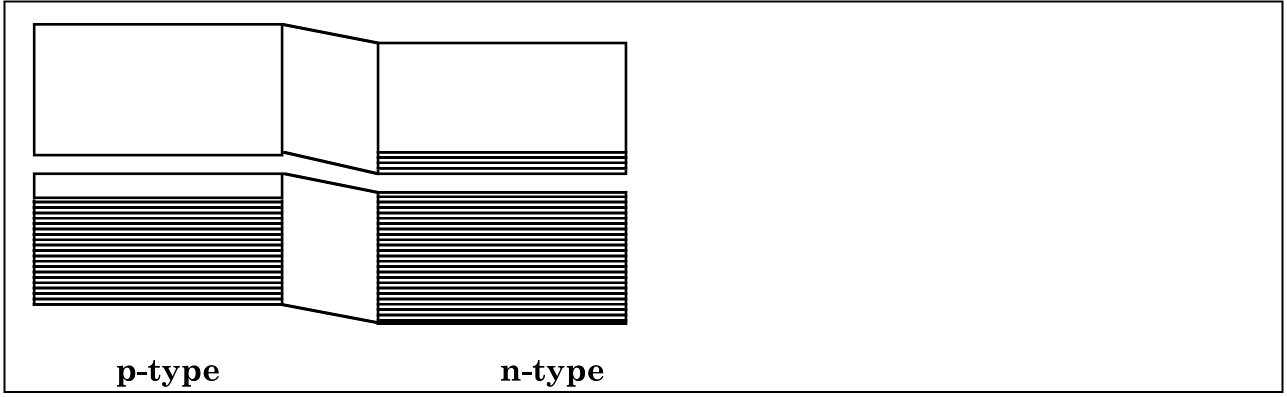
(b) Both of the sketches above are semi-conductors. The one doped with Al or Ga is called a ***p-type semiconductor*** because it amount to silicon with fewer electrons that pure silicon (the "p" stands for "positive" — a misnomer as the substance is neutral — it just looks like silicon with electrons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

F. Diodes: p-n junctions.

1. When p- and n-type semiconductors are joined, the result can be represented as shown below. Label the p-type half and the n-type half. The crooked lines join the two conduction and valence bands.

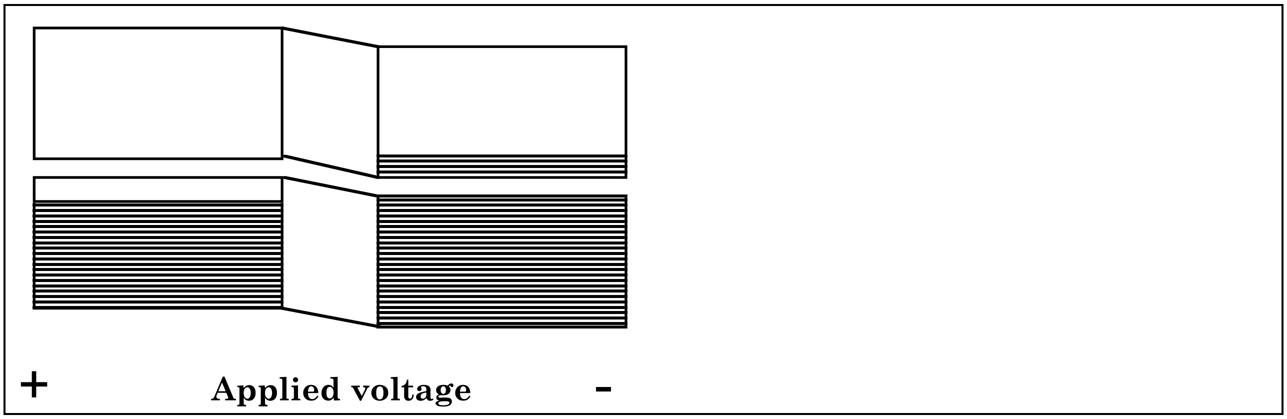


2. Because the p- and n-type are joined, electrons can flow freely in the conduction band. Some electrons from the higher energy orbitals on the n-type (the conduction band) will drop into the lower energy valence band of the p-type where there are empty orbitals available at low energy. This creates a charge on both halves. (a) The p-type semiconductor, originally neutral, is now [positive/negative] and the n-type, also originally neutral is now [positive/negative]. (b) Show on this diagram what has been described above, and (c) Label the charges on both the p- and n- halves. 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.

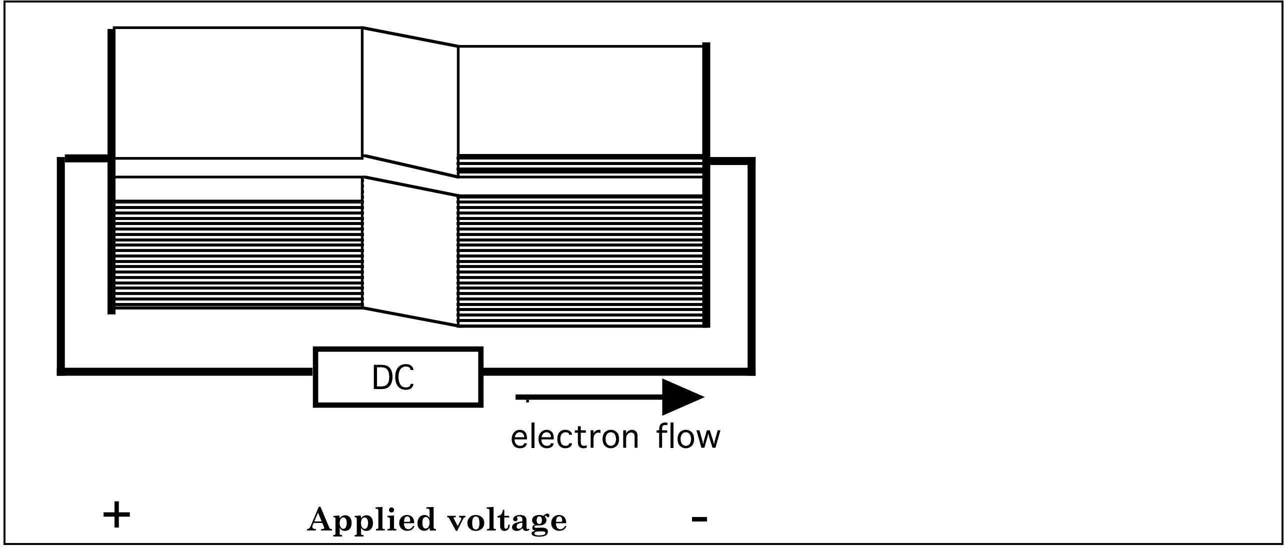


3. At this point, the slightly skewed energy levels can be explained. The energies of the orbitals on any atom change when the atom becomes a cation. We have discussed this before: The energies of orbitals on cations are [higher/lower] than on their neutral or negative counterparts.

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 (left/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.



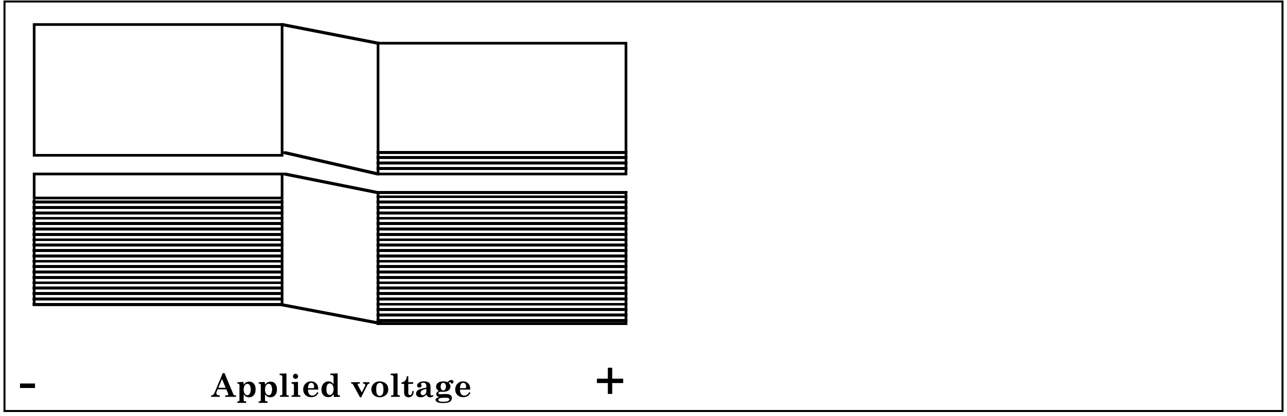
(c) Sketch electron flow when the diode is part of an external circuit.



(d) Why do electrons flow back to the n-half through the valence band? What is the driving force?

When the applied voltage is hooked up this way, it is called a ***forward bias***.

5. Here we've switched the applied voltage — a ***reverse bias*** arrangement. (a) Try to repeat the electron flow sequence described above and describe the problems encountered.

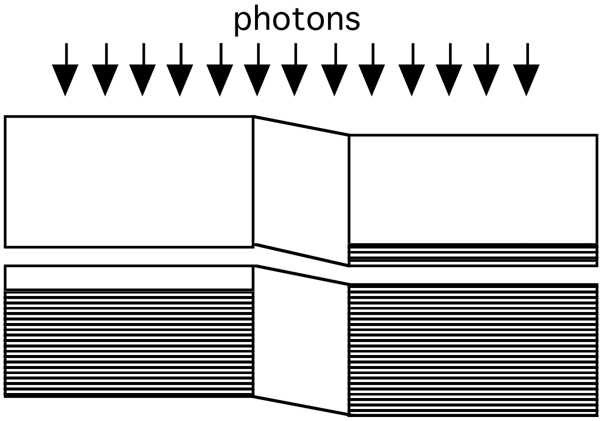


(b) When the applied voltage occurs as shown, does current flow?

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.

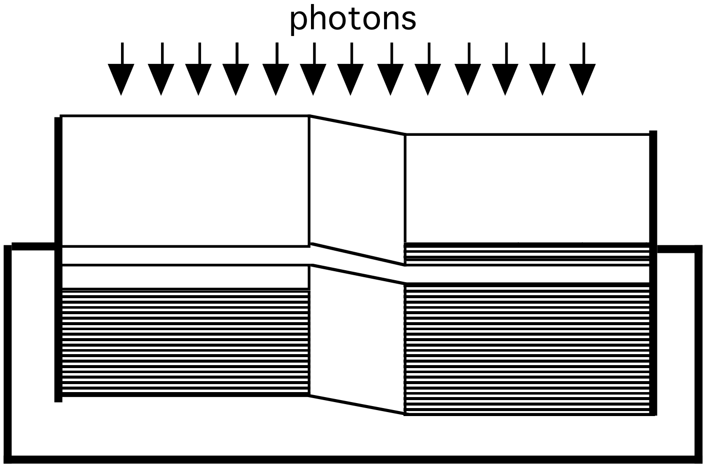
G. Photosensitive switches.

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 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.



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 can flow as long as light is applied.

I. Light-emitting diodes.

LEDs work like photocells, except backwards: they emit light and consume electrical energy. Interested readers can read more about them in a variety of books and on line.

Review for ACS Final Exam: Semiconductors

1. 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

2. 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: A, B