Chem 241

Lecture 23

Announcement

Mistake we have class on the 3rd not 4th

Exam 3

Originally scheduled April 23rd (Friday)

What about April 26th (Next Monday)

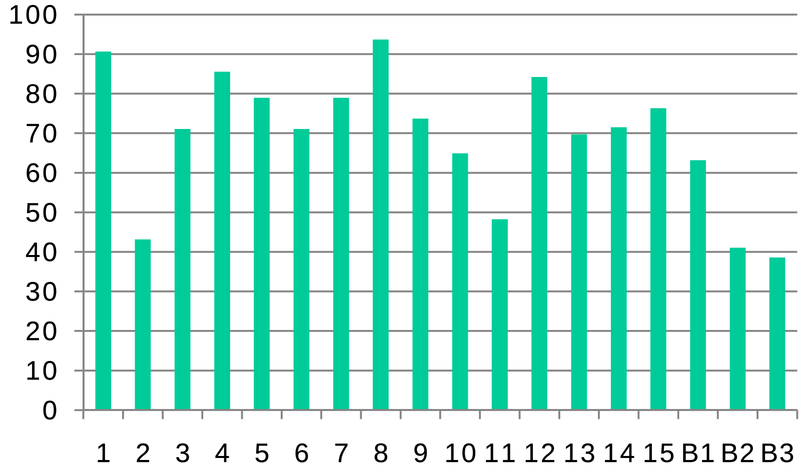
APRIL/MAY

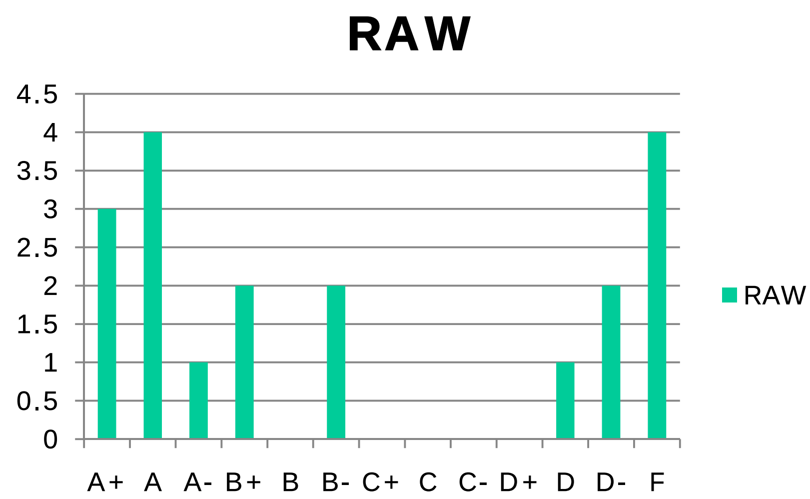
M	T	W	T	F	S	S
19	20	21	22	23	24	25
26	27	28	29	30	1	2
3	4	5	6	7	8	9
10	11	12	13			

Exam Stats

High – 101
Low – 43

Avg – 78
SD – 19.76





Recap

Lattice Energy
Counter Ions
Thermal Stability

Born-Mayer Equation

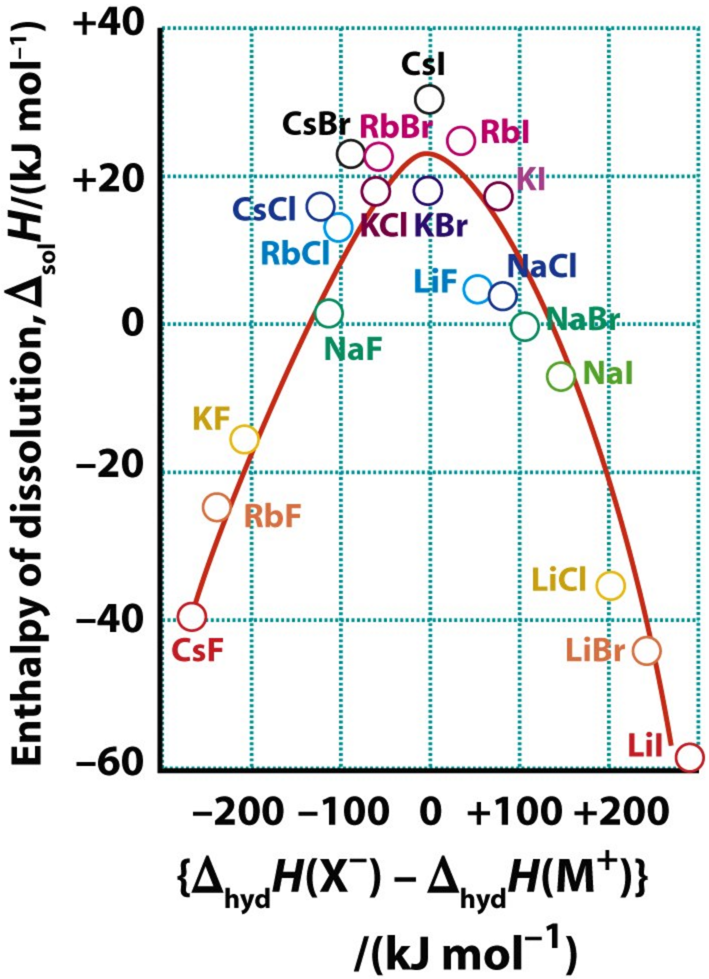
$$\Delta H_L = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d_0}\left(1 - \frac{d}{d_0}\right)A$$

$$\Delta H_L \propto \frac{|z_A z_B|}{d_0}$$

Table 3.8 Madelung constants

Structural type	$\mathcal{A}$
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite	1.638
Wurtzite	1.641

Solubility



$$MX(s) \rightarrow M^+(aq) + X^-(aq)$$

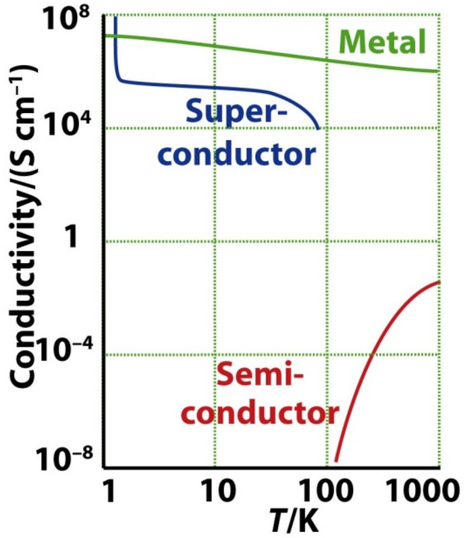
$$\Delta H_L \propto \frac{1}{r_+ + r_-}$$

$$\Delta H_{sol} \propto \frac{1}{r_+} + \frac{1}{r_-}$$

Electronic Structure

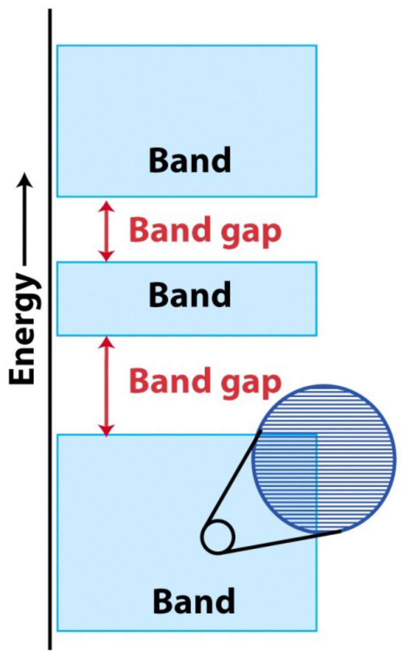
MOT of small molecules can be extended to solids, which consist of an almost infinite number of atoms, ions, etc.

- 1. Particularly useful in explaining the electrical conductivities of materials.
- 2. Types of conductors
    - a. metallic conductor: electrical conductivity decreases with increasing temperature
    - b. semiconductor: electrical conductivity increases with increasing temperature.
    - c. an insulator has very low electrical conductivity
    - d. a superconductor has zero electrical resistance below a critical temperature.



Inorganic solids

Treat solid like a very large molecule that has a nearly infinite number of atoms, and thus a nearly infinite number of bonding MOs and antibonding MOs. (Tight binding approximation).



a. Atomic orbitals of the same type, say the valence s orbitals, give rise to a large number of molecular orbitals that are very similar in energy. This is a **band** of energy levels, the example would be an s-band.

b. The bands are separated from each other by **band gaps**, which are ranges of energies that contain no MOs.

c. Building up bands (# of atoms = # of orbitals)

Inorganic solids

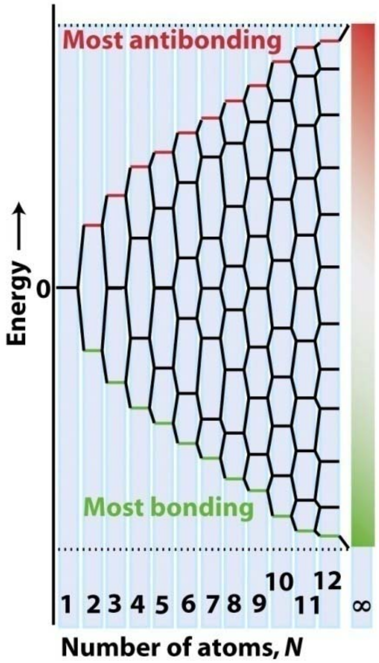
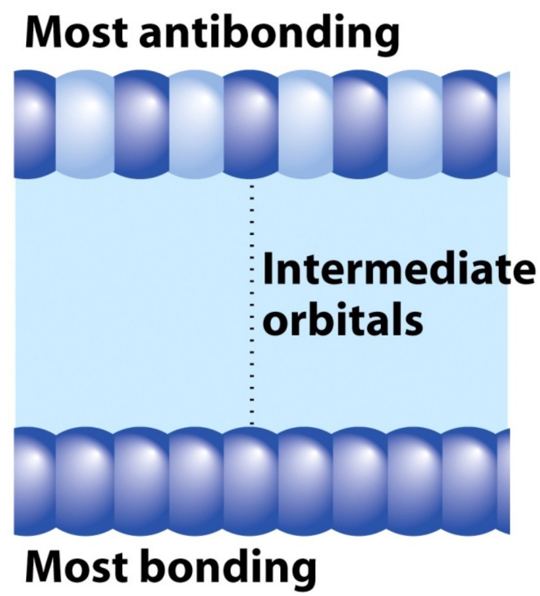


Figure 3-50
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F

d. The result of carrying this out for a large number of atoms, is a large number of orbitals

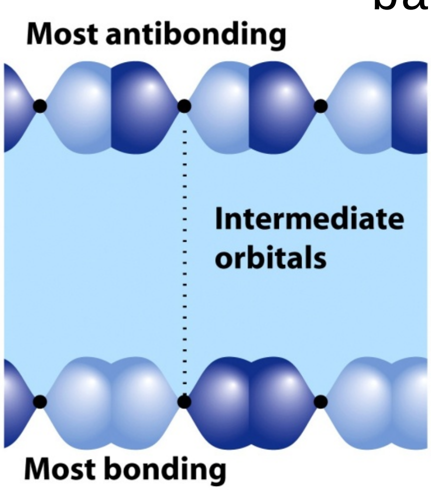
e. The upper and lower energy of the band is constrained by the energy of the most bonding and most antibonding level.

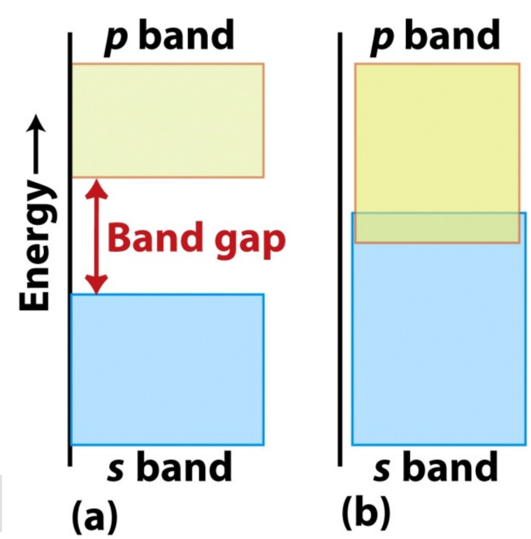
f. since the energy range is finite, and the number of orbitals is the number of atoms in the solid, the band consists of a near-continuum of energy levels.



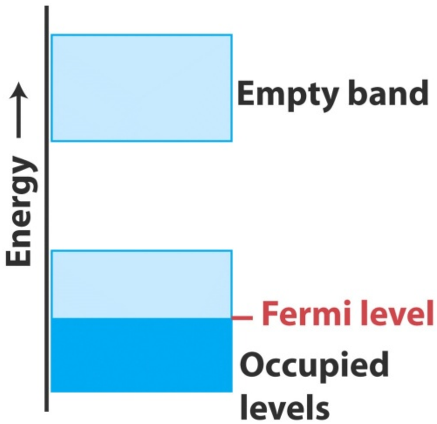
Bands

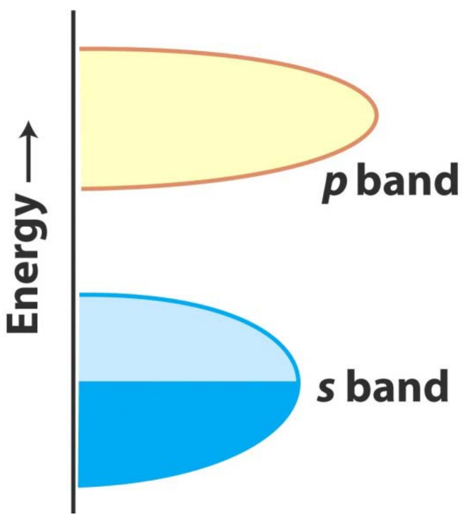
- We can do the same for p-orbitals, d-orbitals, etc. to form p- and d-bands.
  - a. since atomic p-orbitals are higher in energy that s-orbitals, the p-band will lie above the s-band in energy by an amount that is determined by the difference in energy of the atomic orbitals.
  - b. the width (in energy) of a band is determined by the strength of the interaction between the orbitals. If the interaction is strong, the band will be wide. Sometimes the width of the band is sufficient for bands to overlap.





Filling them up





Now we need to put electrons into the bands.

a. The highest level occupied in a band at T = 0 K is the **Fermi level**. In a case where the diatomic would fill the bonding, but not the antibonding, the Fermi level is in the middle of the band.

b. **Conduction band** explains metallic conductors.

c. The ability of the electrons to move in the solid is dependent on the uniformity of the material (purity of the material all atoms the same.

d. the number of energy levels in a given energy range is the density of states, ρ, and is high in the middle of a band, and low at the edges. (0 in a band gap)

Semimetals

In some cases the highest energy level of a filled band is the same as the lowest energy of an empty band (there is no band gap), but since the density of states at the top edge of the lower band and the lower edge of the upper band is very low. Such solids are semimetals (*e.g.*, graphite).

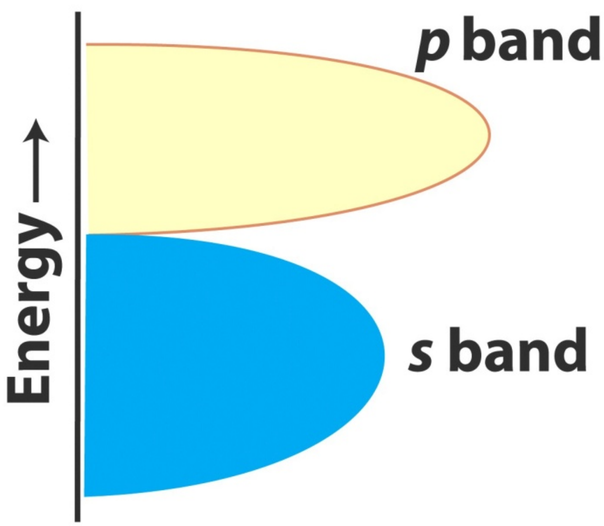


Figure 3-57
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Insulators

•**Insulators** are materials where a filled band is separated in energy from an empty band by a large band gap.

•**Semiconductors** are materials that have small band gaps, where empty bands can be populated thermal excitation of electrons from the filled band to the empty band.

Thus, insulators are just semiconductors with large band gaps.

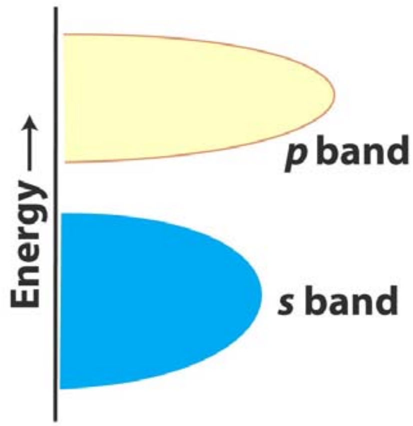


Figure 3-58
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Intrinsic semiconductors

Bands in the pure material are close enough in energy to be thermally populated.

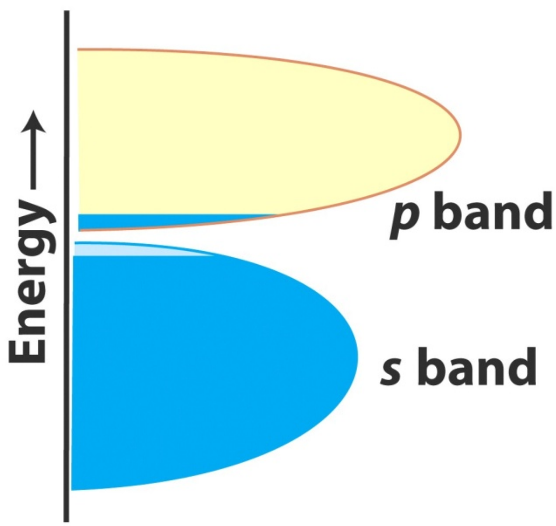


Figure 3-59
Shriver & Atkins Inorganic Chemistry, Fourth Edition

- The promotion of electrons from the filled band into the empty band, introduces electrons into the empty band, and holes in the filled band.

- The population of the upper band has Boltzmann-like temperature dependence, and thus the conductivity shows an exponential dependence with temperature.

$\sigma = \sigma_0 e^{-E_{gap}/2kT}$

-This predicts an activation energy equal to ½ the band gap.

Extrinsic Semiconductors

These are compounds where the semiconductor properties are the result of introducing impurities that produce either occupied donor bands (n-type) or empty acceptor bands (p-type) in the band gap of the pure material.

-the process is called doping

-very low levels of dopant (one atom per 10^9) are required.

- Ex1. If you dope a Si crystal ([Ne]$3s^2 3p^2$) with As ([Ar]$4s^2 4p^3$), you introduce one additional valence e- per As. **n-type**

- Ex2. If you dope a Si crystal ([Ne]$3s^2 3p^2$) with Ga ([Ar]$4s^2 4p^1$), you introduce one additional valence e- per As. **p-type**

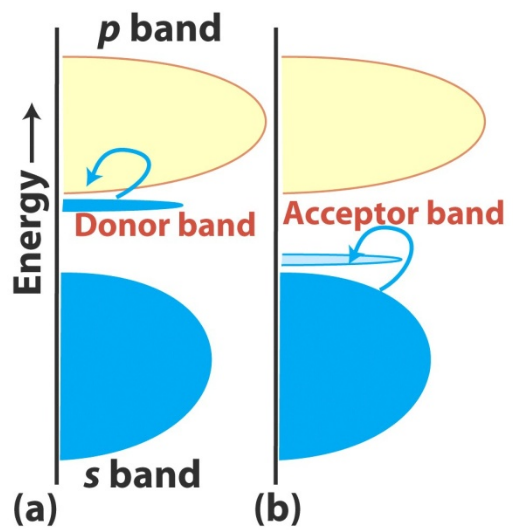


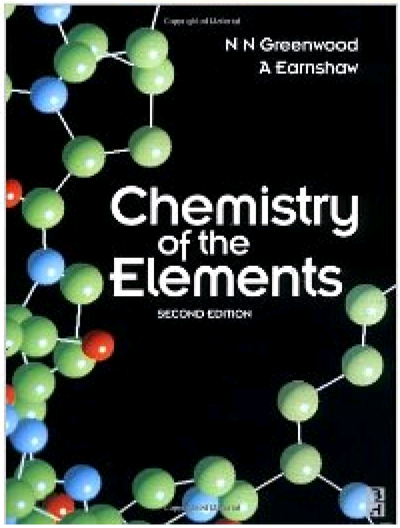
Figure 3-60
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Homework

Chapter 3:

Exercises: 2, 4, 7,9, 16, 17

The Groups

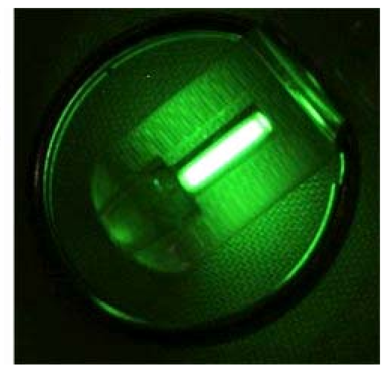


Chemistry of the Elements
A. Earnshaw, Norman Greenwood
ISBN-10: 0750633654

Hydrogen

Does not fit neatly in the periodic table

A. Electronic Configuration: $1s^1$
- Group 1 = ns^1
- Group 17 = needs one more for full shell

3 Useful isotopes

^{1}H – protium

^{2}H – dueterium

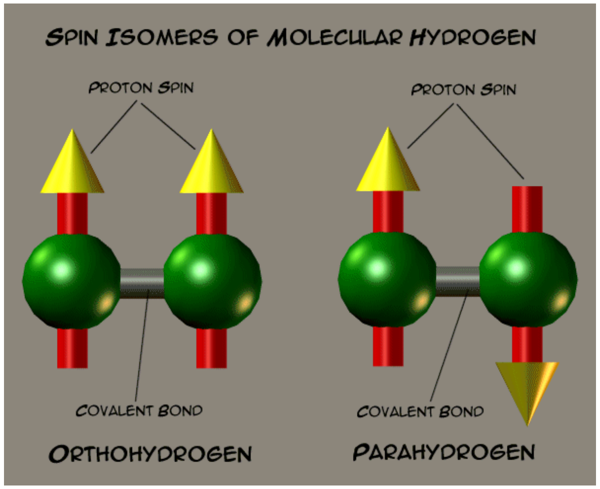
^{3}H – tritium

Used in kinetics isotope effect.

NMR – differ in spins

Ortho-para hydrogen

Dihydrogen can be found in two forms.
Ortho-hydrogen spins are parallel
Para- hydrogen spins are anti-parallel



Two was to look at hydrogen

H^+ - proton - Acts like metals (Lewis Acid)

H^- - hydride – Good nucelophile

- metal hydrides – $LiAlH_4$, NaH,

When assign oxidation number if it is acting like a hydride it is -1 (AlH_3) and when it is acting like a proton +1 (NH_3)

With metals it acts like hydride, more polar bond.

With non-metals it acts more covalent (but polar).

Production and Use

afas