

## Session #8: Homework Solutions

### Problem #1

Two lasers generate radiation of (1) 9.5  $\mu\text{m}$  and (2) 0.1  $\mu\text{m}$  respectively.

- (a) For each of the radiations, determine the photon energy (in eV).
- (b) Will either of the two radiations be able to break (dissociate) the Si–H bond in  $\text{SiH}_4$ ? Given:  $E_{\text{Si-Si}} = 180 \text{ kJ/mole}$

$$E_{\text{H-H}} = 435 \text{ kJ/mole}$$

### Solution

- (a) A give away!

$$E = hv = \frac{hc}{\lambda} \text{ J} \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}}$$

$$E_1 = \frac{hc}{9.5 \times 10^{-6}} \times \frac{1}{1.6 \times 10^{-19}} \text{ eV} = 0.13 \text{ eV}$$

$$E_2 = \frac{hc}{0.1 \times 10^{-6}} \times \frac{1}{1.6 \times 10^{-19}} \text{ eV} = 12.4 \text{ eV}$$

- (b) We have to determine the bond energy, Si–H (from the given data and from x values in the P.T.):  $x_{\text{Si}} = 1.90$ ,  $x_{\text{H}} = 2.20$

$$E_{\text{Si-H}} = \sqrt{E_{\text{Si-Si}} \times E_{\text{H-H}}} = k(x_{\text{H}} - x_{\text{Si}})^2$$

$$= \sqrt{180 \times 435} + 96.2(0.3)^2$$

$$E_{\text{Si-H}} = 288.5 \text{ kJ/mole}$$

To convert the energy into J/mole =  $288.5 \text{ kJ/mole} \times \frac{100}{\text{k}} \times \frac{1 \text{ mole}}{N_A}$

$$E_{\text{Si-H}} = 4.79 \times 10^{-19} \text{ J/bond}$$

$$E_1 \text{ (laser photon energy)} = 0.13 \text{ eV} \times \frac{1.6 \times 10^{-19} \text{ J}}{\text{eV}}$$

$$= 2.08 \times 10^{-20} \text{ J}$$

$$E_2 \text{ (laser photon energy)} = 12.4 \text{ eV} \times \frac{1.6 \times 10^{-18} \text{ J}}{\text{eV}}$$

$$= 1.98 \times 10^{-18} \text{ J}$$

**Only laser no. 2** has a photon energy ( $1.98 \times 10^{-18}$  J) which is in excess of the bond energy Si-H ( $4.79 \times 10^{-19}$ ).

### Problem #2

The equilibrium distance in diatomic LiF is  $1.52 \text{ \AA}$ . Assuming ionic bonding between the two atoms, calculate the energy required to separate them:  $\text{Li}^+ - \text{F}^- \rightarrow \text{Li}^+ + \text{F}^-$ . (Without additional information your answer should be correct to within 10%.)

### Solution

The bond energy for a LiF "molecule" is given as:

$$E = -\frac{e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

We recognize that in this relationship the energy appears as the difference between the attractive and the repulsive term— where the repulsive term

$$E_{\text{rep}} = \frac{e^2}{4\pi\epsilon_0 r_0} \times \frac{1}{n}$$

The repulsive exponent  $n$  is unknown, but is expected to be around 10; this means that, neglecting shell repulsion, the calculated  $E$  value will be higher (by about 10%) than the actual value:

$$E_{\text{approximation}} = + \frac{e^2}{4\pi\epsilon_0 r_0} = \frac{(1.6 \times 10^{-19})^2}{4\pi \cdot 8.85 \times 10^{-12} \times 1.52 \times 10^{-10}}$$

$$E = + 1.5 \times 10^{-18} \text{ J}$$

### Problem #3

Covalent bonds are directional and "saturated"; ionic bonds are "unsaturated" and "non-directional".

(a) Explain why.

(b) What are general consequences of the differences in the bonding characteristics?

### Solution

- (a) Pure covalent bonds can only be formed by the interaction (overlap) of singly occupied orbitals and the maximum number of bonds is given by the number of existing singly occupied orbitals. With bond formation, molecular orbital formation, the bonding capability is saturated. In covalent bond formation, the charge distribution is axial between the reaction partners ( $\sigma$  bond) or lateral between the partners ( $\pi$  bond), the bonding is directional.

Ionic bonds are the result of charge transfer which results in the formation of ions with opposite charge. The electric force fields associated with the ions are non-directional and therefore the bonding capability is not-saturated by the close proximity of oppositely charged species.

- (b) A direct consequence of the directional and saturated nature of covalent bonds is the formation of distinct species (molecule) with a limited number of atoms. (An exception is provided by Group IV elements, for example, where the number of spatial orientation of hybridized bonds permits the formation of covalent solids. A consequence of ion-formation (charge transfer) is in all instances the formation of a solid phase which, because of the principle of energy minimization, exhibits order on the atomic scale, i.e. crystalline structure.

#### Problem #4

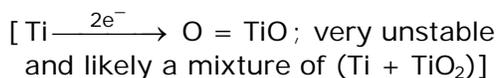
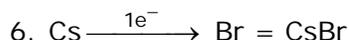
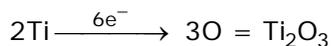
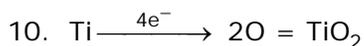
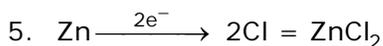
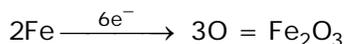
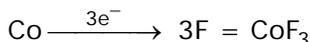
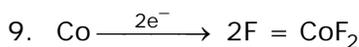
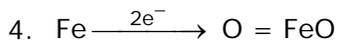
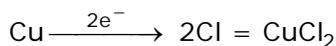
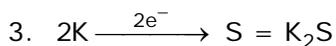
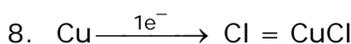
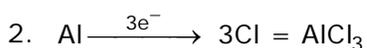
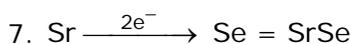
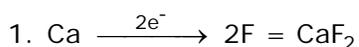
Write the chemical formulas for the *ionic* compound formed by interaction of the elements:

- |                           |                            |
|---------------------------|----------------------------|
| (1) calcium and fluorine  | (6) cesium and bromine     |
| (2) aluminum and chlorine | (7) strontium and selenium |
| (3) potassium and sulfur  | (8) copper and chlorine    |
| (4) iron and oxygen       | (9) cobalt and fluorine    |
| (5) zinc and chlorine     | (10) titanium and oxygen   |

#### Solution

Required: Periodic Table

(A look at the P.T. indicates that more than one oxidation state is encountered in Fe, Cu, Co, Te.)



### Problem #5

Attempt to account for the following properties of an ionic material:

- (a) transparent
- (b) insulators (electric)
- (c) conductors (electric)

[No more than a sketch (if you wish) and four lines of text/answer.]

### Solution

#### Properties of Ionic Materials:

- (a) Transparent: Ionic compounds are formed by charge transfer – which results in “stable” octets on both the cation and the anion. The energy gap between the valence shells (filled) and the next higher (empty) s orbital is so high (about 10 eV) that visible radiation cannot lead to electronic excitation; the radiation is not absorbed – the material appears transparent.
- (b) Insulators: There are no transparent electronic conductors. The argument made above applies here too. For conduction, the electrons under an applied potential must acquire energy – however, the lowest available empty energy states are separated by a large energy gap. No conduction can take place – ionic solids are insulators. The applied electric field exerts a force  $q\epsilon$  on each of the two types of ions in the crystal, but the ions are impeded from movement (ionic conduction) by the surrounding ions. Since, as we will see shortly, there are always some “vacancies” in the solids, small currents are observed. These are not electronic, but ionic, and therefore are associated with mass transport.
- (c) Conductors in the Molten State: The phase transformation solid  $\rightarrow$  liquid takes place when, through a temperature increase (at the melting point), the disruptive thermal forces exceed the attractive bonding forces which hold the “solid state” together. The phase transformation does not affect the electronic shell configurations – which remain octet–stabilized. Upon application of a potential, the anions will move to the anode ( $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ ) and the cations will move to the cathode [ $\text{Na}^+ + 1\text{e}^- \rightarrow \text{Na(m)}$ ].

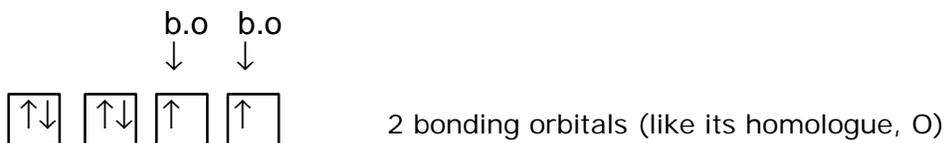
### Problem #6

Hydrogen and selenium react with each other to form a compound.

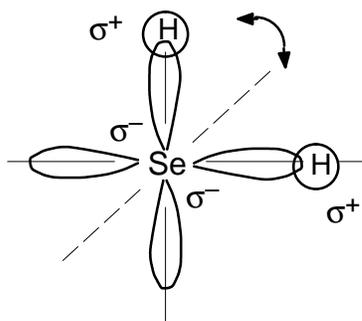
- (a) What is the chemical formula of the compound?
- (b) At room temperature, do you expect this compound to be a solid, a liquid or a gas? Substantiate your answer.

### Solution

(a) Se:  $4s^2p^4$



The relative electro negativity difference  $\Delta X = (2.55 - 2.20) = 0.35$ ; the compound formed will be covalent (polar).



The chemical formula is **H<sub>2</sub>Se**.

(b) We have a discrete covalent molecule which is expected to be a gas at room temperature. A comparative analysis with H<sub>2</sub>O (liquid at R.T.) indicates a decreased dipole moment and the absence of hydrogen bonding. This analysis cannot be quantitative without data – thus, if you make the above analysis and conclude the compound is liquid, you will get full credit. The decreased secondary bonding renders H<sub>2</sub>Se gaseous at room temperature. (You could have found that out by a quick trip to the library – a good place to visit on–and–off.)

### Problem #7

(a) Determine the differences in relative electronegativity ( $\Delta x$  in eV) for the systems H–F and C–F given the following data:

Bond Energy	kJ/mole
H <sub>2</sub>	436
F <sub>2</sub>	172
C–C	335
H–F	565
C–H	410

(b) Taking  $X_H = 2.1$ , determine the relative electronegativities (in eV) for C and F.

### Solution

According to Pauling, the square of the difference in electro negativity for two elements  $(X_A - X_B)^2$  is given by the following relationship:

$$(X_A - X_B)^2 = \left[ \text{Bond Energy (A-B)} - \sqrt{\text{Bond Energy AA} \cdot \text{Bond Energy BB}} \right] \times \frac{1}{96.3}$$

If bond energies are given in kJ.

$$(a) (X_H - X_F)^2 = \left[ 565 - \sqrt{436 \times 172} \right] \frac{1}{96.3} = 3.02$$

$$(X_H - X_F) = \sqrt{3.02} = 1.7$$

$$(X_C - X_H)^2 = \left[ 410 - \sqrt{335 \times 436} \right] \frac{1}{96.3} = 0.29$$

$$(X_C - X_H) = \sqrt{0.29} = 0.54$$

$$(b) \text{ Dilemma: } (2.1 - X_F) = 1.7 ?$$

$$(X_F - 2.1) = 1.7 ?$$

We recognize that  $X_F$  may be either 3.8 or 0.4.

(This dilemma arises from the fact that Pauling had to operate with  $(X_A - X_B)^2$  to avoid the appearance of a negative X value; the proper solution is always obvious considering the position of a given element in the Periodic Table.)

$$X_F = 3.8 ; \text{ the book value is 4.0.}$$

$$(X_C - 2.1) = 0.54$$

$$X_C = 2.64 ; \text{ the book value is 2.5.}$$

### Problem #8

For NaF the repulsive (Born) exponent,  $n$ , is 8.7. Making use of data given in your Periodic Table, attempt to calculate the crystal energy ( $\Delta E_{\text{cryst}}$ ). (What assumption do you have to make to calculate  $\Delta E_{\text{cryst}}$ ?)

### Solution

$$\Delta E = \frac{e^2 N_A M}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

The assumption must be made that the distance of separation of Na-F is given by the sum of the ionic radii (that in a crystal they touch each other – a not unreasonable assumption). Thus,  $r_0 = 0.95 \times 10^{-10} + 1.36 \times 10^{-10} \text{ m} = 2.31 \text{ \AA}$  and you must also assume  $M$  is the same as for NaCl = 1.747:

$$E_{\text{cryst}} = - \frac{(1.6 \times 10^{-19})^2 \cdot 6.02 \times 10^{23} \cdot 1.747}{4\pi \cdot 8.85 \times 10^{-12} \cdot 2.31 \times 10^{-10}} \left(1 - \frac{1}{8.7}\right)$$

$$E_{\text{cryst}} = 927.5 \text{ kJ/mole}$$

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