

Session #9: Homework Solutions

Problem #1

Estimate the ionic radius of Cs^+ . The lattice energy of CsCl is 633 kJ/mol . For CsCl the Madelung constant, M , is 1.763 , and the Born exponent, n , is 10.7 . The ionic radius of Cl^- is known to be 1.81 \AA .

Solution

$$E_{\text{lattice}} = \frac{Mq_1q_2}{4\pi\epsilon_0r_0} \left(1 - \frac{1}{n}\right) \text{ and } r_0 = r_{\text{Cs}^+} + r_{\text{Cl}^-}$$

Solve first for r_0

$$r_0 = \frac{Mq_1q_2N_{\text{Av}}}{4\pi\epsilon_0E_{\text{lattice}}} \left(1 - \frac{1}{n}\right) = \frac{1.763(1.6 \times 10^{-19})^2 6.02 \times 10^{23}}{4\pi(8.85 \times 10^{-12})6.33 \times 10^5} \left(1 - \frac{1}{10.7}\right)$$
$$= 3.50 \times 10^{-10} \text{ m} = 3.50 \text{ \AA} = r_{\text{Cs}^+} + r_{\text{Cl}^-}$$

$$\therefore r_{\text{Cs}^+} = 3.50 - 1.81 = 1.69 \text{ \AA}$$

Problem #2

- CFCs have been implicated in ozone depletion. Show that when Freon 12 (CCl_2F_2) is exposed to ultraviolet radiation, the compound decomposes to produce chlorine.
- Draw the Lewis structure of Freon 12 and indicate the polarities of each bond within this compound.
- Determine the percent ionic character of the C--Cl and C--F bonds.

DATA:

Average Bond Energies (kJ/mol)

Single Bonds

H-H	435
F-F	155
Cl-Cl	242
C-C	347

Multiple Bonds

C = C	610
C \equiv C	836

Solution

- (a) Chlorine will be liberated if the C-Cl bond breaks, therefore, compute its strength and show that ultraviolet photons have enough energy to break the bond.

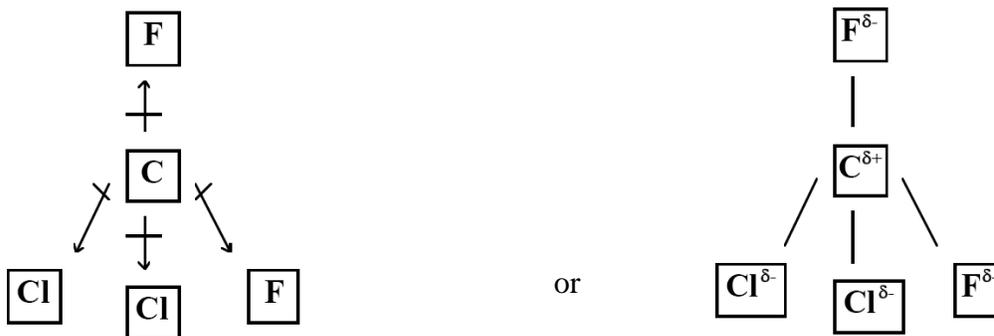
$$\begin{aligned}
 E_{\text{C-Cl}} &= \sqrt{E_{\text{C-C}} \times E_{\text{Cl-Cl}}} + 96.3(\chi_{\text{C}} - \chi_{\text{Cl}})^2 \\
 &= \sqrt{347 \times 242} + 96.3(2.55 - 3.16)^2 \\
 &= 326 \times 10^3 / 6.02 \times 10^{23} = 5.41 \times 10^{-19} \text{ J/bond}
 \end{aligned}$$

photon will break \therefore this bond if $E_{\text{ph}} > E_{\text{bond}} \Rightarrow$ critical λ is

$$\lambda = \frac{hc}{E_{\text{bond}}} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{5.41 \times 10^{-19}} = 3.66 \times 10^{-7} \text{ m}$$

which lies in the u.v. part of the electromagnetic spectrum.

- (b) Draw the Lewis structure of Freon 12 and indicate the polarities of each bond within this compound.

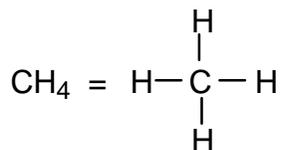


- (c) C-Cl $\Delta\chi = 0.61 \rightarrow \sim 9\%$ ionic character
 C-F $\Delta\chi = 1.43 \rightarrow \sim 40\%$ ionic character

Problem #3

The compound trichloroethylene has the composition $\text{C}_2\text{Cl}_3\text{H}$.

- (a) Formulate this compound in "Lewis" notation. Example:

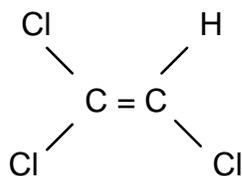


- (b) List the types of atomic orbitals which, upon overlap, lead to the formation of the bonds indicated in (a).

- (c) List all bonds (number and type) involved in the formation of this compound.

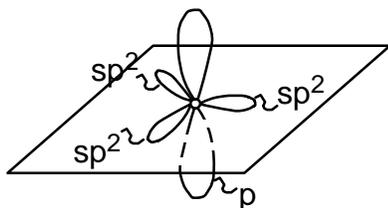
Solution

- (a) C_2Cl_3H in Lewis notation:

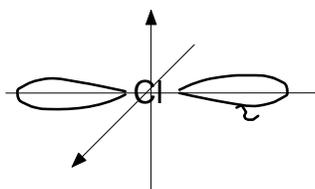


Note that the H may be located on any one of the 4 (sp^2) hybrid orbitals without changing the properties of the compound.

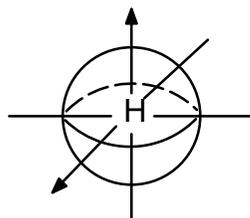
- (b)



On each carbon there are:
three equivalent sp^2 bonding orbitals in a plane and one p orbital normal to the sp^2 plane.



On each chlorine there is:
one singly occupied p orbital.



On the hydrogen we have:
one singly occupied 1s orbital.

(c) $2 sp^2 - sp^2$ orbitals $\rightarrow 1 \sigma C^{\sigma}-C$

$2 p-p$ orbitals $\rightarrow 1 \pi C^{\pi}-C$

6 bonds

$3 sp^2 - p$ orbitals $\rightarrow 3 \sigma C-Cl$

$1 sp^2 - s$ orbitals $\rightarrow 1 \sigma C-H$

Problem #4

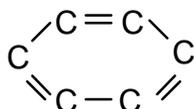
Frequently the statement is made that the crystal energy (ΔE_{cryst}) is predominantly given by the attractive energy term. How can you account for this approximation?

Solution

$E_{\text{cryst}} = K (1 - 1/n) = K - 1/n K$ where $-1/n K$ is the repulsive contribution to E_{cryst} . $1/n \cong 1/8$. This means only $\sim 12\%$ of the total crystal energy.

Problem #5

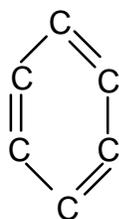
For benzene (C_6H_6), which has a schematic *carbon* arrangement:



- Determine the total number and types of covalent bonds.
- For each bonding type, determine the bonding orbitals which, by overlap, lead to their formation.

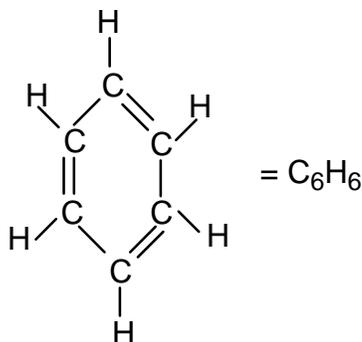
Solution

(a)



From the schematic we recognize three single and three double carbon-to-carbon bonds which are respectively of the σ (sigma) and $\sigma + \pi$ (sigma + pi) variety. Left out in the schematic are the six C-H bonds which are of the σ variety:

In C_6H_6 , we have 12 σ and 3 π bonds.



- In the ring structure of benzene we have three double bonds, which means that all six carbon atoms are sp^2 hybridized. Accordingly:
 3π bonds involve lateral ($p-p$) orbital overlap.
 $6 (C-C) \sigma$ bonds involve (sp^2-sp^2) orbital overlap.

6 (C–H) σ bonds involve (sp^2 –s) orbital overlap.

(It should be noted that the experimentally determined bond energy for the carbon ring is larger than the sum of the bond energies of the double plus single bonds. This increased bond energy is attributed to the existence of alternating double bonds which permit the establishment of "equivalent resonance structures"



in which the double bonds are said to be delocalized:



Problem #6

Why is double bonding encountered in some carbon compounds, but not in germanium compounds – although both exhibit sp^3 hybridization?

Solution

Double bond formation, the result of lateral p orbital overlap, is contingent on close approach of the atoms. Such approach is possible for carbon with its K shell, but not for the larger germanium with its fully occupied M shell.

Problem #7

List the individual steps with the corresponding chemical equations used in constructing a Born-Haber cycle for the formation of CaBr_2 from the element and identify those which you expect to be exothermic.

Solution

- | | |
|---|---|
| 1) $\text{Ca(s)} \rightarrow \text{Ca(v)}$ | $\Delta H_{\text{vap}}(+)$ |
| 2) $\text{Br}_2(\text{g}) \rightarrow 2\text{Br}\cdot$ | $\Delta H_{\text{dissoc}}(+)$ |
| 3) $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$ | |
| 3a) $\text{Ca} \rightarrow \text{Ca}^+ + 1\text{e}^-$ | $\Delta H_{\text{ioniz}}(+)$ |
| 3b) $\text{Ca}^+ \rightarrow \text{Ca}^{++} + 1\text{e}^-$ | $\Delta H_{\text{ioniz}}(+)$ |
| 4) $\text{Br} + 1\text{e}^- \rightarrow \text{Br}^{1-}$ | EA (-) \rightarrow exothermic |
| 5) $\text{Ca}^{2+} + 2\text{Br}^{1-} \rightarrow \text{CaBr}_2$ | $DE_{\text{cryst}}(-) \rightarrow$ exothermic |

$\Delta H_{\text{reaction}} = \Delta H_{\text{vap}} + \Delta H_{\text{dissoc}} + 1\Delta H_{\text{ioniz}} + 2\Delta H_{\text{ioniz}} + 2\text{EA} + \Delta E_{\text{cryst}}$
(it is acceptable to note $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$ if you realize that 1 and 2 ionization is involved)

Problem #8

- (a) Given the ionic radii, $\text{Cs}^+ = 1.67\text{\AA}$, $\text{Cl}^- = 1.81\text{\AA}$, and the Madelung constant $M(\text{CsCl}) = 1.763$, determine to the best of your ability the molar Crystal energy (ΔE_{cryst}) for CsCl.
- (b) Not given additional data, do you expect the value obtained to be larger or smaller than theoretical, and by how many percent do you anticipate to be off?

Solution

- (a) Given the radii $\text{Cs}^+ = 1.67\text{\AA}$ and $\text{Cl}^- = 1.81\text{\AA}$, we can assume that r_0 is the sum of the two. However, we need to know the exponential constant of the repulsive term which is not provided. Considering only the attractive force:

$$\Delta E_{\text{cryst}} = \frac{-e^2 N_A M Q_1 Q_2}{4\pi\epsilon_0 r_0}$$

$$\text{where: } Q_1 = Q_2 = 1$$

$$M = 1.763$$

$$N_A = 6.02 \times 10^{23} \text{ particle/mole}$$

$$\Delta E_{\text{cryst}} = \frac{-(1.6 \times 10^{-19} \text{ coul})^2 \times 6.02 \times 10^{23} \times 1.763 \times 1 \times 1}{4\pi \times 8.85 \times 10^{-12} \times (1.81 + 1.67) \times 10^{-10} \text{ m}}$$

$$= 7.02 \times 10^5 \text{ J/mole}$$

- (b) Because we didn't include the repulsive part, we expect the theoretical energy to be smaller by $1/n$ times than calculated above. Because n is in the range of 10 **we are off by around +10%**

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