

CHAPTER 1

WHERE IT ALL COMES FROM

- 1.1 The solid region of the Earth's crust is the lithosphere, the liquid region is the hydrosphere, and the gaseous region is the atmosphere.
- 1.2 Iron is the primary metal in the Earth's core.
- 1.3 Recovery of elements such as copper and silver is economically feasible because they are found in concentrated form in specific locations.
- 1.4 Minerals are naturally occurring chemical compounds such *bauxite* or *trona*. Rocks contain mixtures of minerals in varying proportions. Ores are materials which contain sufficiently high concentrations of a mineral to make recovery of that mineral economically feasible.
- 1.5 Igneous rocks were formed by solidification of a molten mass.
- 1.6 Sedimentary rocks were formed by compaction of small grains that were deposited as a sediment in a river bed or sea.
- 1.7 Metamorphic rocks have had their composition and structure changed over time by the influences of temperature and pressure.
- 1.8 Some of the important classes of metal compounds found in the lithosphere are the oxides, sulfides, silicates, phosphates, and carbonates.
- 1.9
$$\text{CaO} + \text{CO}_2 \longrightarrow \text{CaCO}_3$$
$$\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2$$
- 1.10 Copper was the first metal to be used extensively because it is found uncombined.
- 1.11 In open pit mining, the ore is recovered by digging in the Earth's surface and removing the top layer of dirt and rock. In shaft mining, a shaft is dug into the Earth to gain access to the ore.
- 1.12 In the flotation process, ore is ground to a powder, mixed with water, oil, and detergents, and beaten to a froth. The metal ore concentrates in the froth and is skimmed off. In the reduction process, a material is added that forms a molten slag with silicate impurities at high temperatures. The molten slag is of lower density than the molten metal and can then be skimmed off or the metal can be drained from the bottom of the furnace. In magnetic separation, magnetic ores are crushed and passed on a conveyor under a magnet. In another method, the ore is crushed and the lighter gangue is washed away leaving behind the heavier ore

particles.

- 1.13 A reducing agent must be inexpensive and available in large quantities in order to be used in the commercial refining of metals.
- 1.14 Pyrometallurgy is the use of high temperatures to smelt and refine metals. Hydrometallurgy is the separation of metal compounds from ores by the use of aqueous solutions. Electrometallurgy is the use of electricity to reduce the metal from its compounds.
- 1.15 Copper was the earliest metal smelted. Iron was not smelted until a later time because reduction of iron requires a higher temperature than that of copper.
- 1.16 Three modern techniques used to shape metals include rolling, forging, and spinning.
- 1.17 Two ancient techniques used to shape metals include hammering (cold working) and forging (hot working).
- 1.18 South Africa is a primary source of manganese (used in special steels, paints, and batteries), diamonds (used in cutting tools and abrasives), fluorite (used in HF and steel making), platinum (used in catalysts, alloys, dental uses, and surgical appliances), and chromium (used in stainless steels, leather tanning, plating, and alloys). The hardest hit area would be the steel industry, which would, in turn, affect manufacture of many durable goods. Fortunately, all of these materials are available from other countries, but the cost of many goods would be driven up.
- 1.19 Elemental sulfur is the starting material in the manufacture of sulfuric acid.
- 1.20 The primary uses for lime, CaO , include glass and cement making.
- 1.21 Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is primarily used in fertilizers.

CHAPTER 2

ATOMIC STRUCTURE AND PROPERTIES

- 2.1
 - (a) For Li, $n = 2, l = 0, m = 0, s = +\frac{1}{2}$
 - (b) For Ca, $n = 4, l = 0, m = 0, s = -\frac{1}{2}$
 - (c) For Sc, $n = 3, l = 2, m = 2, s = +\frac{1}{2}$
 - (d) For Fe, $n = 3, l = 2, m = 2, s = -\frac{1}{2}$

- 2.2
 - Set 1: $n = 5$ $l = 2$ $m = 2$ $s = +\frac{1}{2}$
 - Set 2: $n = 5$ $l = 2$ $m = 1$ $s = +\frac{1}{2}$

- | | | | | |
|---------|---------|---------|----------|--------------------|
| Set 3: | $n = 5$ | $l = 2$ | $m = 0$ | $s = +\frac{1}{2}$ |
| Set 4: | $n = 5$ | $l = 2$ | $m = -1$ | $s = +\frac{1}{2}$ |
| Set 5: | $n = 5$ | $l = 2$ | $m = -2$ | $s = +\frac{1}{2}$ |
| Set 6: | $n = 5$ | $l = 2$ | $m = 2$ | $s = -\frac{1}{2}$ |
| Set 7: | $n = 5$ | $l = 2$ | $m = 1$ | $s = -\frac{1}{2}$ |
| Set 8: | $n = 5$ | $l = 2$ | $m = 0$ | $s = -\frac{1}{2}$ |
| Set 9: | $n = 5$ | $l = 2$ | $m = -1$ | $s = -\frac{1}{2}$ |
| Set 10: | $n = 5$ | $l = 2$ | $m = -2$ | $s = -\frac{1}{2}$ |
- 2.3 (a) O $1s^2 2s^2 2p^4$
 (b) Kr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
 (c) Ni $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
 (d) Ti $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
 (e) Fr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$
- 2.4 (a) Co^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
 (b) Sn^{4+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$
 (c) N^{3-} $1s^2 2s^2 2p^6$
 (d) Se^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
 (e) Fe^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
- 2.5 (a) Mo^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^4$
 (b) Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (Cu has an irregular configuration, $3d^{10} 4s^1$)
 (c) S^{2-} $1s^2 2s^2 2p^6 3s^2 3p^6$
 (d) Mg^{2+} $1s^2 2s^2 2p^6$
 (e) I^- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
- 2.6 Each spinning electron generates a magnetic field that interacts with the magnetic field generated by the orbital motion of the electron. These magnetic interactions are greatest for a half-filled shell that results when Cr has the arrangement $(\text{Ar})3d^5 4s^1$ rather than $(\text{Ar})3d^4 4s^2$. In the case of Cu, the more energetically favorable interaction is with the arrangement $(\text{Ar})3d^{10} 4s^1$ where the $3d$ shell is completed and the $4s$ shell is half-filled rather than $(\text{Ar})3d^9 4s^2$.
- 2.7 (a) Al (b) Ca (c) Kr (d) Cl (e) N
- 2.8 The valence shell of Be is $2s^2$, a closed shell. For B, the configuration $2s^2 2p^1$ has one electron outside of the filled $2s$ shell, which makes it easier to remove the electron from the $2p$ orbital.
- 2.9 These elements all have configurations that have closed shells.
- 2.10 (a) Endothermic; removal of an electron is always requires energy.
 (b) Exothermic; addition of an electron to Cl forms Cl^- that has a closed

shell arrangement of electrons, which is a more energetically favorable arrangement.

- (c) Endothermic; addition of an electron to a species that is already negatively charged always requires energy.
- (d) Exothermic; addition of an electron to Na forms Na^- that has a closed shell arrangement of electrons, which is a more energetically favorable arrangement than the half-filled shell.
- (e) Endothermic; removal of an electron is always requires energy.

2.11 (a) Cl (b) F (c) C (d) O

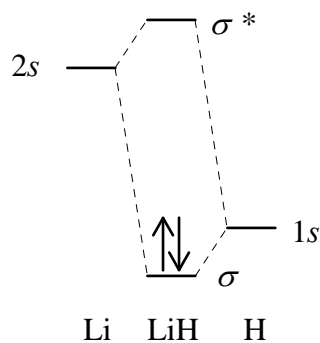
2.12 Nitrogen has the half-filled $2p$ outer shell. If another electron is added, that electron enters an orbital that already contains another electron and forces pairing. For carbon, one $2p$ orbital is empty and can readily accept an electron. For oxygen, the pairing has already occurred in one $2p$ orbital and oxygen has a higher nuclear charge than nitrogen.

CHAPTER 3 COVALENT BONDING AND MOLECULAR STRUCTURE

3.1

$\begin{array}{c} \text{--- } \sigma^* \\ \uparrow\downarrow \quad \uparrow \quad \pi^* \end{array}$	$\begin{array}{c} \text{--- } \sigma^* \\ \text{--- } \text{--- } \pi^* \end{array}$	$\begin{array}{c} \text{--- } \sigma^* \\ \text{--- } \text{--- } \pi^* \end{array}$	$\begin{array}{c} \text{--- } \sigma^* \\ \text{--- } \text{--- } \pi^* \end{array}$	$\begin{array}{c} \text{--- } \sigma^* \\ \text{--- } \text{--- } \pi^* \end{array}$
$\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \pi \\ \uparrow\downarrow \quad \sigma \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \pi \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \pi \end{array}$	$\begin{array}{c} \text{--- } \sigma \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \pi \end{array}$	$\begin{array}{c} \text{--- } \sigma \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \pi \end{array}$
$\begin{array}{c} \uparrow\downarrow \quad \sigma^* \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma^* \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma^* \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma^* \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma^* \end{array}$
$\begin{array}{c} \uparrow\downarrow \quad \sigma \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \end{array}$	$\begin{array}{c} \uparrow\downarrow \quad \sigma \end{array}$
F_2^+ B.O. = 1.5 Paramagnetic	CN^- B.O. = 3 Diamagnetic	C_2^{2-} B.O. = 3 Diamagnetic	CN^+ B.O. = 2 Diamagnetic	BN B.O. = 2 Diamagnetic

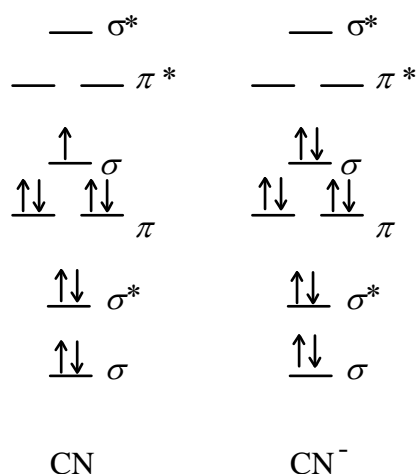
3.2 In Li_2 and H_2 , the atomic orbitals used are identical so the molecular orbital contains equal contribution from each atom. In LiH , the bonding σ orbital more closely resembles the H $1s$ orbital than the Li $2s$ orbital. Therefore, the energy of the σ orbital is much closer in energy to that of the H $1s$ orbital.



3.3

NO ⁻	C ₂ ⁻	BN ²⁻	O ₂ ⁺
B.O. = 2	B.O. = 2.5	B.O. = 3	B.O. = 2.5
Paramagnetic	Paramagnetic	Diamagnetic	Paramagnetic

3.4



The band seen at $9,000 \text{ cm}^{-1}$ for CN is due to the excitation of an electron from the π to the σ orbital. CN^- has no transitions in this region of the spectrum because the σ orbital is already filled.

- 3.5 (a) % Ionic Character = $16|\chi_{\text{Cl}} - \chi_{\text{F}}| + 3.5|\chi_{\text{Cl}} - \chi_{\text{F}}|^2$
 % I.C. = $16|3.2 - 4.0| + 3.5|3.2 - 4.0|^2$
 % I.C. = 15%
- (b) q = fraction ionic character \times charge on electron
 $q = 0.15 \times 4.8 \times 10^{-10} \text{ esu} = 7.2 \times 10^{-11} \text{ esu}$
 $\mu = q \times r = (7.2 \times 10^{-11} \text{ esu}) \times (2.12 \times 10^{-8} \text{ cm})$
 $\mu = 1.5 \times 10^{-18} \text{ esu cm} = 1.5 \text{ Debye}$

3.6 $\lambda = 0.50$

$$\% \text{ Ionic Character} = \frac{100\lambda^2}{1^2 + \lambda^2} = \frac{100(0.50)^2}{1 + (0.50)^2}$$

% I.C. = 20%

$$\begin{aligned}
 q &= \text{fraction ionic character} \times \text{charge on electron} \\
 q &= 0.20 \times 4.8 \times 10^{-10} \text{ esu} = 9.6 \times 10^{-11} \text{ esu} \\
 \mu &= q \times r = (9.6 \times 10^{-11} \text{ esu}) \times (1.50 \times 10^{-8} \text{ cm}) \\
 \mu &= 1.4 \times 10^{-18} \text{ esu cm} = 1.4 \text{ Debye}
 \end{aligned}$$

- 3.7 a) % Ionic Character = $16|\chi_{\text{A}} - \chi_{\text{B}}| + 3.5|\chi_{\text{A}} - \chi_{\text{B}}|^2$
 % I.C. = $16|1.2| + 3.5|1.2|^2$
 % I.C. = 24%
- (b) q = fraction ionic character \times charge on electron
 $q = 0.24 \times (4.8 \times 10^{-10} \text{ esu}) = 1.15 \times 10^{-11} \text{ esu}$
 $\mu = q \times r = (1.15 \times 10^{-11} \text{ esu}) \times (1.50 \times 10^{-8} \text{ cm})$
 $\mu = 1.7 \times 10^{-18} \text{ esu cm} = 1.7 \text{ Debye}$
- (c) The additional contribution to the A–B bond (Δ_{AB}) caused by the

interaction of the atoms of different electronegativities is

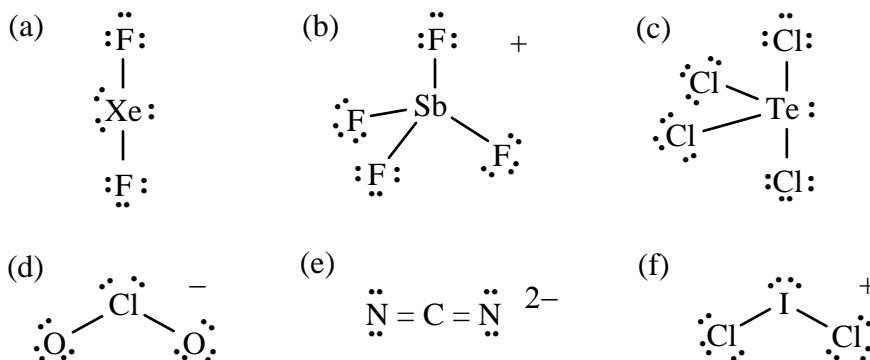
$$\Delta_{AB} = 96.48|\chi_A - \chi_B|^2 = 96.48|1.2|^2 = 139 \text{ kJ mol}^{-1}$$

$$\Delta_{AB} = D_{AB} - \frac{1}{2}[D_{AA} + D_{BB}]$$

$$139 = D_{AB} - \frac{1}{2}[240 + 425]$$

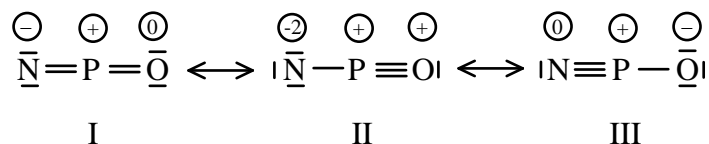
$$D_{AB} = 472 \text{ kJ mol}^{-1}$$

3.8



- 3.9 (a) XeF₂ has one C_∞ axis, ∞ C_2 axes, ∞ σ_v planes, one σ_h plane, and a center of symmetry. It belongs to the $D_{\infty h}$ point group.
- (b) SbF₄⁺ has four C_3 axes, three C_2 axes, six σ_v planes, and three S_4 axes. It belongs to the T_d point group.
- (c) TeCl₄ has one C_2 axis and two σ_v planes. It belongs to the C_{2v} point group.
- (d) ClO₂⁻ has one C_2 axis and two σ_v planes. It belongs to the C_{2v} point group.
- (e) CN₂²⁻ has one C_∞ axis, ∞ C_2 axes, ∞ σ_v planes, one σ_h plane, and a center of symmetry. It belongs to the $D_{\infty h}$ point group.
- (f) ICl₂⁺ has one C_2 axis and two σ_v planes. It belongs to the C_{2v} point group.

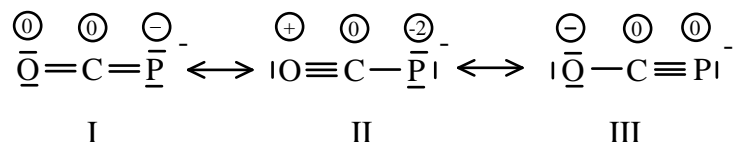
3.10 The most favorable arrangement of atoms will be the structure in which the least electronegative atom is in the center. In this case, the phosphorus atom will be in the center because it is the least electronegative atom of the three.



Resonance structure II would contribute the least to the actual structure because it has the highest formal charges, has adjacent positive formal charges, and has a positive formal charge on the most electronegative atom, oxygen.

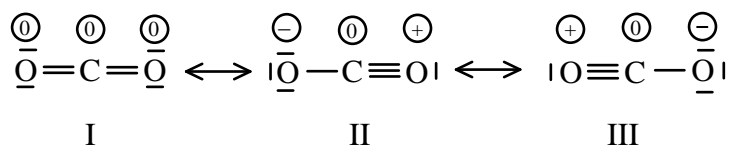
3.11 The most favorable arrangement of atoms would be with the carbon atom in the

center because it is the least electronegative atom of the three.

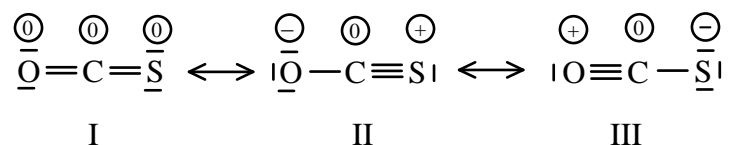


Resonance structure II would contribute least to the actual structure because it has the highest formal charges and has a positive formal charge on the most electronegative atom, oxygen.

3.12

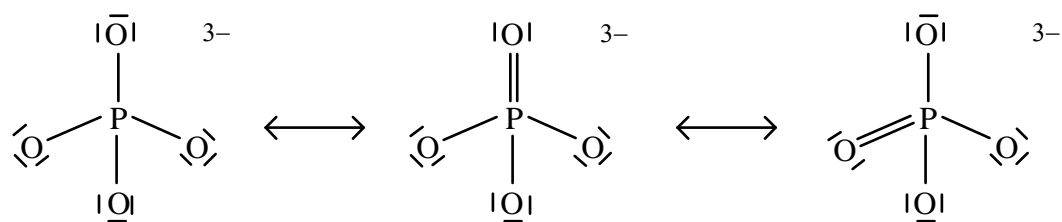


For CO₂, structure I shows no charge separation. Even though structures II and III do show charge separation, the effects cancel and the molecule is nonpolar.



Although structure I shows a zero formal charge on all of the atoms, structures II and III do not. However, structure II contributes to a greater extent than does structure III so the molecule is slightly polar with the oxygen end representing the negative end.

- 3.13 (a) The bond lengths for both PO₄³⁻ and SiO₄⁴⁻ are shorter than single bond lengths because there will be some contribution from resonance structures that have double bonds.



The resonance structures for SiO₄⁴⁻ would be similar.

- (b) In the case of the SiO₄⁴⁻, the resonance structures showing double bonds would contribute less to the actual structure, because, in the single bond structure, the Si has a formal charge of zero, and all of the oxygen atoms have formal charges of -1.