3.1 Lewis structures and VSEPR theory?

(a) GeCl₃⁻? Only one resonance structure is important (each atom has an octet).

\[
\begin{array}{c}
:Cl-\text{Ge}-Cl:- \\
\vdots \\
:Cl-
\end{array}
\]

GeCl₃⁻

(b) FCO₂⁻? With two resonance contributors to account for the equivalence of the two C-O bonds. Each atom has an octet.

\[
\begin{array}{c}
:F-\text{C}=\text{O}: \\
\equiv \\
:F-\text{C}=\text{O}:
\end{array}
\]

FCO₂⁻

(c) CO₃²⁻? Three resonance structures are necessary to account for the fact that the three C-O bonds in the carbonate anion are equivalent, and these are shown below. Each atom has an octet in all three resonance structures.

\[
\begin{array}{c}
:O-\text{C}=\text{O}: \\
\equiv \\
:O-\text{C}=\text{O}:
\end{array}
\]

CO₃²⁻
d) \( \text{AlCl}_4^- \)? Only one resonance structure is necessary to achieve an octet around each atom and to account for the equivalence of the four Al-Cl bonds, and it is shown below.

\[
\begin{align*}
\vdots \quad \vdots \quad \vdots \\
\vdots \quad \text{Al} \quad \vdots \\
\vdots \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{align*}
\]

\( \text{AlCl}_4^- \)

(e) \( \text{FNO}^- \)? The least electronegative atom is likely to be the central atom. The Lewis structure of this molecule is shown above, requiring only one resonance structure to achieve an octet around all three atoms.

3.2 Lewis structures and formal charges?

(a) \( \text{ONC}^- \)? With one O atom, one N atom, one C atom, and a -1 charge, the ONC anion has 16 valence electrons. You can arrange them in two resonance forms as follows:

\[
\begin{align*}
\vdots \quad \text{N} \equiv \text{C} \equiv \vdots \\
-1 & \quad +1 & \quad -1 \\
\end{align*}
\]

The nonzero formal charges for the atoms are given. These were calculated using the formula in Section 3.1(b), Formal charges. The number of lone pair electrons (not the number of lone pairs) and half the number of shared electrons are subtracted from the number of valence electrons on the parent atom. The resonance structure on the left is likely to be the dominant one, since it contains smaller formal charges. In addition, the resonance structure on the right is probably not very important because it puts a high negative formal charge on the least electronegative atom.
(b) NCO? This ion also has 16 electrons, and the two most important resonance structures are shown below. The nonzero formal charges are given. The resonance structure on the left is likely to be the dominant one, since it puts the negative formal charge on 0, the most electronegative atom.

![Resonance structures for NCO](attachment:image.png)

3.3 Formal charges and oxidation numbers of NO$_2$? The resonance structures, nonzero formal charges, and oxidation numbers for nitrite ion are shown below:

<table>
<thead>
<tr>
<th>Formal Charges</th>
<th>Oxidation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>-2  +3  -2</td>
</tr>
<tr>
<td>-1</td>
<td>-2  +3  -2</td>
</tr>
</tbody>
</table>

The two structures shown are similar in that they both contain a N-O single bond and a N=O double bond. Therefore, they each contribute equally. The nitrogen atom in nitrite ion can be oxidized or reduced, since it is in the +3 oxidation state and since nitrogen can have oxidation numbers that range from -3 to +5. Both the oxidation number (+3) and the formal charge (0) on the nitrogen atom fail to give an accurate picture of its actual charge, which is slightly negative (that is, the negative charge is shared by all three atoms).

3.4 More Lewis structures?
(a) XeF$_4$? There is a straight-forward way to draw Lewis F structures with a central atom and some number of atoms. In this case, start with the Lewis structure of a xenon atom. Then consider how many fluorine atoms there are in the molecule, and use one of xenon’s electrons for each Xe-F bond. The complete Lewis structure of XeF$_4$ is shown below.

![Lewis structure of XeF$_4$](attachment:image.png)
(b) PF$_5$? The Lewis structure shows that the central P atom is surrounded by five bonding electron pairs.

\[ \text{PF}_5 \]

(c) BrF$_3$? Like the P atom in PF$_5$, the Br atom in BrF$_3$ is surrounded by five electron pairs, three bonding pairs and two lone pairs.

\[ \text{BrF}_3 \]

(d) TeCl$_4$? The Lewis structure for this molecule is shown below.

\[ \text{TeCl}_4 \]

(e) ICl$_2$? The central I atom has five electron pairs.

\[ \text{ICl}_2^- \]
3.5 What shape would you expect for:
(a) $\text{SO}_3$? With three bonds and no lone pairs, you should expect a trigonal-planar geometry (like $\text{BF}_3$). The shape of $\text{SO}_3$ is also shown below.

(b) $\text{SO}_3^{2-}$? With three bonds and one lone pair, you should expect a trigonal-pyramidal geometry (like $\text{NH}_3$). The shape of $\text{SO}_3^{2-}$ is also shown below.
(c) IF$_5$? With five a bonds and one lone pair, you should expect a square-pyramidal geometry.

3.6 The shapes of PC$_14$ and PC$_16$?
With four a bonds and no lone pairs for PC$_14^+$ and six bonds and no lone pairs for PC$_16^-$, the expected shapes are tetrahedral (like CC$_4^+$) and octahedral (like SF$_6^-$), respectively. In the tetrahedral PC$_14^+$ ion, all P-Cl bonds are the same length and all Cl-P-Cl bond angles are 109.5°. In the octahedral PC$_16^-$ ion, all P-Cl bonds are the same length and all Cl-P-Cl bond angles are either 90° or 180°. The P-Cl bond distances in the two ions would not necessarily be the same length.

3.7 Calculate bond lengths:
(a) CC$_4$ (observed value = 1.77 Å)? From the covalent radii values given in Table 3.4, 0.77 Å for C and 0.99 Å for Cl, the C-Cl bond length in CC$_4$ is predicted to be 0.77 Å + 0.99 Å = 1.76 Å. The agreement with the experimentally observed value is excellent.

(b) SiC$_4$ (observed value = 2.01 Å)? The covalent radius for Si is 1.18 Å. Therefore, the Si—Cl bond length in SiC$_4$ is predicted to be 1.18 Å + 0.99 Å = 2.17 Å. This is 8% longer than the observed bond length, so the agreement is not as good in this case.
(c) GeCl₄ (observed value = 2.10 Å)? The covalent radius for Ge is 1.22 Å. Therefore, the Ge-Cl bond length in GeCl₄ is predicted to be 2.21 Å. This is 5% longer than the observed bond length.

3.8 Si=O or Si—O in silicon-oxygen compounds?
This question is similar to the one addressed in Example 3.4. You need to consider the enthalpy difference between one mole of Si=O double bonds and two moles of Si-O single bonds. The difference is:

\[
2(\text{Si—O}) - (\text{Si=O}) = 2(466 \text{ kJ}) - (640 \text{ kJ}) = 292 \text{ kJ}
\]

Therefore, the two single bonds will always be better enthalpically than one double bond. If silicon atoms only have single bonds to oxygen atoms in silicon-oxygen compounds, the structure around each silicon atom will be tetrahedral: each silicon will have four single bonds to four different oxygen atoms.

3.9 Why is elemental nitrogen N₂ and elemental phosphorus P₄?
Diatomic nitrogen has a triple bond holding the atoms together, whereas six P-P single bonds hold together a molecule of P₄. If N₂ were to exist as N₄, N molecules with the P₄ structure, then two NN triple bonds would be traded for six N-N single bonds, which are intrinsically weak. The net enthalpy change can be estimated from the data in Table 3.5 to be \(2(945 \text{ kJ}) - 6(163 \text{ kJ}) = 912 \text{ kJ}\), which indicates that the tetramerization of nitrogen is very unfavorable. On the other hand, multiple bonds between period 3 and larger atoms are not as strong as two times the analogous single bond, so P₂ molecules, each with a PP triple bond, would not be as stable as P₄ molecules, containing only P-P single bonds. In this case, the net enthalpy change for \(2\text{P}_2 \rightarrow \text{P}_4\) can be estimated to be \(2(481 \text{ kJ}) - 6(201 \text{ kJ}) = -244 \text{ kJ}\).
3.10 Calculate $\Delta H$ from mean bond enthalpies?
For the reaction:

$$2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$$

Since you must break two moles of H-H bonds and one mole of 0=0 bonds on the left-hand side of the equation and form four moles of 0-H bonds on the right-hand side, the enthalpy change for the reaction can be estimated as:

$$2(436 \text{ kJ}) + 497 \text{ kJ} - 4(463 \text{ kJ}) = -483 \text{ kJ}$$

The experimental value is -484 kJ, which is in closer agreement with the estimated value than ordinarily expected. Since Table 3.5 contains average bond enthalpies, there is frequently a small error when comparing estimates to a specific reaction.

3.12 How many unpaired electrons?
(a) $\text{O}_2^-$?
You must write the electron configurations for each species, using Figure 3.14, and then apply the Pauli exclusion principle to determine the situation for incompletely filled degenerate orbitals. In this case the electron configuration is

$$1\sigma_g^2 2\sigma_u^2 2\pi_g^2 1\pi_u^4 1\pi_g^3$$

With three electrons in the pair of $2\pi_g$ molecular orbitals, one electron must be unpaired. Thus, the superoxide anion has a single unpaired electron.

(b) $\text{O}_2^+$?
The configuration is

$$1\sigma_g^2 2\sigma_u^2 2\pi_g^2 1\pi_u^4 1\pi_g^1$$

so the oxygenyl cation also has a single unpaired electron.

(c) BN?
You can assume that the energy of the $3\sigma_g$ molecular orbital is higher than the energy of the $1\pi_u$ orbitals, since that is the case for CO (see Figure 3.22). Therefore, the configuration is

$$1\sigma_g^2 2\sigma_u^2 1\pi_u^4$$

and, as observed, this diatomic molecule has no unpaired electrons. If the configuration were

$$1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$$

the molecule would have two unpaired electrons since each of the $1\pi_u$ orbitals would contain an unpaired electron, in accordance with the Pauli exclusion principle.

(d) NO-$^-$?
The exact ordering of the $3\sigma_g$ and $1\pi_u$ energy levels is not clear in this case, but it is not relevant either as far as the number of unpaired electrons is concerned. The configuration is either

$$1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 2\pi_g^2$$

or it is

$$1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^2$$

In either case, this anion has two unpaired electrons, and these electrons occupy the set of antibonding $2\pi_g$ molecular orbitals.
3.13 Writing electron configurations?
(a) Be₂? Only four valence electrons for two Be atoms gives the electron configuration
\[ l\sigma_g^2 l\sigma_u^2 \]
(b) B₂? The electron configuration is
\[ l\sigma_g^2 l\sigma_u^2 l\pi_u^2 \]
(c) C₂⁻? The electron configuration is
\[ l\sigma_g^2 l\sigma_u^2 l\pi_u^4 2\sigma_g^1 \]
(d) F₂⁺? The electron configuration is
\[ l\sigma_g^2 l\sigma_u^2 2\sigma_g^2 l\pi_u^4 l\pi_g^3 \]

3.14 Determining bond orders? The Lewis structures for the three species are shown below:

(a) S₂? The electron configuration of this diatomic molecule is
\[ l\sigma_g^2 l\sigma_u^2 2\sigma_g^2 l\pi_u^4 l\pi_g^2 \]
The bonding molecular orbitals are \( l\sigma_g, 2\sigma_g \) and \( l\pi_u \), while the antibonding molecular orbitals are \( l\sigma_u, \) and \( l\pi_g \). Therefore, the bond order is 
\[ \frac{1}{2}(2 + 4 + 2) - (2 + 2) = 2, \]
which is consistent with the double bond between the S atoms suggested by the Lewis structure.

(b) Cl₂? The electron configuration is
\[ l\sigma_g^2 l\sigma_u^2 2\sigma_g^2 l\pi_u^4 l\pi_g^4 \]
The bonding and antibonding orbitals are the same as for \( S_2 \), above. Therefore, the bond order is 
\[ \frac{1}{2}((2 + 4 + 2) - (2 + 4)) = 1 \]
which is in harmony with the single bond between the Cl atoms indicated by the Lewis structure.

(c) NO⁻? The electron configuration is
\[ l\sigma_g^2 2\sigma_g^2 3\sigma_g^2 l\pi_u^4 2\pi_g^4 \]
which is the same as the configuration for \( S_2 \), shown above. Thus, the bond order for NO⁻ is 2, as for \( S_2 \), once again in harmony with the conclusion based on the Lewis structure.
3.16 Linear H₄ MOs?
Four atomic orbitals can yield four independent linear combinations. The four relevant ones in this case, for a hypothetical linear H₄ molecule, are shown below in order of increasing energy. The most stable orbital has the fewest nodes (i.e. the electrons in this orbital are not excluded from the internuclear regions), the next orbital in energy has only one node, and so on to the fourth and highest energy orbital, with three nodes (a node between each of the four H atoms).

![Energy Diagram](image)

3.18 Average bond order in NH₃?
The molecular orbital energy diagram for ammonia is shown in Figure 3.33. The interpretation given in the text was that the 2a₁ molecular orbital is almost nonbonding, so the electron configuration 1a₁⁴₂e⁴2a₁⁴ results in only three bonds ((2 + 4)/2 = 3). Since there are three N-H “links”, the average N-H bond order is 1 (3/3 = 1).

3.22 Distinguish between a metal and a semiconductor?
(a) Simple band picture? The band pictures for a metal and for two types of semiconductors are shown below:

![Band Diagrams](image)

The band gap, $E_g$, for semiconductors is an important property. For the one on the left, $E_g$ is about the same size as $RT_{room}$ and its conductivity will be much larger than for the one on the right, for which $E_g >> RT_{room}$. 
(b) **Temperature dependence?** The electrical conductivity of a metal decreases as the temperature is increased. This is because increasing the temperature increases lattice vibrations, which reduce the freedom of electrons to move through the solid. In contrast, the electrical conductivity of a semiconductor increases as the temperature is increased. This is because increasing the temperature increases the thermal energy of the electrons in the solid. Thus, more electrons are excited from the filled valence band to the empty conduction band, which more than offsets the effect of lattice vibrations. Therefore, at higher temperatures more charge carriers are present in a semiconductor and the conductivity increases. Over a broad temperature range, this thermal promotion of electrons has a greater influence on conductivity than the vibrations which decrease conductivity.

(c) **Insulator vs. semiconductor?** The conductivity of an insulator is very low but it does increase as the temperature is increased. Therefore, it is not possible to distinguish between a semiconductor and an insulator by the temperature dependence of their conductivities. In fact, the two types of materials are both thought of as semiconductors. They correspond to the two different situations shown in the band pictures above (the insulator has $E_g > RT_{\text{room}}$).