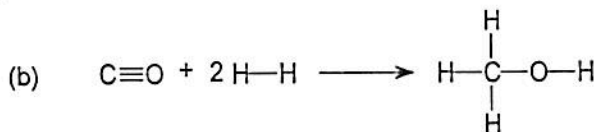8.63   *Plan.* Draw structural formulas so bonds can be visualized. Then use Table 8.4 and Equation
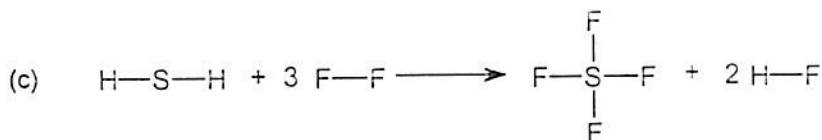
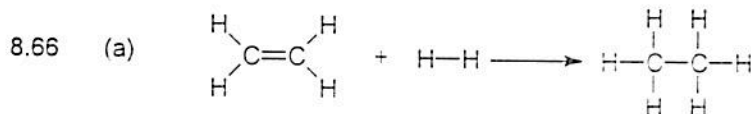8.11.   *Solve:*

(a)   2 Br—N—Br + 3 F—F ⟶ 2 F—N—F + 3 Br—Br
　　　　　　|　　　　　　　　　　　　　　　|
　　　　　　Br　　　　　　　　　　　　　　F

　　　　$\Delta H = 6D(N\text{-}Br) + 3D(F\text{-}F) - 6D(N\text{-}F) - 3D(Br\text{-}Br)$
　　　　　　$= 6(243) + 3(155) - 6(272) - 3(193) = -288$ kJ

(b)   C≡O + 2 H—H ⟶ H—C—O—H (with H above and H below the C)

　　　　$\Delta H = D(C \equiv O) + 2D(H\text{-}H) - 3D(C\text{-}H) - D(C\text{-}O) - D(O\text{-}H)$
　　　　　　$= 1072 + 2(436) - 3(413) - 358 - 463 = -116$ kJ

(c)   H—S—H + 3 F—F ⟶ F—S—F + 2 H—F (with F above and F below the S)

　　　　$\Delta H = 2D(S\text{-}H) + 3D(F\text{-}F) - 4D(S\text{-}F) - 2D(H\text{-}F)$
　　　　　　$= 2(339) + 3(155) - 4(327) - 2(567) = -1299$ kJ

8.66   (a)   H₂C=CH₂ + H—H ⟶ H—C—C—H (ethane)

　　　　$\Delta H = 4D(C\text{-}H) + D(C=C) + D(H\text{-}H) - 6D(C\text{-}H) - D(C\text{-}C)$
　　　　　　$= D(C=C) + D(H\text{-}H) - 2D(C\text{-}H) - D(C\text{-}C)$
　　　　$\Delta H = 614 + 436 - 2(413) - 348 = -124$ kJ

(b) $\Delta H° = \Delta H_f° \ C_2H_6(g) - \Delta H_f° \ C_2H_4(g) - \Delta H_f° \ H_2(g)$
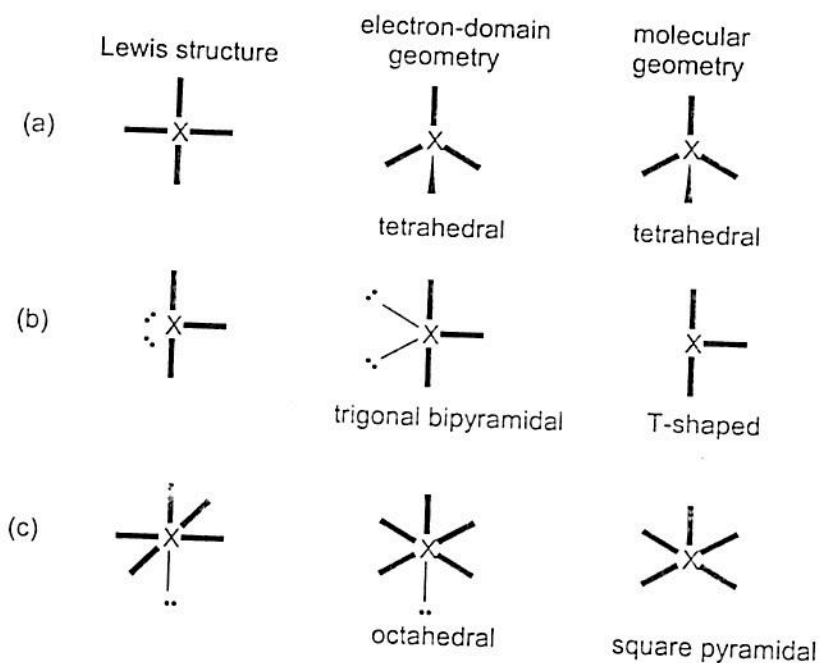　　　　　　$= -84.68 - 52.30 - 0 = -136.98$ kJ

The values of ΔH for the reaction differ because the bond enthalpies used in part (a) are average values that can differ from one compound to another. For example, the exact enthalpy of a C–H bond in C_2H_4 is probably not equal to the enthalpy of a C–H bond in C_2H_6. Thus, reaction enthalpies calculated from average bond enthalpies are estimates. On the other hand, standard enthalpies of formation are measured quantities and should lead to accurate reaction enthalpies. The advantage of average bond enthalpies is that they can be used for reactions where no measured enthalpies of formation are available.

9.2   In a symmetrical tetrahedron, the four bond angles are equal to each other, with values of 109.5°. The H–C–H angles in CH_4 and the O–Cl–O angles in ClO_4^- will have values close to 109.5°.

9.9   Analyze/Plan. See Table 9.3. *Solve:*

	Lewis structure	electron-domain geometry	molecular geometry

(a)

tetrahedral   tetrahedral

(b)

trigonal bipyramidal   T-shaped

(c)

octahedral   square pyramidal

9.14   (a)   electron-domain geometries: i, octahedral; ii, tedrahedral; iii, trigonal bipyramidal
       (b)   nonbonding electron domains: i, 2; ii, 0; iii, 1
       (c)   S or Se. Shape iii has 5 electron domains, so A must be in or below the third row of the periodic table. This eliminates Be and C. Assuming each F atom has 3 nonbonding electron domains and forms only single bonds with A, A must have 6 valence electrons to produce these electron-domain and molecular geometries.
       (d)   Xe. (See Table 9.3) Assuming F behaves typically, A must be in or below the third row and have 8 valence electrons. Only Xe fits this description. (Noble gas elements above Xe have not been shown to form molecules of the type AF_4. See Section 7.8.)
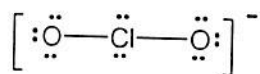
9.16   (a)   1 – 109°, 2 – 120°   (b) 3 – 109°, 4 – 120°
       (c)   5 – 109°, 6 – 109°   (d) 7 – 180°, 8 – 109°

9.28 Each C–Cl bond is polar. The question is whether the vector sum of the C–Cl bond dipoles in each molecule will be nonzero. In the *ortho* and *meta* isomers, the C–Cl vectors are at 60° and 120° angles, respectively, and their resultant dipole moments are nonzero. In the *para* isomer, the C–Cl vectors are opposite, at an angle of 180°, with a resultant dipole moment of zero. The *ortho* and *meta* isomers are polar, the *para* isomer is nonpolar.

PS
#13

9.18 (a) ClO_2^- 20 e⁻, 10 e⁻ pr

NO_2^- 18 e⁻, 9 e⁻ pr

$$\left[:\ddot{O}\!-\!\ddot{C}l\!-\!\ddot{O}: \right]^- \qquad \left[\ddot{O}\!=\!\ddot{N}\!-\!\ddot{O}: \right]^- \longleftrightarrow \left[:\ddot{O}\!-\!\ddot{N}\!=\!\ddot{O} \right]^-$$
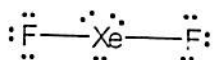
4 e⁻ domains around Cl
tetrahedral e⁻ domain geometry
bent molecular geometry
bond angle ≤ 109.5°
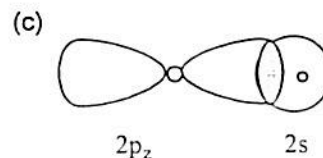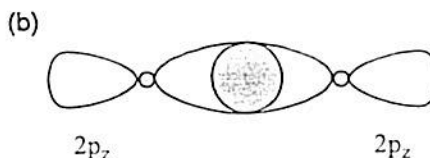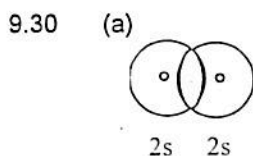
3 e⁻ domains about N
(both resonance structures)
trigonal planar e⁻ domain geometry
bent molecular geometry
bond angle ≤ 120°

Both molecular geometries are described as 'bent" because both molecules have two nonlinear bonding electron domains. The bond angles (the angle between the two bonding domains) in the two ions are different because the total number of electron domains, and thus the electron domain geometries are different.
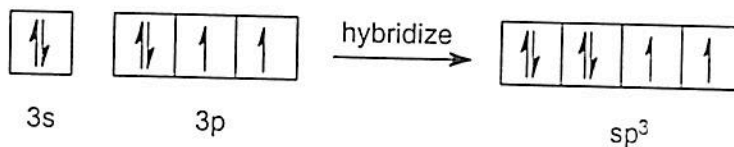
(b) XeF_2 22 e⁻, 11 e⁻ pr

$$:\ddot{F}\!-\!\ddot{Xe}\!-\!\ddot{F}:$$

5 e⁻ domains around Xe
trigonal bipyramidal e⁻ domain geometry
linear molecular geometry

9.30 (a)   (b)   (c)

2s   2s $2p_z$ $2p_z$ $2p_z$ 2s

9.36 (a)   S: [Ne]$3s^23p^4$

$$\boxed{\uparrow\downarrow}\quad \boxed{\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow\,|\;} \xrightarrow{\text{hybridize}} \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow\,|\;}$$
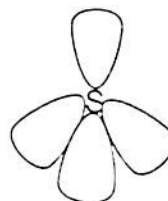
3s   3p   sp³

(b)   The hybrid orbitals are called sp³.   (c)
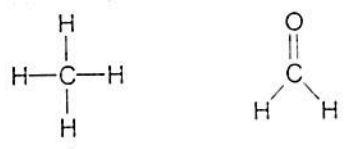
(d)   The hybrid orbitals formed in (a) would not be appropriate for SF_4. There are 5 electron domains in SF_4, 4 bonding and one nonbonding, so 5 hybrid orbitals are required. A set of 4 sp³ hybrid orbitals could not accommodate all the electron pairs around S.

9.41 (a)

H—C—H (with H on top and H on bottom)   O=C (with H and H below)

(b) sp^3 sp^2

(c)   The C atom in CH_4 is sp^3 hybridized; there are no unhybridized p orbitals available for the π overlap required by multiple bonds. In CH_2O, the C atom is sp^2 hybridized, with 1 p atomic orbital available to form the π overlap in the C=O double bond.
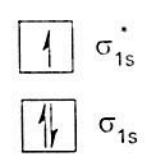
9.44 (a)   The C bound to H has 3 electron domains and is sp^2 hybridized.
The C bound to O has 2 electron domains and is sp hybridized.

(b) C_2H_2O has $2(4) + 2(1) + 6 = 16$ valence electrons.

(c)   4 pairs or 8 total valence electrons form σ bonds

(d)   2 pairs or 4 total valence electrons form π bonds

(e)   2 pairs or 4 total valence electrons are nonbonding

9.52 (a)

H_2^-

(b)   ↑ σ^*_{1s}

↑↓ σ_{1s}
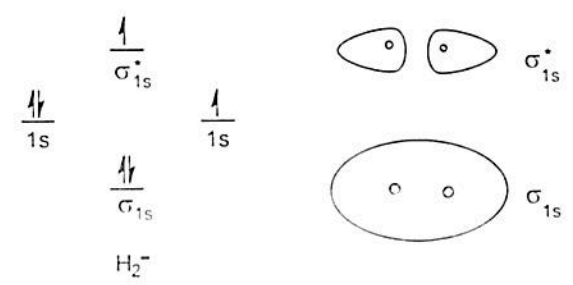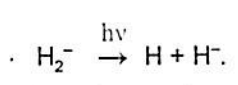
(c) Bond order $= 1/2 (2-1) = 1/2$

(d)   If 1 electron moves from σ_{1s} to σ^*_{1s}, the bond order becomes -1/2. There is a net increase in energy relative to isolated H atoms, so the molecule will decompose.
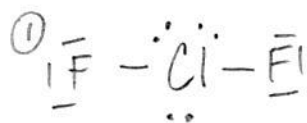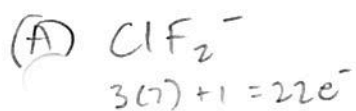
$H_2^- \xrightarrow{h\nu} H + H^-$.

9.56   (a) O_2^{2-} has a bond order of 1.0, while O_2^- has a bond order of 1.5. For the same bonded atoms, the greater the bond order the shorter the bond, so O_2^- has the shorter bond.

       (b)   The two possible orbital energy level diagrams are:

	σ_{2p}^{*}		σ_{2p}^{*}
□		□	
□□	π_{2p}^{*}	□□	π_{2p}^{*}
□□	π_{2p}	□	σ_{2p}
⬍	σ_{2p}	↑ ↑	π_{2p}
⬍	σ_{2s}^{*}	⬍	σ_{2s}^{*}
⬍	σ_{2s}	⬍	σ_{2s}
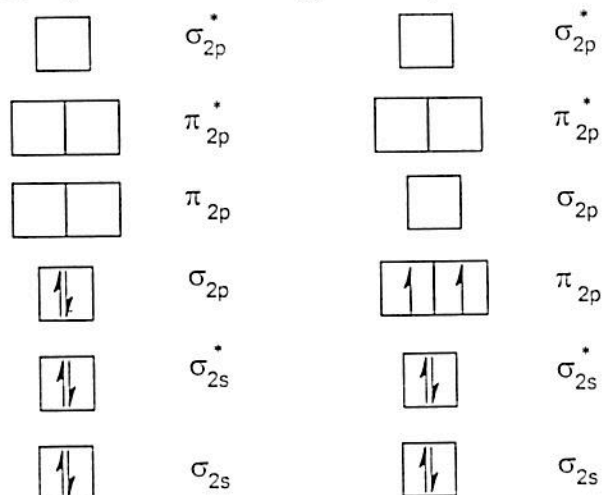
If the σ_{2p} molecular orbital is lower in energy than the π_{2p} orbitals, there are no unpaired electrons, and the molecule is diamagnetic. Switching the order of σ_{2p} and π_{2p} gives 1 unpaired electron in each degenerate π_{2p} orbital and explains the observed paramagnetism of B_2 (see Figure 9.41).
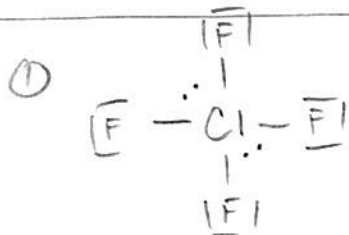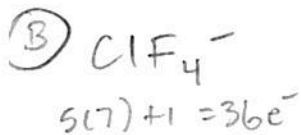
MORE FUN!! <u>KEY</u>

(A) ClF_2^-
3(7)+1 = 22e⁻

① $|\overline{F} - \overset{..}{\underset{..}{Cl}} - \overline{F}|$

② trigonal bipyramidal

③ linear

$\overset{F}{\underset{F}{\underset{|}{\overset{|}{\overset{..}{\underset{..}{Cl}}}}}} :$

④ 180° ⑤ Sp^3d ⑥ nonpolar

(B) ClF_4^-
5(7)+1 = 36e⁻

① $\overline{F} - \overset{\overline{|F|}}{\underset{|\underline{F}|}{\overset{|}{\underset{|}{Cl}}}} - \overline{F}|$

② octahedral

③ $\underset{F}{\overset{F}{\underset{F}{\overset{\,\,\,\,\,\,\,\,\,\,\,}{Cl}}}} \text{IIII} F$

SQUARE planar

④ 90°

⑤ Sp^3d^2

⑥ non-polar

© ClF_3
4(7) = 28e⁻

① $\overset{\overline{|F|}}{\underset{\underline{|F|} \quad \underline{F|}}{:Cl:}}$
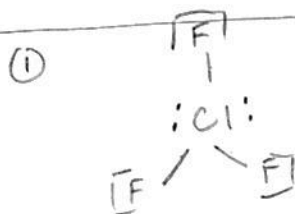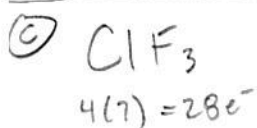
② trig. bipyramidal

③ $\overset{F}{\underset{F}{\overset{|}{\underset{|}{::Cl - F}}}}$ "T" shape

④ 90°/180° Actually slightly less

⑤ Sp^3d

⑥ polar.

(D) ClF_5
6(7) = 42e⁻

① $\overset{\overline{|F|}}{\underset{\underline{|F|} \quad \underline{F|}}{\overset{(F \quad \overline{F|})}{:Cl}}}$

② octahedral

③ $\underset{F}{\overset{F}{\underset{F}{\overset{|}{Cl}}}} \text{IIII} F$
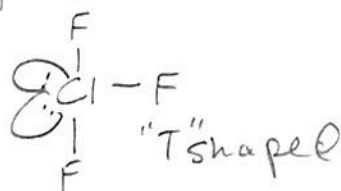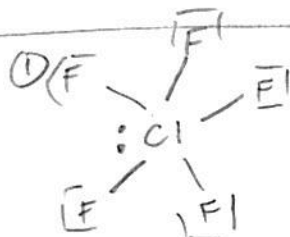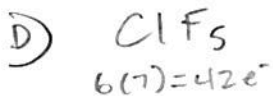
SQUARE pyramidal

④ 90°, slightly less than 90° on top angle

⑤ Sp^3d^2

⑥ polar ↑

(F) $ASO(OH)_3$
5+6 + 3(7) = 32e⁻

① $H - \overset{..}{\underset{..}{O}} - \overset{|\overline{O}|}{\underset{\underset{H}{\overset{..}{\underset{..}{O}}}}{\overset{|}{\underset{|}{As}}}} \text{---} \overset{..}{\underset{..}{O}} \text{---} H$
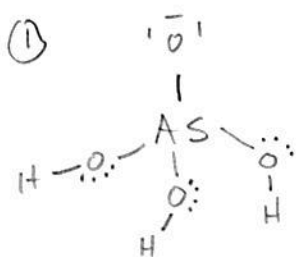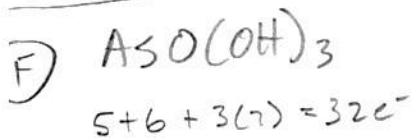
② (As) tetrahedral

③ (As) tetrahedral
OH bent

$H - \overset{..}{O} \overset{\overset{|\overline{O}|}{\underset{\overset{..}{\underset{..}{O}}}{\overset{|}{As}}}}{} \text{IIII} \overset{..}{O} - H$
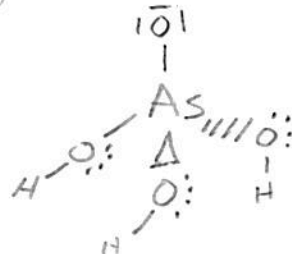
④ 109.5° tetrah (As)
~104.5 OH bent

⑤ Sp^3 (As)
Sp^3 (O)

⑥ POLAR ↑

(2) Ⓐ ~120° Ⓑ ~120° Ⓒ ~120° Ⓓ ≲120° ⓔ <109.5°

B ① sp^2 ② sp^2 ③ sp^2 ④ sp^2

Ⓒ $C=O$, $N-H$, $N-C$, $C-H$, $C-C$
most polar ← $\longleftrightarrow$ → least polar

Ⓓ 17σ , 4π

---

(3) AsF_3
$5(+21) = 26e$

Ⓐ

tetrahedral
w/ lone free
PAIR

AsF_5
$5 + 35$
$= 40e$

symmetrical trigonal
bi-pyramidal
(non-polar)

Ⓑ

$2(6)+5+1$
$= 18\acute{e}$

resonance, single/double
bonds are averaged due
to delocalized p orbitals
= same length
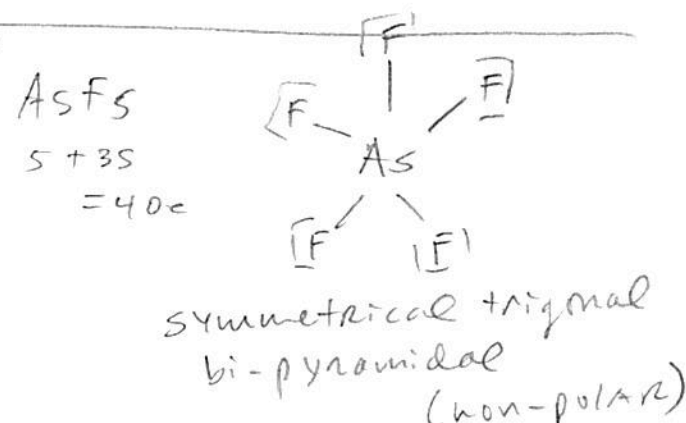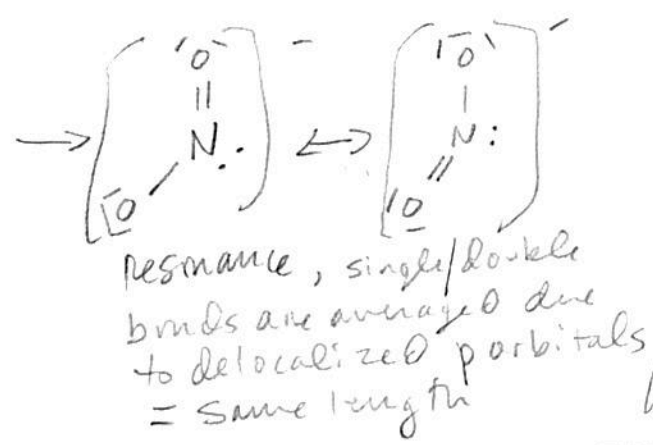
$18e^-$
HNO_2
NO resonance, no bond
ave.
$\ddot{O}=\ddot{N}-\ddot{O}-H$ ← no formal charges

note: this structure (below)
is not correct due to
Formal charges

$+1$ -1

$2(7)+6 = 20$

Ⓒ SF_2

$[F-\ddot{S}-\ddot{F}]$
tetrahedral.

$4(7)+6 = 34$

SF_4

See
SAW

SF_6

octahedral.

Oxygen has no expanded octet (2nd n value)
therefore it cannot be a seesaw or
an octahedral