FOCUS 2

MOLECULES

2A.1 (a) 5; (b) 4; (c) 7; (d) 3

2A.3 (a) [Ar]; (b) [Ar]$3d^{10}4s^2$; (c) [Kr]$4d^5$; (d) [Ar]$3d^{10}4s^2$

2A.5 (a) [Ar] $3d^{10}$; (b) [Xe]$4f^{14}5d^{10}6s^2$; (c) [Ar] $3d^{10}$; (d) [Xe] $4f^{14}5d^{10}$

2A.7 (a) [Kr]$4d^{10}5s^2$; same; In^+ and Sn^{2+} lose 5p valence electrons; (b) none; (c) [Kr]$4d^{10}$; Pd

2A.9 (a) Co^{2+}; (b) Fe^{2+}; (c) Mo^{2+}; (d) Nb^{2+}

2A.11 (a) Co^{3+}; (b) Fe^{3+}; (c) Ru^{3+}; (d) Mo^{3+}

2A.13 (a) 4s; (b) 3p; (c) 3p; (d) 4s

2A.15 (a) -2; (b) -2; (c) $+1$; (d) $+3$; (e) $+2$

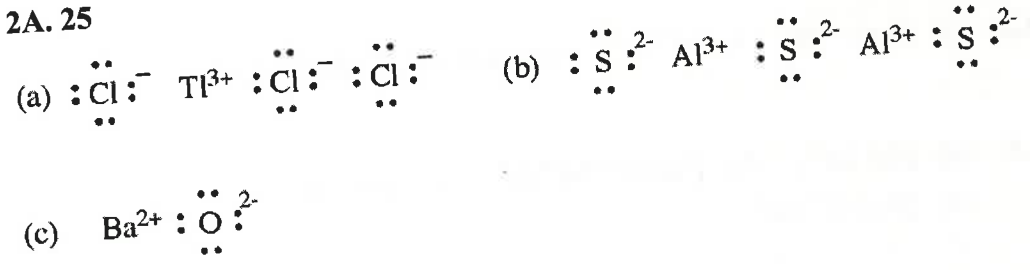
2A.17 (a) 3; (b) 6; (c) 6; (d) 2

2A.19 (a) [Kr] $4d^{10}5s^2$; no unpaired electrons; (b) [Kr]$4d^{10}$; no unpaired electrons; (c) [Xe]$4f^{14}5d^4$; four unpaired electrons; (d) [Kr]; no unpaired electrons; (e) [Ar] $3d^8$; two unpaired electrons

2A.21 (a) [Ar]; no unpaired electrons; (b) [Kr]$4d^{10}5s^2$; no unpaired electrons; (c) [Xe]; no unpaired electrons; (d) [Kr]$4d^{10}$; no unpaired electrons

2A.23 (a) Mg_3As_2; (b) In_2S_3; (c) AlH_3; (d) H_2Te; (e) BiF_3

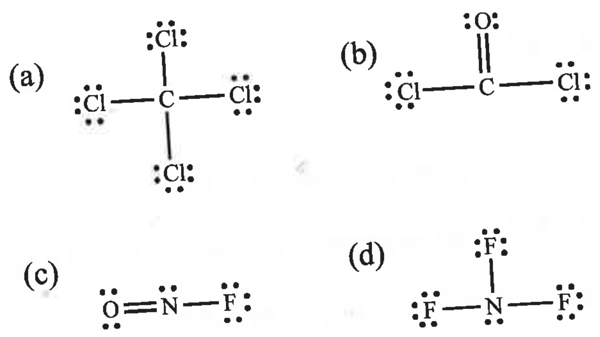
2A. 25



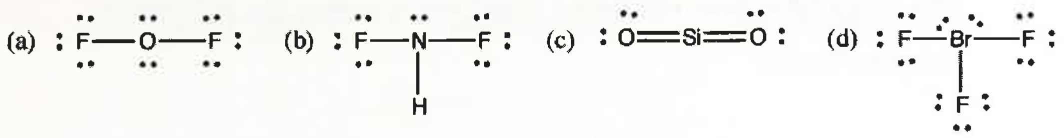
2A.27 The coulombic attraction is directly proportional to the charge on each ion (Equation 1) so the ions with the higher charges will give the greater coulombic attraction. The answer is therefore (b) Ga^{3+}, O^{2-}.

2A.29 The Li^+ ion is smaller than the Rb^+ ion (58 vs 149 pm). Because the lattice energy is related to the coulombic attraction between the ions, it will be inversely proportional to the distance between the ions (see Equation 2). Hence the larger rubidium ion will have the lower lattice energy for a given anion.

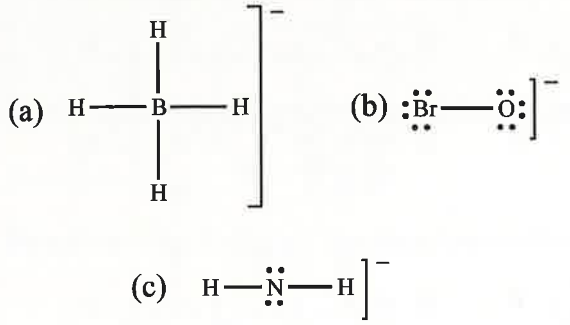
2B.1



2B.3

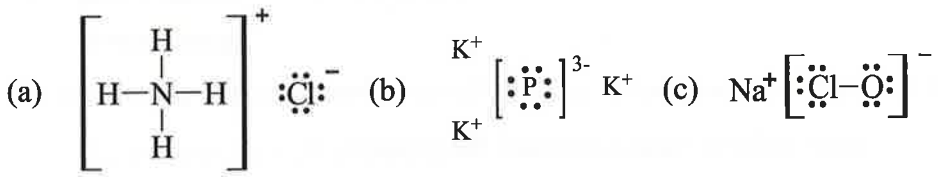


2B.5

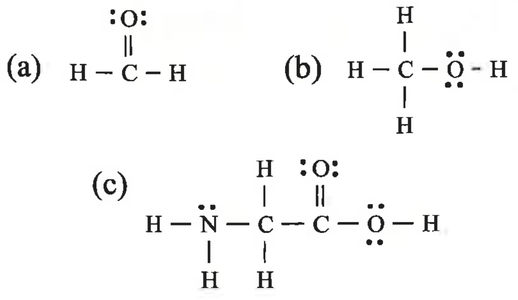


2B.7 The structure has a total of 32 electrons; of these, 21 are accounted for by the chlorines (three Cl × seven valence electrons each); of the 11 electrons remaining, six come from the oxygen. This leaves five electrons unaccounted for; these must come from E. Therefore, E must be a member of the nitrogen family and since it is a third period element E must be phosphorous (P).

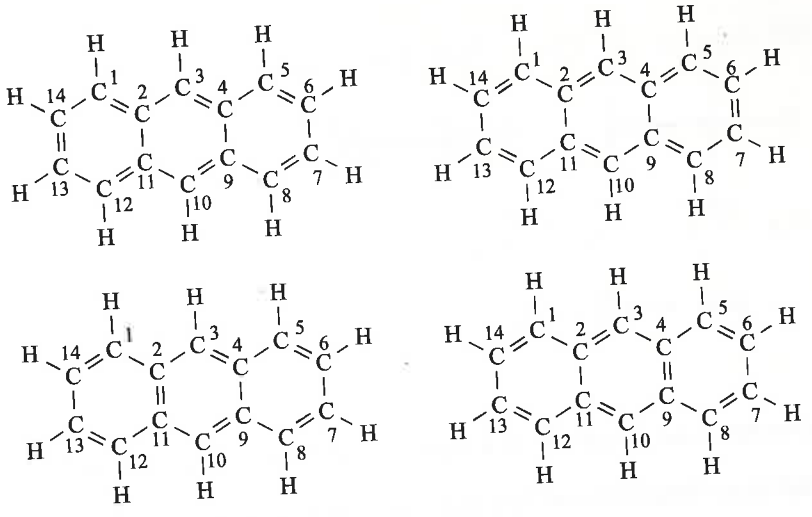
2B.9



2B.11



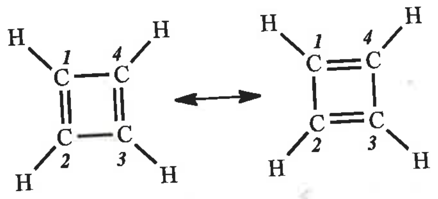
2B.13 There are four possible resonance structures one can draw for anthracene (the atoms have been numbered to aid you in seeing the differences between them):



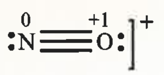
2B.15

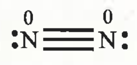
In both structures the N has a formal charge of +1 and the singly bound O has a formal charge of −1. All other atoms have formal charge of 0.

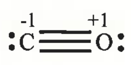
2B.17 The two resonance structures for cyclobutadiene are shown below (the carbons have been numbered for clarity):



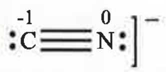
2B.19

(a) 

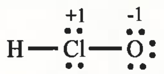
(b) 

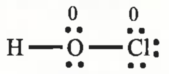
(c) 

(d) 

(e) 

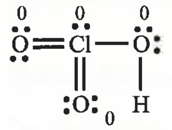
2B.21 Two possible structures for hypochlorous acid are:



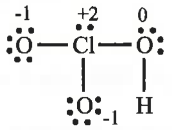


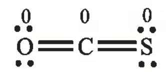
Based on formal charge, the structure on the right is the most likely.

2B.23

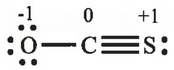
(a) 

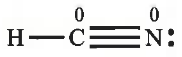
lower energy



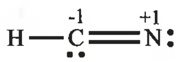
(b) 

lower energy



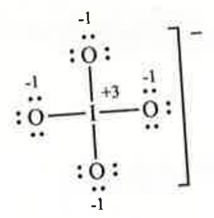
(c) 

lower energy

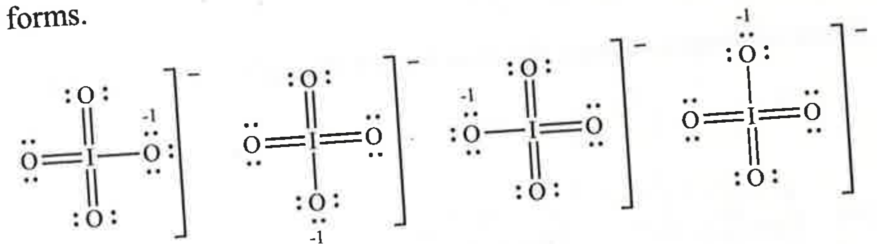


2C.1 Radicals are species with an unpaired electron, therefore only (b) and (c) are radicals since they have an odd number of electrons. (a) and (d) have an even number of electrons allowing Lewis structures to be drawn with all electrons paired.

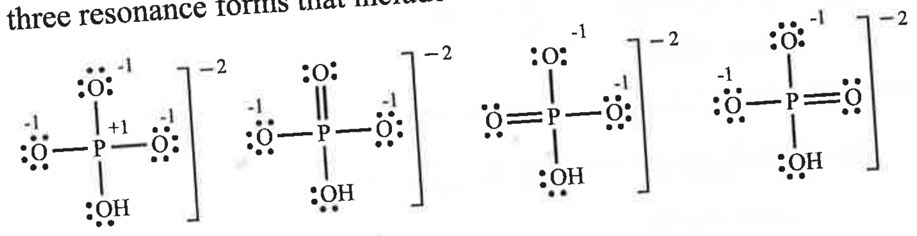
2C.3 (a) The periodate ion has one Lewis structure that obeys the octet rule:



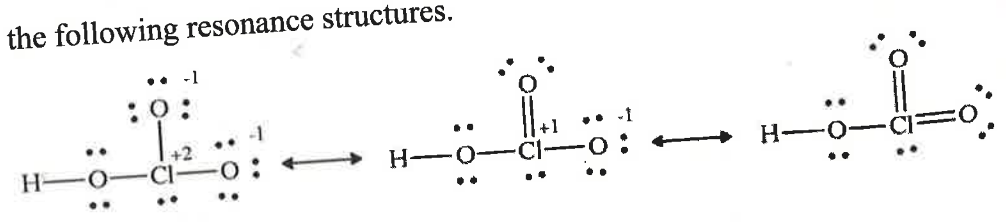
The formal charge of at I can be reduced to from +3 to 0 by including three double-bond contributions, thereby giving rise to four resonance forms.



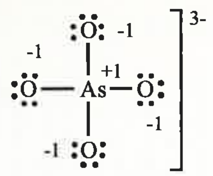
(b) The hydrogen phosphate ion has one Lewis structure that obeys the octet rule (the first structure shown below). The inclusion of one double bond to oxygen lowers the formal charge at P from +1 to 0. There are three resonance forms that include this contribution.



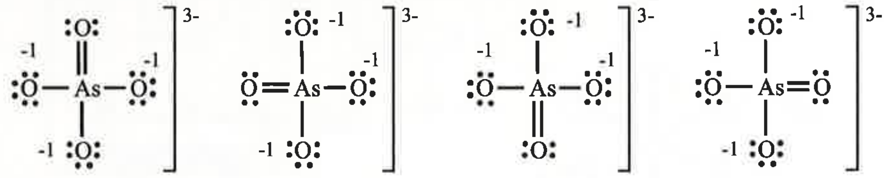
(c) There is one Lewis structure that obeys the octet rule shown below at the left. The formal charge at chlorine can be reduced to +1 by including one double bond contribution. The formal charge can be reduced to 0 if there are two double bond contributions. These contributions give rise to the following resonance structures.



(d) The arsenate ion has one Lewis structure that obeys the octet rule.

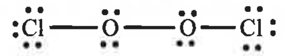


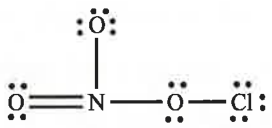
Just as in part (a), including one double bond to oxygen lowers the formal charge at As from +1 to 0. There are four resonance forms that include this contribution.



2C.5 The Lewis structures are

(a) 

(b) 

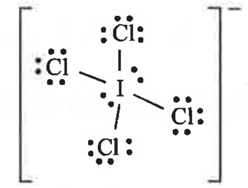
(c) 

Radicals are species with an unpaired electron, therefore only (a) is a radical.

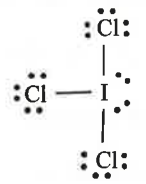
2C.7

(a) 

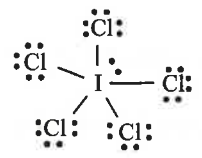
I has 2 bonding pairs
and 2 lone pairs

(b) 

I has 4 bonding pairs
and 2 lone pairs

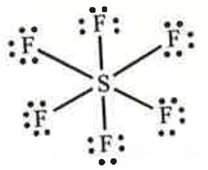
(c) 

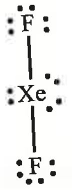
I has 3 bonding pairs
and 2 lone pairs

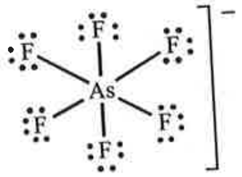
(d) 

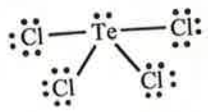
I has 5 bonding pairs
and 1 lone pair

2C.9

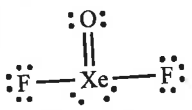
(a)

12 electrons

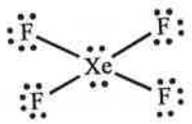
(b)

10 electrons

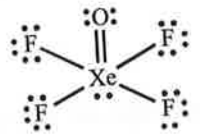
(c)

12 electrons

(d)

10 electrons

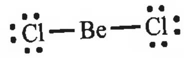
2C.11

(a)

2 lone pair

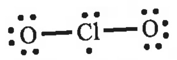
(b)

2 lone pair

(c)

1 lone pair

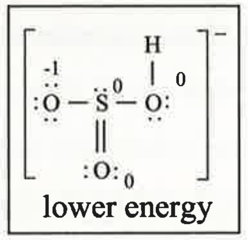
2C.13 (a) In $BeCl_2$, there are 4 electrons around the central beryllium:

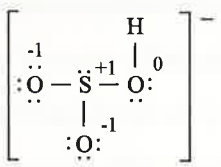


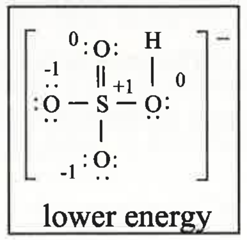
(b) In ClO_2 there are an odd number of electrons around the central chlorine:

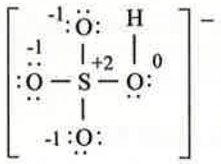


2C.15

(a)

lower energy



(b)

lower energy



2C.17 (a) In the first structure, the formal charges at Xe and F are 0, whereas, in the second structure, Xe is −1, one F is 0, and the other F is +1. The first structure is favored on the basis of formal charges. (b) In the first structure, all of the atoms have formal charges of 0, whereas, in the second structure, one O atom has a formal charge of +1 and the other O has a formal charge of −1. The first structure is thus preferred.

2D.1 In (1.78) < Sn (1.96) < Sb (2.05) < Se (2.55)

2D.3 $BaBr_2$ would have bonds that are primarily ionic. The electronegativity difference is greater between Ba and Br than between B or Be and Br, making the Ba—Br bond more ionic.

2D.5 (a) The bond in HCl would be more ionic. The electronegativity difference is greater between H and Cl than between H and I, making the H—Cl bond more ionic.

(b) The bonds in CF_4 would be more ionic. The electronegativity difference is greater between C and F than between C and H, making the C—F bonds more ionic.

(c) C and S have nearly identical electronegativities, so the C—S bonds would be expected to be almost completely covalent, whereas the C—O bonds would be more ionic.

2D.7 (a) The electronegativity difference between K and Cl (2.34) is greater than that between Al and Cl (1.55), so KCl should be more soluble in water than $AlCl_3$. (b) The electronegativity difference between Mg and O is 2.13 while it is 2.55 when comparing Ba and O, therefore BaO should be more water soluble than MgO.

2D.9 $Rb^+ < Sr^{2+} < Be^{2+}$; smaller, more highly charged cations have greater polarizing power. The ionic radii are 149 pm, 116 pm, 27 pm, respectively.

2D.11 $O^{2-} < N^{3-} < Cl^- < Br^-$; the polarizability increases as the ion gets larger and less electronegative. The ionic radii for these species are 140 pm, 171 pm, 181 pm, 196 pm, respectively.

2D.13 (a) $CO_3^{2-} > CO_2 > CO$

CO_3^{2-} will have the longest C—O bond length. In CO there is a triple bond and in CO_2 the C—O bonds are double bonds. In carbonate, the bond is an average of three Lewis structures in which the bond is double in one form and single in two of the forms. We would thus expect the bond order to be approximately 1.3. Because the bond length is inversely related to the number of bonds between the atoms, we expect the bond length to be longest in carbonate.

(b) $SO_3^{2-} > SO_2 \sim SO_3$

Similar arguments can be used for these molecules as in part (a). In SO_2 and SO_3, the Lewis structures with the lowest formal charge at S have double bonds between S and each O. In the sulfite ion, however, there are

three Lewis structures that have a zero formal charge at S. Each has one S—O double bond and two S—O single bonds. Because these S—O bonds would have a substantial amount of single bond character, they would be expected to be longer than those in SO_2 or SO_3. This is consistent with the experimental data that show the S—O bond lengths in SO_2 and SO_3 to be 143 pm, whereas those in SO_3^{2-} range from about 145 pm to 152 pm depending on the compound.

(c) $CH_3NH_2 > CH_2NH > HCN$

The C—N bond in HCN is a triple bond, in CH_2NH it is a double bond, and in CH_3NH_2 it is a single bond. The C—N bond in the last molecule would, therefore, be expected to be the longest.

2D.15 Of CF_4, CCl_4, and CBr_4, CF_4 is predicted to have the strongest C—X bond; it is the shortest of the three bonds. Note that electronegativity and polarity arguments would predict the C—F bond to be the weakest.

2D.17 (a) The C—O bonds in carbon dioxide are double bonds. The covalent radius for doubly bonded carbon is 67 pm and that of O is 60 pm. Thus we predict the C=O in CO_2 to be ca. 127 pm. The experimental bond length is 116.3 pm.

(b) The C—O bond is a double bond so it would be expected to be the same as in (a), 127 ppm. This is the experimentally found value. The C—N bonds are single bonds and so one might expect the bond distance to be the sum of the single bond C radius and the single bond N radius (77 plus 75 pm) which is 152 pm. However, because the C atom is involved in a multiple bond, its radius is actually smaller. The sum of that radius (67 pm) and the N single bond radius gives 142 pm, which is close to the experimental value of 133 pm.

(c) The O—Cl bond is a single bond so we expect the bond distance to be 74 pm + 98 pm or 172 pm. The experimental value is 169 pm.

(d) The N—Cl bond is a single bond so we predict the bond distance to be 75 pm + 98 pm or 173 pm. However, because the N atom is involved in a multiple bond with oxygen, its radius should actually be smaller. The sum of that radius (60 pm) and the Cl single bond radius gives a predicted bond length of 158 pm.

NOTE: Parts (b) and (d) of this question raise an interesting point concerning the radius to use for the A—X single bond in Y=A—X. The double bond that A forms with Y shrinks the A atom down to a smaller size, and even though the A—X link is a single bond, there is a strong argument for using the double-bond radius of A in predicting the A—X bond length. In many cases this assumption compares reasonably well with the experimental values seen, suggesting that the A atom has indeed been shrunk by its formation of a neighboring double bond. A caveat does warrant mention here: this assumption is based on a high degree of covalent character being present in the A—X bond; as the amount of ionic character increases, so does the bond length. This is reflected in the actual experimental value of 198 pm seen for the N—Cl bond. In fact. NOCl behaves as if it was actually O=N$^+$— C$^-$ in many of the reactions it undergoes, demonstrating that there exists a high degree of ionic character not accounted for in the simple model used here.

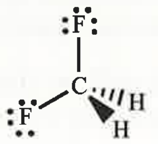
2D.19 (a) 77 pm + 58 pm = 135 pm; (b) 111 pm + 58 pm = 169 pm; (c) 141 pm + 58 pm = 199 pm. Bond distance increases with atomic size going down Group 14/IV.

2E.1 (a) Must have lone pairs; (b) May have lone pairs.

2E.3

(a) :N≡C—H linear

(b)



tetrahedral

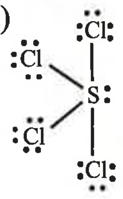
2E.5 (a) The shape is angular; the electron pair on the central Cl atom results in a trigonal planar arrangement. (b) The bond angle will be slightly less than 120°.

2E.7 (a) The shape of the thionyl chloride molecule is trigonal pyramidal. (b) The O—S—Cl angles are identical. The lone electron pair repels the bonded electron pairs equally thus, all O—S—Cl bond angles are compressed equally. (c) The expected bond angle is slightly less than 109.5°.

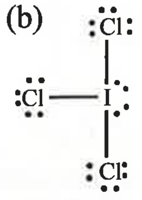
2E.9 (a) T-shaped; (b) slightly less than 90°

2E.11

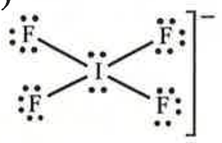
(a)



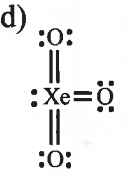
(b)



(c)



(d)



(a) The sulfur atom will have five pairs of electrons about it: one nonbonding pair and four bonding pairs to chlorine atoms. The arrangement of electron pairs will be trigonal bipyramidal; the nonbonding pair of electrons will prefer to lie in an equatorial position, because in that location the e-e repulsions will be lowest. The actual structure is described as a seesaw. AX_4E.

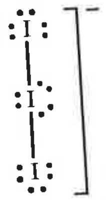
(b) Like the sulfur atom in (a), the iodine in iodine trichloride has five pairs of electrons about it, but here there are two lone pairs and three bonding pairs. The arrangement of electron pairs will be the same as in (a), and again the lone pairs will occupy the equatorial positions. Because the name of the molecule ignores the lone pairs, it will be classified as T-shaped. AX_3E_2.

(c) There are six pairs of electrons about the central iodine atom in IF_4^-. Of these, two are lone pairs and four are bonding pairs. The pairs will be placed about the central atom in an octahedral arrangement with the lone pairs opposite each other. This will minimize repulsions between them. The name given to the structure is square planar. AX_4E_2.

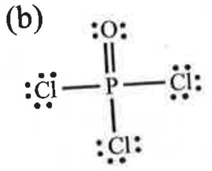
(d) In determining the shape of a molecule, double bonds count the same as single bonds. The XeO_3 structure has four "objects" about the central Xe atom: three bonds and one lone pair. These will be placed in a tetrahedral arrangement. Because the lone pair is ignored in naming the molecule, it will be classified as trigonal pyramidal. AX_3E.

2E.13 The Lewis structures are:

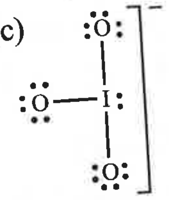
(a)



(b)

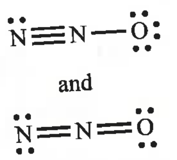


(c)



(resonance forms possible)

(d)



(a) The I_3^- molecule is predicted to be linear, so the I—I—I angle should equal 180°. AX_2E_3.

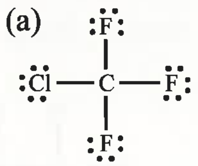
(b) The $POCl_3$ molecule is tetrahedral. All bond angles should be 109.5°. AX_4.

(c) The shape of IO_3^- will be a trigonal pyramid, so the O—I—O bond angles should be less than 109.5°. AX_3E.

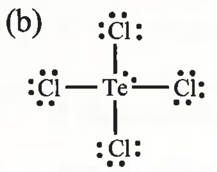
(d) The structure of N_2O is linear with a bond angle of 180°. AX_2.

2E.15 The Lewis structures are

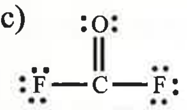
(a)



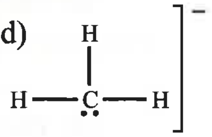
(b)



(c)



(d)



(a) The shape of CF_3Cl is tetrahedral; all halogen—C—halogen angles should be approximately 109.5°. AX_4;

(b) $TeCl_4$ molecules will be seesaw-shaped with Cl—Te—Cl bond angles of approximately 90° and 120°. AX_4E;

(c) COF_2 molecules will be trigonal planar with F—C—F and O—C—F angles of 120°. AX_3;

(d) CH_3^- ions will be trigonal pyramidal with H—C—H angles of slightly less than 109.5°. AX_3E.

2E.17 (a) slightly less than 120°; (b) 180°; (c) 180°; (d) slightly less then 109.5°

2E.19 (a) tetrahedral, bond angle of 109.5°

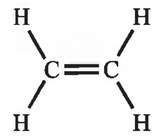
(b) tetrahedral about the carbon atoms (109.5°); C—Be—C angle of 180°

(c) angular, H—B—H angle slightly less than 120°

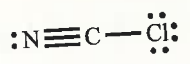
(d) angular, Cl—Sn—Cl angle slightly less than 120°

2E.21

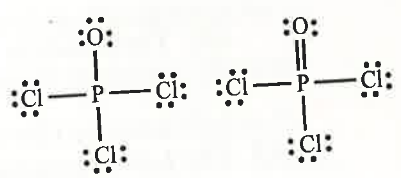
(a) H—C—H and H—C—C angles of 120°.



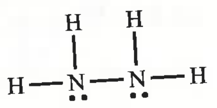
(b) Linear, 180°



(c) Tetrahedral, 109.5° (Note: Both are acceptable Lewis structures; the presence of the double bond makes the second molecule the more stable Lewis structure.)

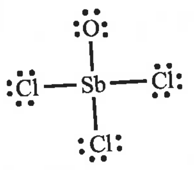


(d) The arrangement of atoms about each N is trigonal pyramidal giving H—N—H and H—N—N bond angles of approximately 107°.



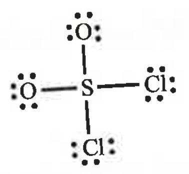
2E.23

(a)



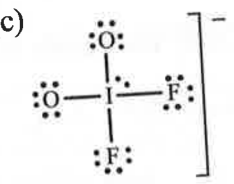
tetrahedral

(b)



tetrahedral

(c)

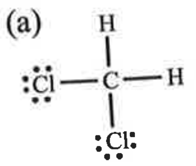


see-saw

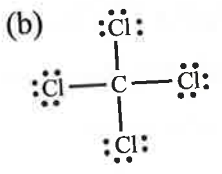
Note: Other acceptable Lewis structures are possible (those with double bonds between the central atom and oxygen, which are more stable structures due to the lowering of formal charge) but they do not change the shape of the molecule

2E.25 The Lewis structures are

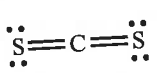
(a)



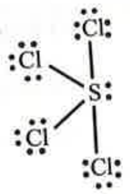
(b)



(c)



(d)



Molecules (a) and (d) are polar; (b) and (c) are nonpolar.

2E.27 (a) pyridine: polar; (b) ethane: nonpolar; (c) trichloromethane: polar

2E.29 (a) Of the three forms, **1** and **2** are polar; only **3** is nonpolar. This is because the C—Cl bond dipoles are pointing in exactly opposite directions in **3**. (b) The dipole moment for **1** would be the largest because the C—Cl bond vectors are pointing most nearly in the same direction in **1** (60° apart) whereas in **2** the C—Cl vectors point more away from each other (120°), giving a larger cancellation of dipole.

2F.1 (a) sp^3, orbitals oriented toward corners of a tetrahedron (109.5° apart);
(b) sp, orbitals oriented directly opposite to each other (180° apart);
(c) sp^{3}d^2, orbitals oriented toward the corners of an octahedron (interorbital angles of 90° and 180°);
(d) sp^2, orbitals oriented toward the corners of an equilateral triangle trigonal planar array (angles = 120°); trigonal planar

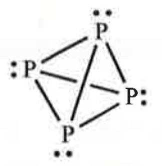
2F.3 (a) 2 σ bonds. 0 π bonds (b) 2 σ bonds. 1 π bonds, there is also a resonance structure that includes 2 σ bonds. 2 π bonds.

2F.5 (a) sp; (b) sp^2; (c) sp^3; (d) sp^3

2F.7 (a) sp^2; (b) sp^3; (c) sp^{3}d; (d) sp^3

2F.9 (a) sp^3; (b) sp^{3}d^2; (c) sp^{3}d; (d) sp^3

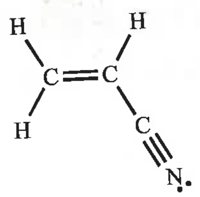
2F.11 The Lewis structure of tetrahedral P_4 is:



(a) Each phosphorous is attached to three other phosphorous atoms and a single lone pair, therefore its hybridization is sp^3.

(b) While each P within this structure is polar (due to the presence of a single lone pair on each phosphorous), P_4 is nonpolar due to the 3D orientations of those lone pairs.

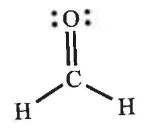
2F.13



The first two carbons (CH_2 and CH) are sp^2 hybridized with H—C—H and C—C—H angles of 120°. The third carbon (bonded to N) is sp hybridized with a C—C—N angle of 180°.

2F.15 As the s-character of a hybrid orbital increases, the bond angle increases.

2F.17 In formaldehyde, both the C and the O are sp^2 hybridized. The H—C—O bond angle is 120°; the molecule has three sigma bonds (one each connecting the two H and O to the C) and one pi bond (between the C and the O).



2F.19 Atomic orbitals a and b are mutually orthogonal if $\int a \cdot b \; d\tau = 0$ (assuming $a \neq b$) where the integration is over all space.

Furthermore, an orbital, a, is normalized if $\int a^2 \; d\tau = 1$.

In this problem, the two hybrid orbitals are: $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x + p_y - p_z$. Therefore, to show these two orbitals are orthogonal we must show $\int h_1 h_2 \; d\tau = 0$.

$$\int h_1 h_2 \; d\tau = \int (s + p_x + p_y + p_z)(s - p_x + p_y - p_z) d\tau =$$

$$\int (s^2 - sp_x + sp_y - sp_z + sp_x - p_x^2 + p_x p_y - p_x p_z + sp_y -$$

$$p_x p_y + p_y^2 - p_y p_z + sp_z - p_z p_x + p_z p_y - p_z^2) d\tau$$

Of course, this integral of a sum may be written as a sum of integrals:

$$\int s^2 d\tau - \int sp_x d\tau + \int sp_y d\tau - \int sp_z d\tau + \ldots$$

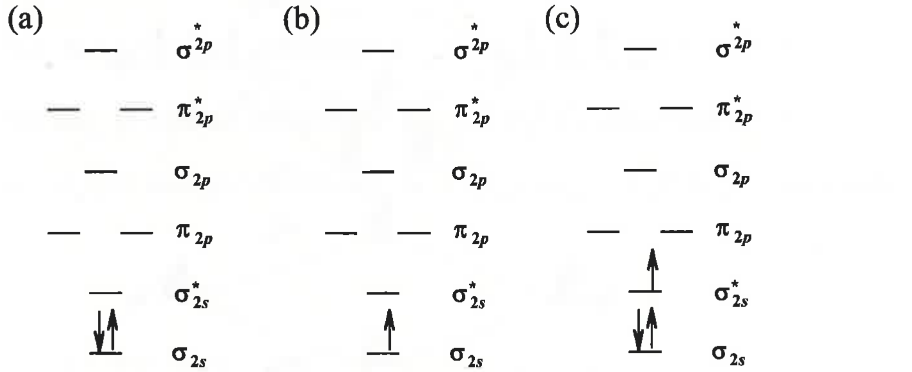
Because the hydrogen wavefunctions are mutually orthogonal, the members of this sum which are integrals of a product of two different wavefunctions are zero. Therefore, this sum of integrals simplifies to:

$$\int s^2 d\tau - \int p_x^2 d\tau + \int p_y^2 d\tau - \int p_z^2 d\tau = 1 - 1 + 1 - 1 = 0$$

(recall that the integral of the square of a normalized wavefunction is one.)

2F.21 We are given: $\lambda = -\dfrac{\cos\theta}{\cos^2(\frac{1}{2}\theta)}$. In the H_2O molecule, the bond angle is 104.5°. Therefore, $\lambda = 0.67$ and the hybridization is $sp^{0.67}$.

2G.1 The molecular orbital diagrams are as follows (only the valence electrons are shown):



(a) Li_2 $BO = \frac{1}{2}(2) = 1$; diamagnetic, no unpaired electrons

(b) Li_2^+ $BO = \frac{1}{2}(1) = \frac{1}{2}$; paramagnetic, one unpaired electron

(c) Li_2^- $BO = \frac{1}{2}(2-1) = \frac{1}{2}$; paramagnetic, one unpaired electron

2G.3 (a) (i) $(\sigma_{2s})^2(\sigma_{2s}{*})^2(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}{*})^4(\sigma_{2p}{*})^1$

(ii) $(\sigma_{2s})^2(\sigma_{2s}{*})^2(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}{*})^3$

(iii) $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}{}^*)^4(\sigma_{2p}{}^*)^2$

(b) (i) 0.5; (i) 1.5; (iii) 0

(c) (i) and (ii) are paramagnetic, with one unpaired electron each

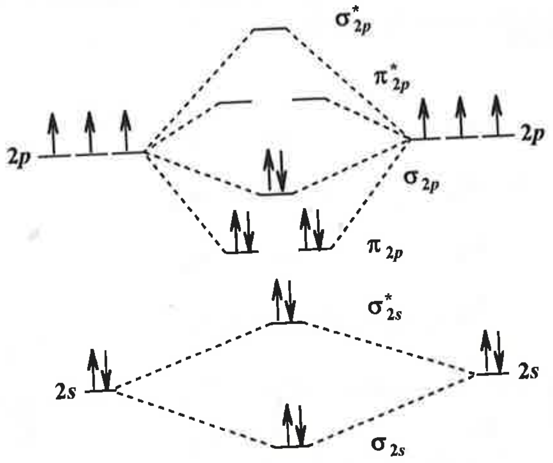
(d) σ for (i) and (iii), π for (ii)

2G.5 The charge on C_2^{n-} is –2 and the bond order is 3

$$\left(BO=\frac{1}{2}(2+4+2-2)=3\right).$$

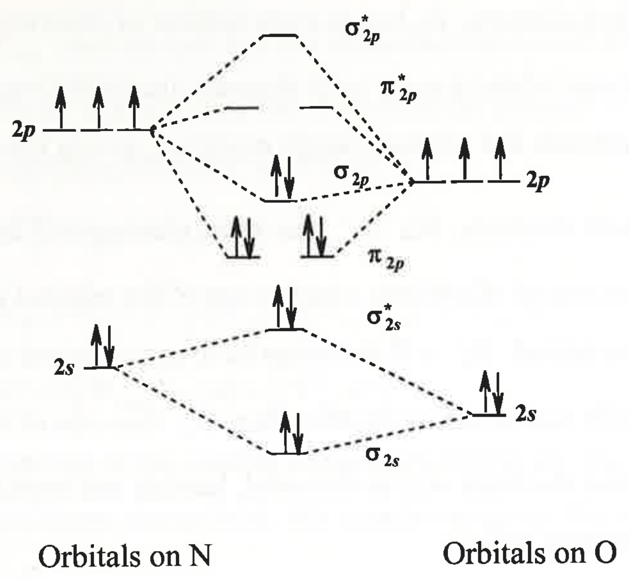
2G.7 HeH^- would not be expected to exist because its bond order is 0; BO = ½ (2 – 2) = 0. HeH^+ on the other hand would have a bond order of 1 and thus be lower in energy.

2G.9 (a) The energy level diagram for N_2 is as follows:



(b) The oxygen atom is more electronegative, which will make its orbitals lower in energy than those of N. The revised energy-level diagram is shown below. This will make all of the bonding orbitals closer to O than to N in energy and will make all the antibonding orbitals closer to N than to O in energy.

Energy level diagram for NO^+



(c) The electrons in the bonding orbitals will have a higher probability of being at O because O is more electronegative and its orbitals are lower in energy.

2G.11 (a) B_2 (6 valence electrons): $(\sigma_{2s})^2\,(\sigma_{2s}^*)^2\,(\pi_{2p})^2$, bond order = 1

(b) Be_2 (4 valence electrons): $(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2$, bond order = 0

(c) F_2 (14 valence electrons): $(\sigma_{2s})^2\,(\sigma_{2s}^*)^2\,(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}^*)^4$, bond order = 1

2G.13

CO: $\left(\sigma_{2s}\right)^2\left(\sigma_{2s}^*\right)^2\left(\pi_{2p}\right)^4\left(\sigma_{2p}\right)^2$; bond order = 3

CO^+: $\left(\sigma_{2s}\right)^2\left(\sigma_{2s}^*\right)^2\left(\pi_{2p}\right)^4\left(\sigma_{2p}\right)^1$; bond order = 2.5

Due to the higher bond order for CO, it should form a stronger bond and therefore have the higher bond enthalpy

2G.15 (a) – (c) All of these molecules possess unpaired electrons and therefore are paramagnetic. B_2^- and B_2^+ have an odd number of electrons and must, therefore, have at least one unpaired electron; indeed, both have only one unpaired electron. B_2 has an even number of electrons, but in its molecular orbital energy level diagram, the HOMO is a degenerate set of π_{2p} orbitals that are each singly occupied, giving this molecule two unpaired electrons. For B_2^-, one more electron will be placed in this degenerate set of orbitals, causing one of the original unpaired electrons to now be paired. B_2^- will therefore have one unpaired electron. Likewise, B_2^+ will have one less electron than B_2; thus one of the originally unpaired electrons will be removed, leaving one unpaired electron in this molecule as well.

2G.17 (a) F_2 with 14 valence electrons has a valence electron configuration of $(\sigma_{2s})^2(\sigma_{2s}*)^2(\sigma_{2p})^2\,(\pi_{2p})^4\,(\pi_{2p}*)^4$ with a bond order of 1. After forming F_2^- from F_2, an electron is added into a σ_{2p}^* orbital. The addition of an electron to this antibonding orbital will result in a reduction of the bond order to 1/2 (See Problem 2G.3). F_2 will have the stronger bond. (b) B_2 will have an electron configuration of $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^2$ with a bond order of 1. Removing one electron to form B_2^+ will eliminate one electron in the bonding orbitals, creating a bond order of 1/2. B_2 will have the stronger bond.

2G.19 C_2^+ $(\sigma_{2s})^2(\sigma_{2s}*)^2\,(\pi_{2p})^3$;

C_2 $(\sigma_{2s})^2(\sigma_{2s}*)^2\,(\pi_{2p})^4$;

C_2^- $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4\,(\sigma_{2p})^1$;

C_2^- is expected to have the lowest ionization energy because its electron is lost from a higher energy MO (σ_{2p}) than either C_2^+ or C_2 (π_{2p_y}).

2G.21 Given the overlap integral $S = \int \Psi_{A1s}\Psi_{B1s}d\tau$, the bonding orbital $\Psi = \Psi_{A1s} + \Psi_{B1s}$, and the fact that the individual atomic orbitals are normalized, we are asked to find the normalization constant N which will normalize the bonding orbital Ψ such that:

$$\int N^2\Psi^2 d\tau = N^2\int(\Psi_{A1s} + \Psi_{B1s})^2 d\tau = 1$$

$$N^2\int(\Psi_{A1s} + \Psi_{B1s})^2 d\tau = N^2\int(\Psi^2_{A1s} + 2\Psi_{A1s}\Psi_{B1s} + \Psi^2_{B1s})d\tau$$

$$= N^2\left(\int\Psi^2_{A1s}d\tau + 2\int\Psi_{A1s}\Psi_{B1s}d\tau + \int\Psi^2_{B1s}d\tau\right)$$

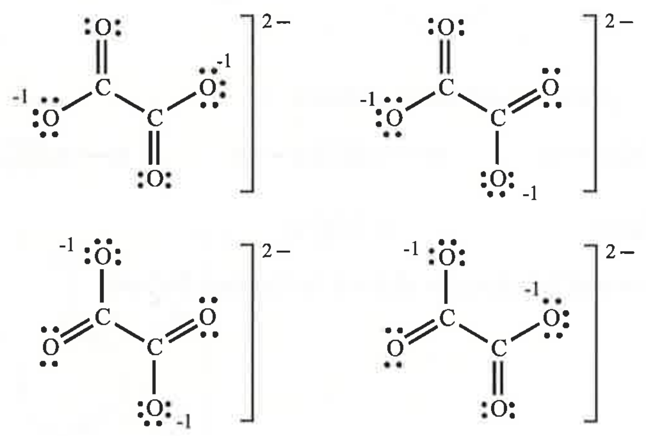
Given the definition of the overlap integral above and the fact that the individual orbitals are normalized, this expression simplifies to:

$$N^2(1 + 2S + 1) = 1$$

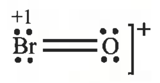
Therefore, $N = \sqrt{\dfrac{1}{2+2S}}$

2.1 Atoms for which no formal charge is shown have a charge of zero:

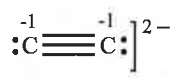
(a)



(b)

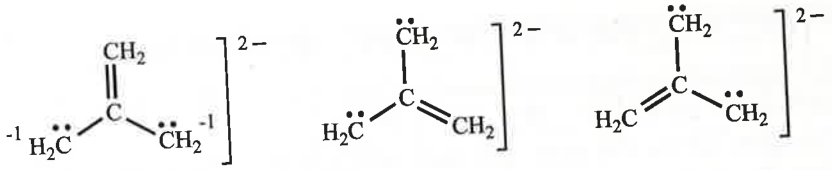


(c)

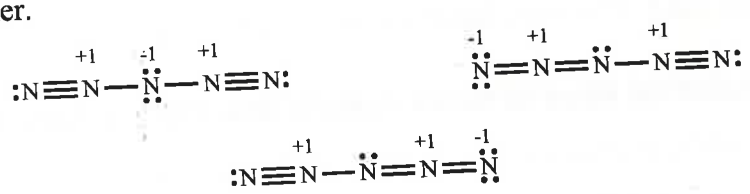


2.3 Iron(III) chloride would be expected to have the greater lattice energy. The iron(III) ion is higher in charge and smaller in size then the iron(II) ion, thus the attraction between it and the chloride ion will be greater and hence the lattice energy will be greater.

2.5



2.7 The Lewis structure for N_5^+ is possible without having multiple formal charges present. The first of the three resonance structures shown below is the most important Lewis structure, since in it no two like charges are near each other.



$$:N\equiv\overset{+1}{N}-\overset{-1}{\ddot{N}}-\overset{+1}{N}\equiv N:\qquad \overset{-1}{\ddot{N}}=\overset{+1}{N}=\ddot{N}-\overset{+1}{N}\equiv N:$$

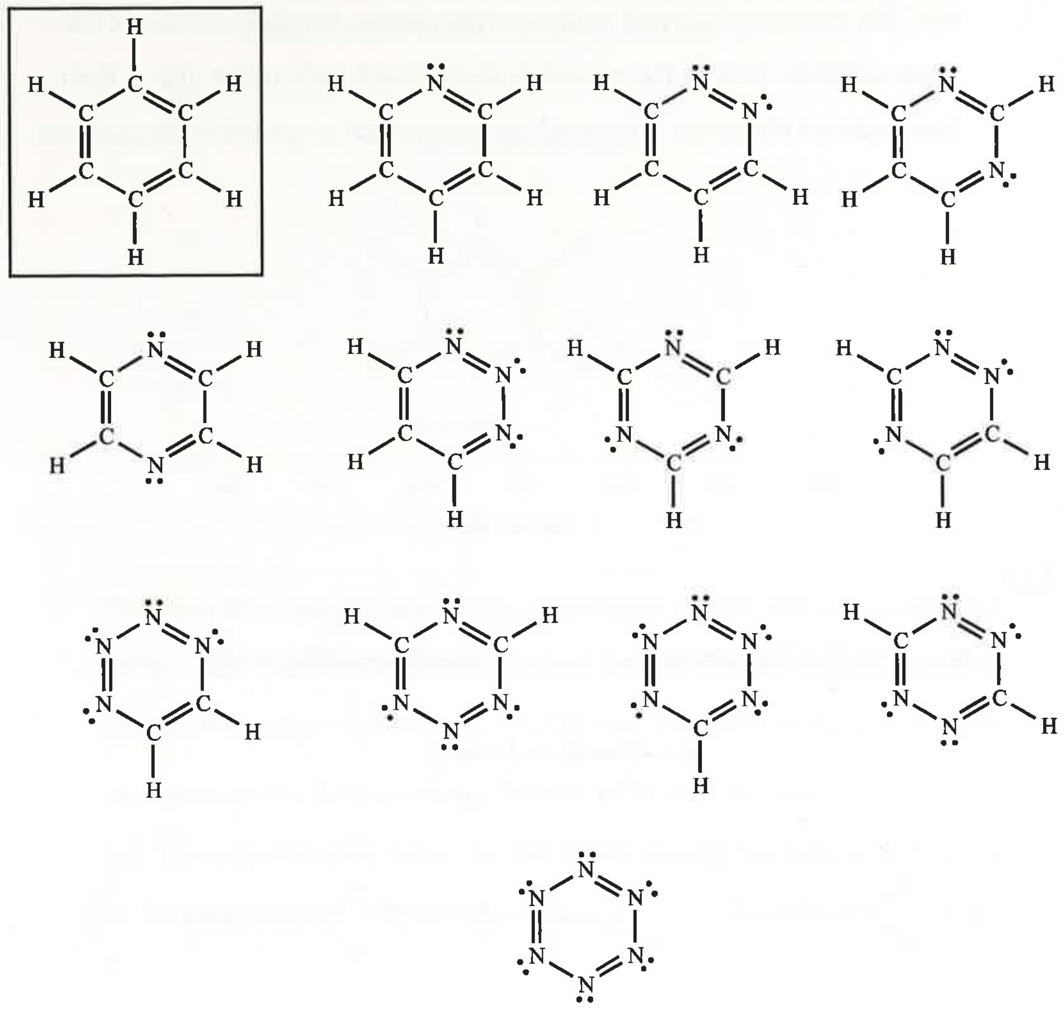
$$:N\equiv\overset{+1}{N}-\ddot{N}=\overset{+1}{N}=\overset{-1}{\ddot{N}}$$

2.9

(a) $H-C\equiv C-H$ $\quad H-C\equiv Si-H$ $\quad H-Si\equiv Si-H$

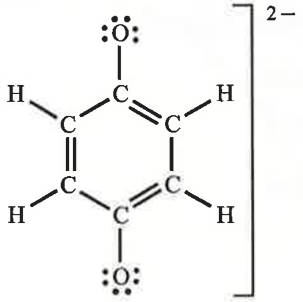
$H-C\equiv N:$ $\quad :N\equiv N:$

(b) The structure of benzene is shown in the box below:



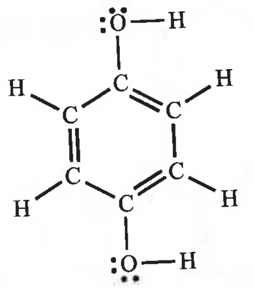
(+ suitable resonance forms)

2.11 (a)



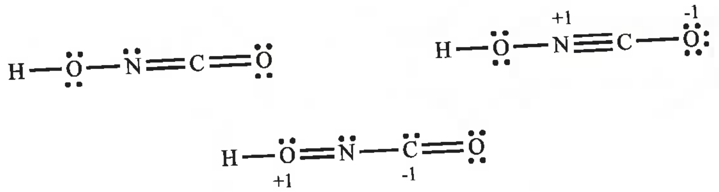
(b) All the atoms have formal charge 0 except the two oxygen atoms, which are -1. The negative charge is most likely to be concentrated at the oxygen atoms.

(c) The protons will bond to the oxygen atoms. Oxygen atoms are the most negative sites in the molecule and act as Lewis bases due to their lone pairs of electrons. The resulting compound is named hydroquinone.

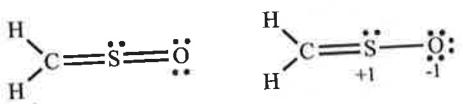


2.13

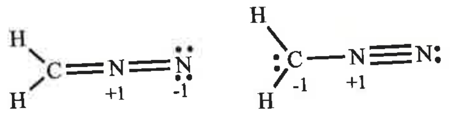
(a)



(b)



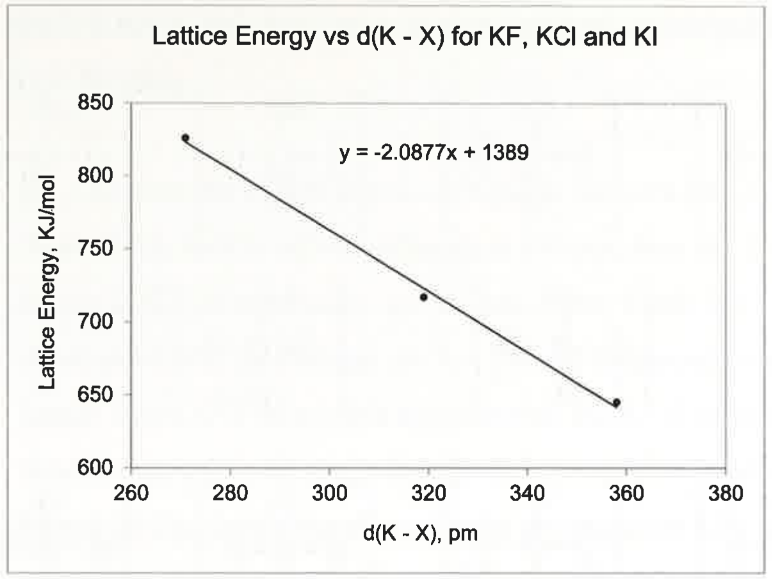
(c)



(d)

2.15

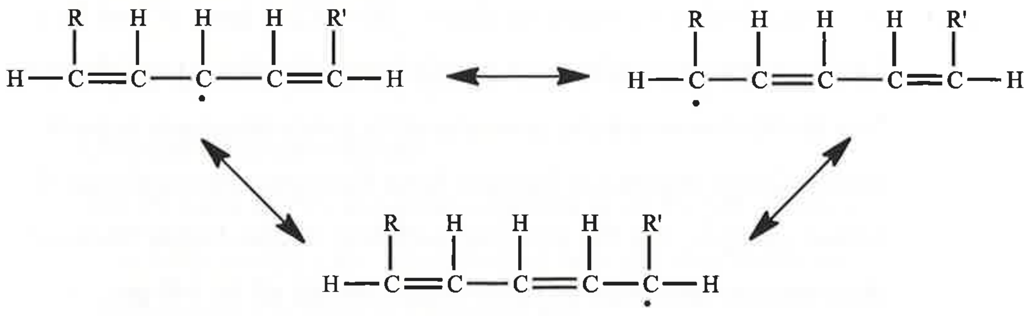
	d(K – X)	Lattice Energy, kJ/mol
Fluoride	271 pm	826
Chloride	319 pm	717
Iodide	358 pm	645



The data fit a straight line with a correlation coefficient of greater than 99%. (b) From the equation derived for the straight line relationship Lattice Energy $=-1.984\,d_{\text{M-X}}+1356$ and the value of $d_{\text{K-Br}}=338\text{ pm}$, we can estimate the lattice energy of KBr to be $693\ \text{kJ}\cdot\text{mol}^{-1}$.

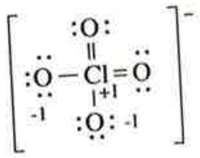
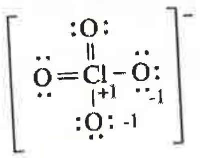
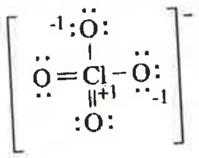
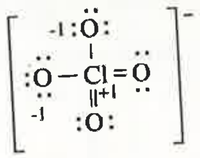
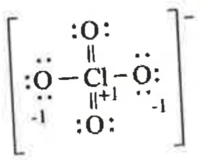
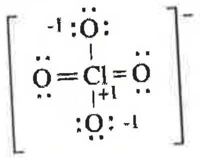
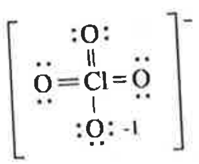
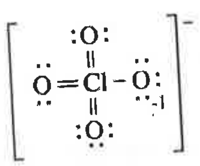
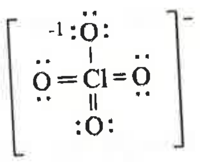
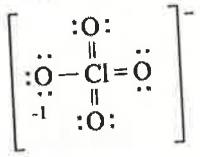
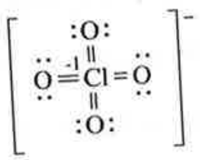
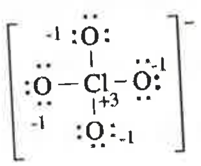
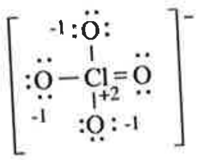
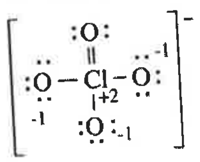
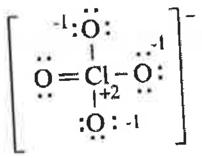
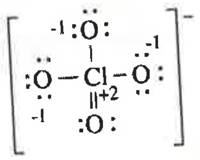
(c) The experimental value for the lattice energy for KBr is $689\ \text{kJ}\cdot\text{mol}^{-1}$, so the agreement is very good.

2.17



2.19 (a) I: Tl_2O_3; II: Tl_2O; (b) +3; +1; (c) $[\text{Xe}]4f^{14}5d^{10}$; $[\text{Xe}]\,4f^{14}5d^{10}6s^2$; (d) Because compound II has a lower melting point, it is probably more covalent, which is consistent with the fact that the +3 ion is more polarizing.

2.21 (a)

The four structures with three double bonds (third row) and the one with four double bonds are the most plausible Lewis structures according to formal charge arguments because these five structures minimize the formal charges. (b) The structure with four double bonds fits these observations best since its bond lengths would all be 140 pm, or only 4 pm shorter than the observed length. However, the four structures with three double bonds also fit because, if the double bonds are delocalized by resonance, we can estimate the average bond length to be $\frac{1}{4}(170\text{ pm})+\frac{3}{4}(140\text{ pm})=147.5\text{ pm}$, or just 3.5 pm longer than observed.

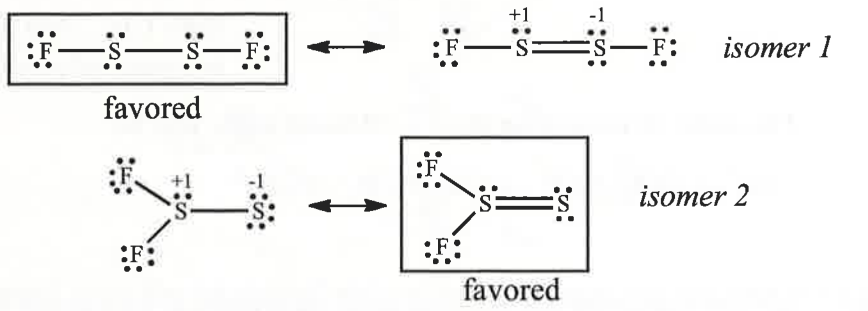
(c) +7; The structure with all single bonds fits this criterion best.

(d) Approaches (a) and (b) are consistent but approach (c) is not. This

result is reasonable because oxidation numbers are assigned by assuming ionic bonding.

2.23 (a) Compare the length of a S—S bond to that of a Cl—Cl bond. From Table 2D.3, the Cl—Cl bond length is 199 pm; here the S—S bond length in S_2F_2 is reported to be 190 pm. From Table 2D.3 it can be determined that, on average, an X—Y bond is approximately 20 pm longer that a X=Y bond; this suggests that the S—S bond (which is 9 pm shorter than a Cl—Cl single bond) has some double bond character.

(b) and (c) The Lewis structures for the two possible S_2F_2 are:

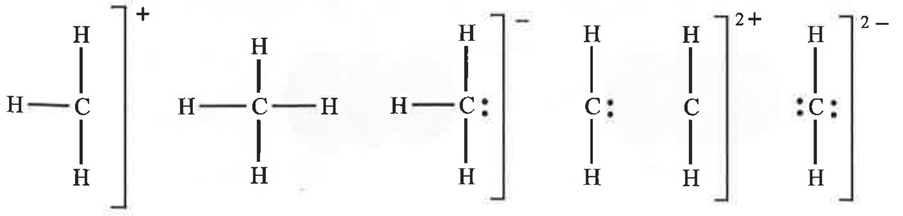


If resonance is occurring, then one would expect that the S—S bond length is indeed between a single and a double bond in length.

2.25 (a) The CN bond in CH_3NH_2 would be expected to be longer. The C—N bond in HCN is a triple bond, in CH_3NH_2 it is a single bond, thus it would be expected to be longer.

(b) The PF bond in PF_3 would be expected to be longer. Bond distance increases with atomic size. Phosphorous is larger then nitrogen, thus it would be expected to have the longer bond.

2.27 (a) The Lewis structures are:



(b) All of these species are expected to be diamagnetic. None are radicals.

(c) The predicted bond angles in each species based upon the Lewis structure and VSEPR theory will be

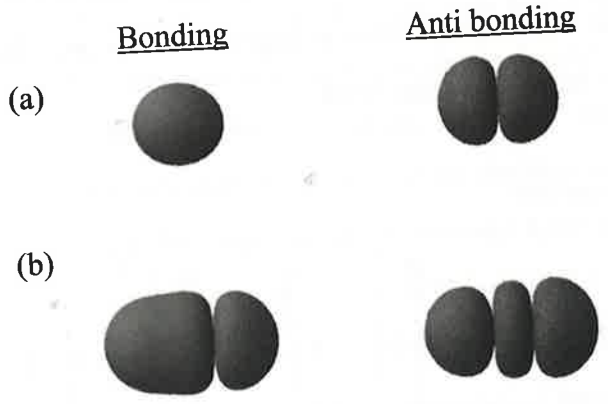
CH_3^+	AX_3	trigonal planar 120°	
CH_4	AX_4	tetrahedral	109.5°
CH_3^-	AX_3E	pyramidal	slightly less than 109.5°
CH_2	AX_2E	angular	slightly less than 120°
CH_2^{2+}	AX_2	linear	180°
CH_2^{2-}	AX_2E_2	angular	less than 109.5°, more so than CH_3^- due to the presence of two lone pairs

The order of increasing H—C—H bond angle will be

$CH_2^{2-} < CH_3^- < CH_4 < CH_2 < CH_3^+ < CH_2^{2+}$

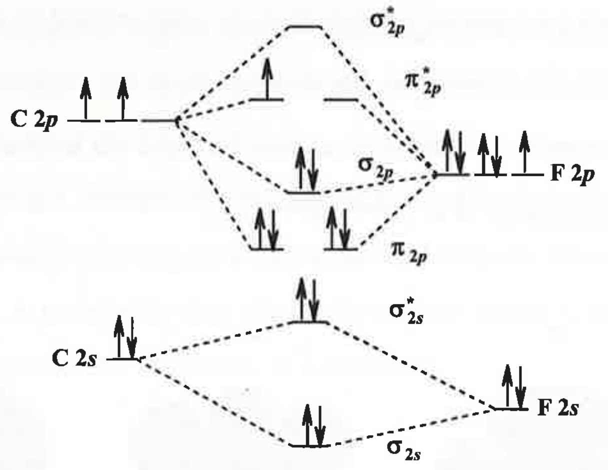
2.29 (a) The elemental composition gives an empirical formula of CH_4O, which agrees with the molar mass. There is only one reasonable Lewis structure; this corresponds to the compound methanol. All of the bond angles about carbon should be 109.5°. The bond angles about oxygen should be close to 109.5° but will be somewhat less, due to the repulsions by the lone pairs. (b) Both carbon and oxygen are sp^3 hybridized. (c) The molecule is polar.

2.31



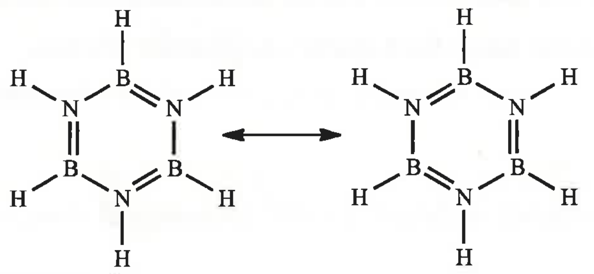
(c) The bonding and antibonding orbitals for HF appear different because a p-orbital from the F atom is used to construct bonding and antibonding orbitals whereas in the H_2 molecule s-orbitals on each atom are used to construct bonding and antibonding orbitals.

2.33 (a) The expected molecular orbital diagram for CF is



The bond order for the neutral species is 2.5 because one electron occupies a π_{2p}*-orbital. Adding an electron to form CF^- will reduce the bond order by 1/2 to 2, while removing an electron from form CF^+ will increase the bond order to 3. Because bond lengths increase as bond order decreases, the C—F bond length varies in these molecules in the following manner: $CF^+ < CF < CF^-$. (b) The CF^+ ion will be diamagnetic but both CF and CF^- will have unpaired electrons (one in the case of CF and two in the case of CF^-).

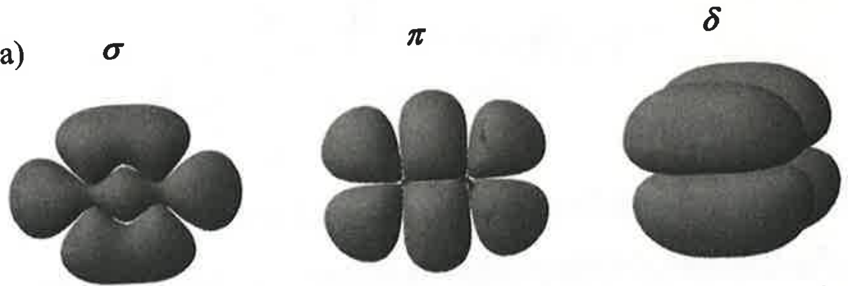
2.35 The Lewis structure of borazine is:



It is nearly identical to that of benzene. It is obtained by replacing alternating C atoms in the benzene structure with B and N (although not shown, each B has a formal charge of -1 and each N has a formal charge of +1). The orbitals at each B and N atom will be sp^2 hybridized.

2.37 The antibonding molecular orbital is obtained by taking the difference between two atomic orbitals that are proportional to e^{-r/a_0}. Halfway between the two nuclei, the distance from the first nucleus, r_1, is equal to the distance to the second nucleus, r_2, and the antibonding orbital is proportional to $\Psi \propto e^{-r/a_0} - e^{-r/a_0} = 0$.

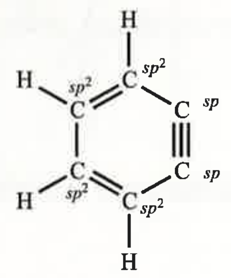
2.39 (a)



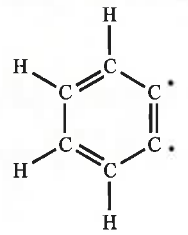
(b) The overlap between the orbitals will decrease as one goes from σ to π to δ, so we expect the bond strengths to decline in the same order.

2.41 The effect of changes (a) and (b) will be similar. The overall bond order will change. In the first case, electrons will be removed from π-orbitals so that the net π-bond order will drop from three to two. The same thing will happen in (b), but because two electrons are added to antibonding orbitals, a net total of one π-bond will be broken. Based on this simple model, the ions formed should be paramagnetic because the electrons are added to or taken from doubly degenerate orbitals.

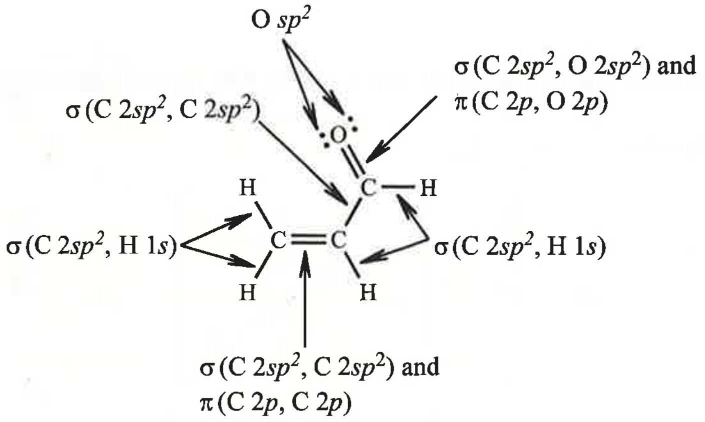
2.43 (a) The Lewis structure of benzyne is



(b) Benzyne would be highly reactive because the two carbon atoms that are *sp* hybridized are constrained to have a very strained structure compared with what their hybridization would like to adopt—namely a linear arrangement. Instead of 180° angles at these carbon atoms, the angles by necessity of being in a six-membered ring are constrained to be close to 120°. A possibility that allows the carbon atoms to adopt more reasonable angles is the formation of a diradical:

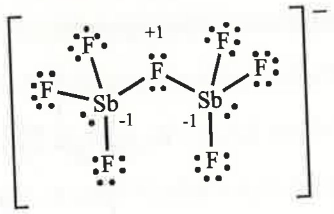


2.45



All atoms in this molecule have a formal charge of zero.

2.47 (a) A possible Lewis structure for $[Sb_2F_7]^-$ based on the information provided is as follows:

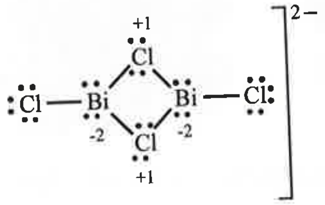


Each Sb has a formal charge of -1 while the bridging F has a formal charge of +1.

(b) Each Sb atom in this structure has a hybridization of sp^3d.

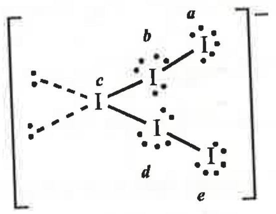
(NOTE: the crystal structure of this ion has been done for both the potassium and the cesium salt; to read more about this controversial ion, see S.H. Mastin and R.R. Ryan (1971) "Crystal Structure of KSb_2F_7. On the Existence of the $[Sb_2F_7]^-$ ion", *Inorganic Chemistry*, **10**, 1757.

2.49 A possible Lewis structure for $[Bi_2Cl_4]^{2-}$ is as follows:



Formal charges for the bridging Cl atoms and the two Bi are shown.

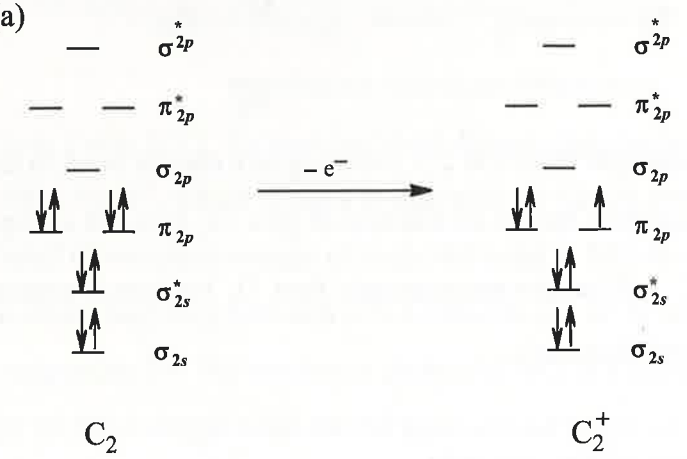
2.51 A possible Lewis structure for I_5^- that fits the conditions given in the problem is:



In this structure, two atoms (I_b and I_d) have a formal charge of −1, one atom (I_c) has a formal charge of +1, and two atoms (I_a and I_e) have no formal charge; the ion has an overall charge of −1. To explain the shape, I_b and I_d are sp^3d hybridized (trigonal bipyramid) with the attached atoms occupying axial positions, which results in a bond angle of 180° around each axial atom. I_c has a VSEPR formula of AX_2E_2; its four electron pairs adopt a tetrahedral electron geometry, which is consistent with sp^3 hybridization.

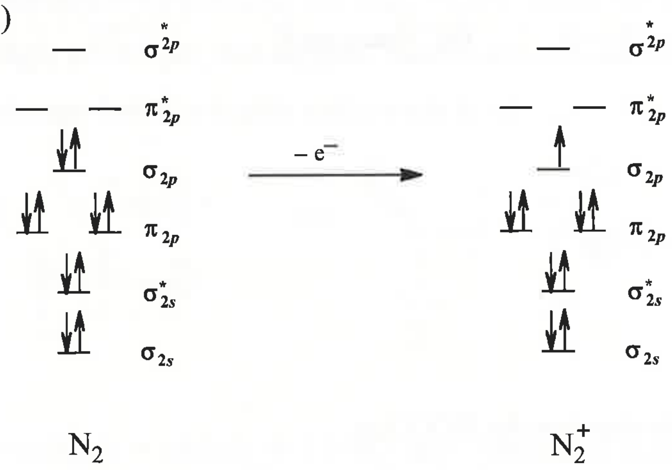
2.53 The molecular orbital diagrams for each of diatomics and their respective cations are shown below:

(a)



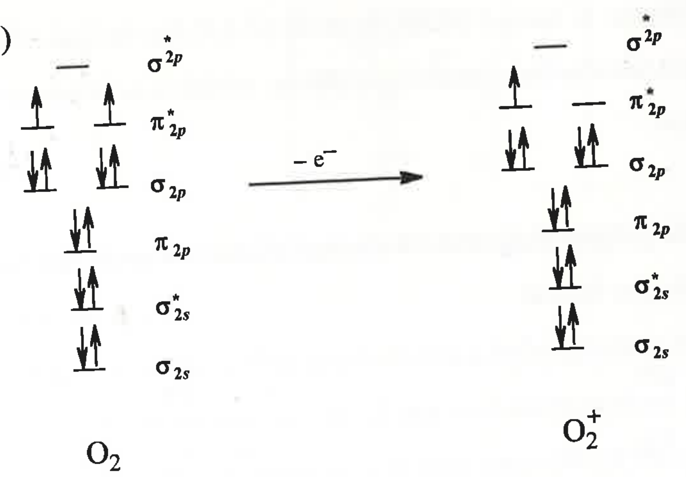
Bond order changes from 2 to 1.5, resulting in a longer bond in the cation. C_2 is diamagnetic; loss of an electron to give C_2^+ makes that species paramagnetic.

(b)



Bond order changes from 3 to 2.5, resulting in a longer bond in the cation. N_2 is diamagnetic; loss of an electron to give N_2^+ makes that species paramagnetic.

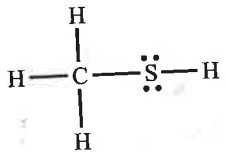
(c)

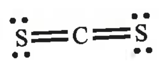


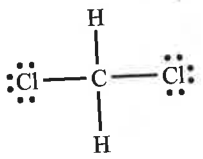
Bond order changes from 2 to 2.5, resulting in a shorter bond in the cation. O_2 is paramagnetic; loss of an electron to give O_2^+ does not change that (although O_2^+ will be less paramagnetic than O_2 because it possesses fewer unpaired electrons).

2.55 (a) sp^3d^3 ; (b) sp^3d^3f ; (c) sp^2d

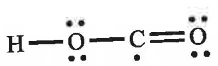
2.59

(a) 

(b) 

(c) 

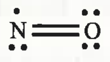
2.61 (a) The Lewis structure for HOCO is:



(b) It is a radical since the C has an unpaired electron on it.

2.63 Angles a and c are expected to be approximately 120°. Angle b is expected to be around 109.5°.

2.65 (a) The Lewis structures of NO and NO_2 are:

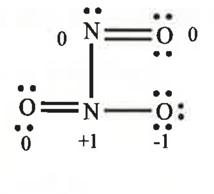


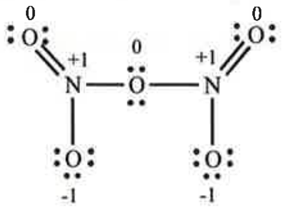
(best possible structure)

(equivalent resonance structures)

From Table 2D.2, the average bond dissociation energy of a N=O bond is 630 kJ mol^{-1}, which is right in line with the Lewis structure of NO. The bond dissociation energy of each NO bond in NO_2 is 469 kJ mol^{-1}, which is about half-way between a N–O double and an N–O single bond, suggesting that the resonance picture of NO_2 is a reasonable one.

(b) An N–O single bond should have a bond length of 149 pm while an N–O double bond should have a bond length of 120 pm (values are obtained by summing the respective covalent radii values from Figure 2D.11). From Table 2D.3 the length of a N–O triple bond can be estimated to be between 105 and 110 pm. Since NO itself has a bond length of 115 pm, this suggests that its actual bond order is somewhere between that of a double and a triple bond.

(c) 

(d) 

(e) $N_2O_5(g) + H_2O(l) \rightarrow 2\ HNO_3(aq)$; Nitric acid is produced

(f)

$$4.05\text{ g }N_2O_5 \times \frac{1\text{ mol }N_2O_5}{108.02\text{ g }N_2O_5} \times \frac{2\text{ mol }HNO_3}{1\text{ mol }N_2O_5} = 7.50 \times 10^{-2}\text{ mol }HNO_3$$

$$\text{Molarity} = \frac{7.50 \times 10^{-2}\ \text{mol HNO}_3}{1.00\ \text{L}} = 7.50 \times 10^{-2}\ \text{mol}\cdot\text{L}^{-1}\ \text{HNO}_3$$

(g) The oxidation number of nitrogen for the various nitrogen oxides are as follows: NO: +2; NO_2: +4; N_2O_3: +3; and N_2O_5: +5. An oxidizing agent is a species that wants to gain electrons; based on oxidation number, N_2O_5 should be the most potent oxidizing agent of the nitrogen oxides, as it possesses the most positive oxidation number for N of the group.

FOCUS 3

STATES OF MATTER

3A.1 (a) 8×10^9 Pa; (b) 80 kbar; (c) 6×10^7 Torr; (d) 1×10^6 lb·in^{-2}

3A.3 Pressure is defined as the total weight of the air, which is proportional to total air molecules, per unit area. At a higher altitude, there are fewer air molecules per unit area than a same unit area at a lower altitude.

3A.5 (a) The difference in column height will be equal to the difference in pressure between atmospheric pressure and pressure in the gas bulb. If the pressures were equal, the height of the mercury column on the air side and on the apparatus side would be the same. The pressure in the gas bulb is $0.890\ \text{atm or}\ 0.890\times760\ \ \text{Torr}\cdot\text{atm}^{-1} = 676\ \text{Torr}$. The difference would be $762\ \text{Torr} - 676\ \text{Torr} = 86\ \text{Torr} = 86\ \text{mm Hg}$. (b) The side attached to the bulb will be higher because the neon pressure is less than the pressure of the atmosphere. (c) If the student had recorded the level in the atmosphere arm to be higher than the level in the bulb arm by 86 mmHg then the pressure in the bulb would have been reported as 762 Torr + 86 Torr = 848 Torr.

3A.7 $d_1h_1 = d_2h_2$

$$74.7\ \text{cm}\times\frac{13.6\ \text{g}\cdot\text{cm}^{-3}}{1.10\ \text{g}\cdot\text{cm}^{-3}} = 924\ \text{cm or } 9.24\ \text{m}$$

3A.9 $(20.\ \text{in})(10.\ \text{in})(14.7\ \text{lb}\cdot\text{in}^{-2}) = 2.9\times10^3\ \text{lb}$