CHAPTER 2

CHEMICAL BONDS

2.1 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-}.

2.3 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.

2.5 (a) 5; (b) 4; (c) 7; (d) 3

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

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

2.11 (a) $[Kr]4d^{10}5s^2$; same (b) none (c) $[Kr]4d^{10}$; Pd

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

2.15 (a) Co^{3+}; (b) Fe^{3+}; (c) Ru^{3+}; (d) Mo^{3+}

2.17 (a) $4s$; (b) $3p$; (c) $3p$; (d) $4s$

2.19   (a) −1;   (b) −2;   (c) +1;   (d) +3 (+1 sometimes observed);

(e) +2

2.21   (a) 3;   (b) 6;   (c) 6;   (d) 2

2.23   (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

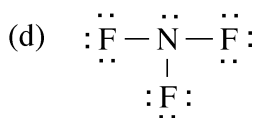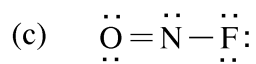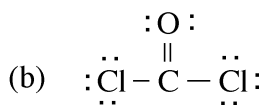unpaired electrons;   (e) $[Ar]3d^8$; two unpaired electrons

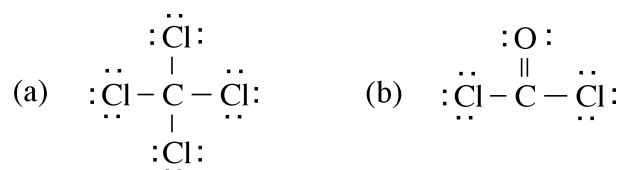**2.25**   (a) $3p$;   (b) $5s$;   (c) $5p$;   (d) $4d$

2.27   (a) +7;   (b) −1;   (c) [Ne] for +7, [Ar] for −1;   (d) electrons are lost

or added to give noble-gas configuration.

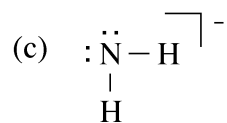**2.29**   (a) Mg_3As_2;   (b) In_2S_3;   (c) AlH_3;   (d) H_2Te;   (e) BiF_3

2.31   (a) Bi_2O_3;   (b) PbO_2;   (c) Tl_2O_3

2.33

(a) $\ddot{:}\underset{\displaystyle :\underset{\cdot\cdot}{\ddot{C}l}:}{\overset{\displaystyle :\ddot{C}l:}{\underset{\cdot\cdot}{C}}}\ddot{Cl}:$

(b) $:\ddot{Cl}-\overset{\displaystyle :O:}{\overset{\|}{C}}-\ddot{Cl}:$

(c) $\ddot{O}=\ddot{N}-\ddot{F}:$

(d) $:\ddot{F}-\underset{\displaystyle :\ddot{F}:}{N}-\ddot{F}:$

2.35

(a)
$$\left[\begin{array}{c} H \\ | \\ H-B-H \\ | \\ H \end{array}\right]^{-}$$

(b)
$$\left[:\overset{..}{\underset{..}{Br}}-\overset{..}{\underset{..}{O}}:\right]^{-}$$

(c)
$$\left[:\overset{..}{N}-H \atop | \atop H\right]^{-}$$

2.37

(a)
$$\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array}\right]^{+} :\overset{..}{\underset{..}{Cl}}:^{-}$$

(b)
$$K^{+}\left[:\overset{..}{\underset{..}{Br}}:\right]^{3-}$$
$$K^{+}$$
$$K^{+}$$

(c)
$$Na^{+}\left[:\overset{..}{\underset{..}{Cl}}-\overset{..}{\underset{..}{O}}:\right]^{-}$$

2.39

2.41

$$\overset{\displaystyle :\overset{..}{Cl}:}{\underset{\overset{..}{\underset{..}{O}}=N-\overset{..}{\underset{..}{O}}:}{|}} \qquad \overset{\displaystyle :\overset{..}{Cl}:}{\underset{:\overset{..}{\underset{..}{O}}-N=\overset{..}{\underset{..}{O}}}{|}}$$

2.43

(a) $[:N\equiv O:]^+$ (b) $:N\equiv N:$ (a) $:C\equiv O:$

     0   +1   0   0   -1   +1

(a) $[:C\equiv C:]^{2-}$ (a) $[:C\equiv N:]^{-}$

     -1   -1   -1   0

2.45

(a) $\ddot{O}=Cl\quad \ddot{O}:$ $:\ddot{O}-Cl-\ddot{O}:$

        $:O:\ H$ $:O:\ H$

       lower energy

(b) $\ddot{O}=C=\ddot{S}$ $:\ddot{O}\quad C\quad \ddot{S}-$

     lower energy

(c) $H\quad C\quad N:$ $H\quad C-N:$

     0   0   0   0   1

     lower energy
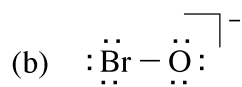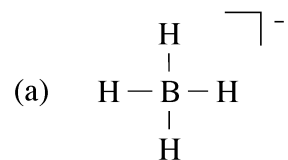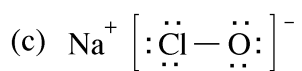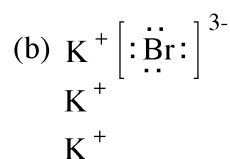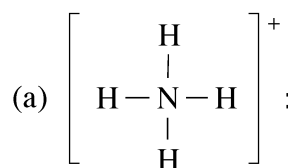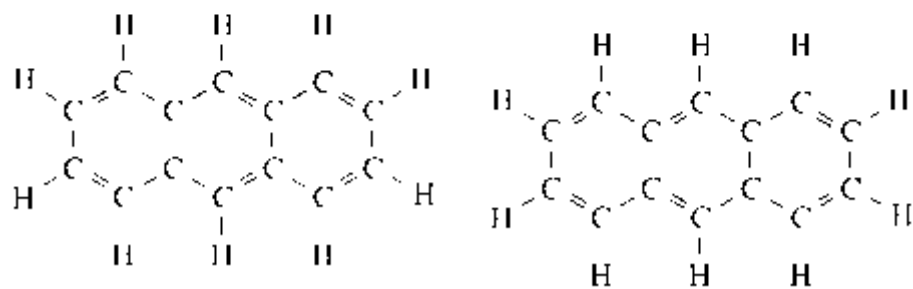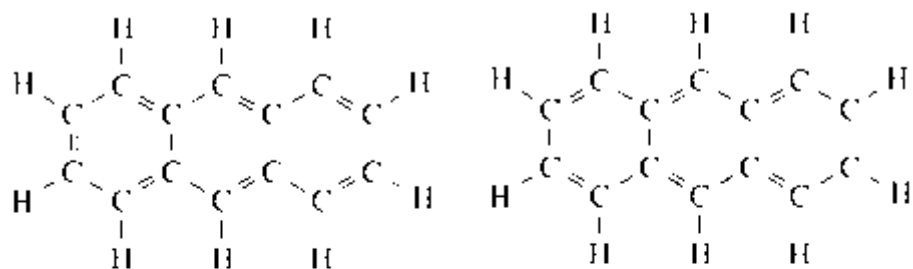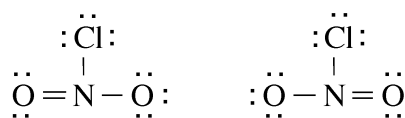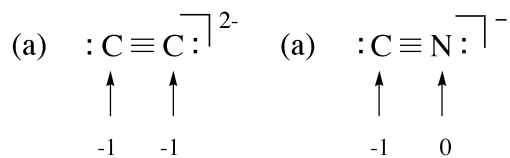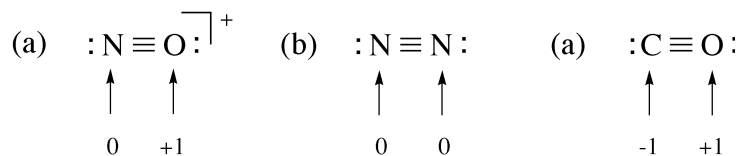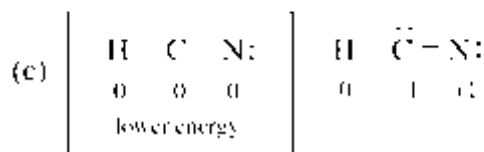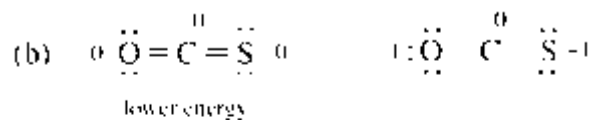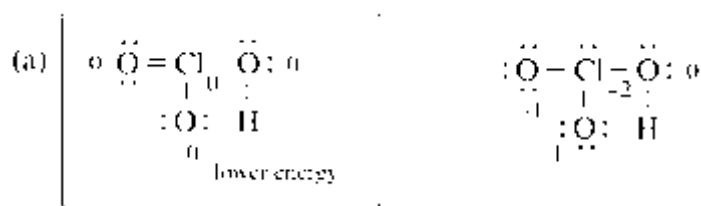
2.47 (a) In the first structure, the formal charges at Xe and F are 0, whereas, in the second structure, Xe is -1, one F is 0, and the other F is $+1$. The first structure is favored on the basis of formal charges. (b) In the first structure, all of the atoms have formal charges of 0, whereas, in the 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.

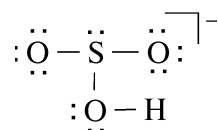**2.49**   (a) The sulfite ion has one Lewis structure that obeys the octet rule:

$$\left[:\ddot{O} - \ddot{S} - \ddot{O}: \atop \underset{:\ddot{O}:}{\overset{|}{}} \right]^{2-}$$
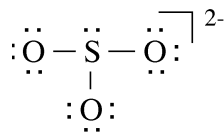
and three with an expanded octet:

$$\left[\ddot{O} = \ddot{S} - \ddot{O}: \atop \underset{:\ddot{O}:}{\overset{|}{}} \right]^{2-} \qquad \left[:\ddot{O} - \ddot{S} = \ddot{O} \atop \underset{:\ddot{O}:}{\overset{|}{}} \right]^{2-} \qquad \left[:\ddot{O} - \ddot{S} - \ddot{O}: \atop \underset{:\ddot{O}:}{\overset{\|}{}} \right]^{2-}$$
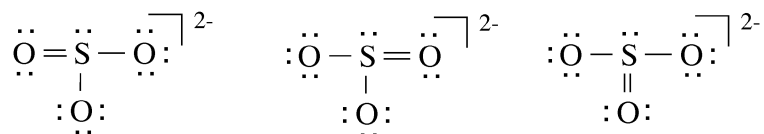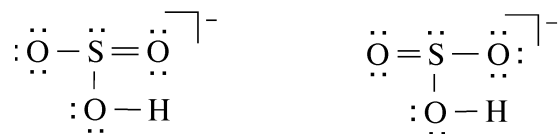
The structures with expanded octets have lower formal charges.

(b) There is one Lewis stucture that obeys the octet rule:

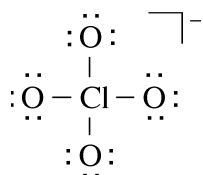$$\left[:\ddot{O} - \ddot{S} - \ddot{O}: \atop \underset{:\ddot{O} - H}{\overset{|}{}} \right]^{-}$$

The formal charge at sulfur can be reduced to 0 by including one double bond contribution. This change gives rise to two expanded octet structures.

$$\left[:\ddot{O} - \ddot{S} = \ddot{O} \atop \underset{:\ddot{O} - H}{\overset{|}{}} \right]^{-} \qquad \left[\ddot{O} = \ddot{S} - \ddot{O}: \atop \underset{:\ddot{O} - H}{\overset{|}{}} \right]^{-}$$

Notice that, unlike the sulfite ion, which has three resonance forms, the presence of the hydrogen ion restricts the electrons to the oxygen atom to which it is attached. Because H is electropositive, its placement near an oxygen atom makes it less likely for that oxygen atom to donate a lone pair to an adjacent atom.

(c) The perchlorate ion has one Lewis structure that obeys the octet rule:

$$\left[\underset{:\ddot{O}:}{\overset{:\ddot{O}:}{:\ddot{O} - Cl - \ddot{O}:}} \right]^{-}$$

The formal charge at Cl can be reduced to 0 by including three double-bond contributions, thereby giving rise to four resonance forms.
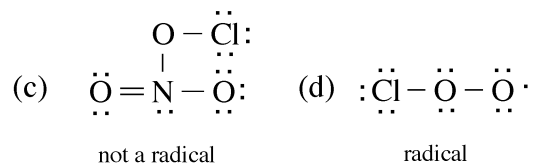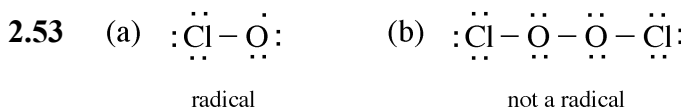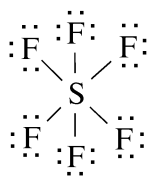
$$
\left[\ddot{O} = \overset{\overset{\displaystyle :O:}{\|}}{\underset{\underset{\displaystyle :\ddot{O}:}{|}}{Cl}} = \ddot{O} \right]^{-}
\qquad
\left[:\ddot{O} - \overset{\overset{\displaystyle :O:}{\|}}{\underset{\underset{\displaystyle :O:}{\|}}{Cl}} = \ddot{O} \right]^{-}
$$

$$
\left[\ddot{O} = \overset{\overset{\displaystyle :O:}{\|}}{\underset{\underset{\displaystyle :O:}{\|}}{Cl}} - \ddot{O}: \right]^{-}
\qquad
\left[\ddot{O} = \overset{\overset{\displaystyle :\ddot{O}:}{|}}{\underset{\underset{\displaystyle :O:}{\|}}{Cl}} = \ddot{O} \right]^{-}
$$
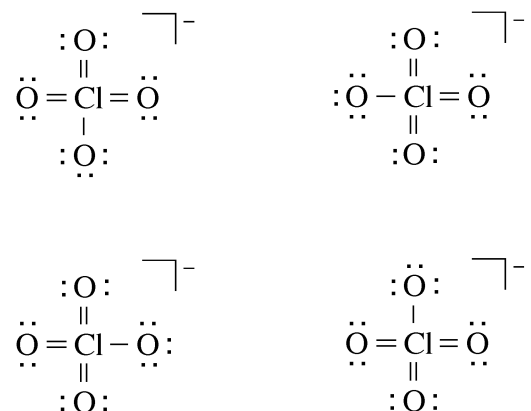
For the nitrite ion, there are two resonance forms, both of which obey the octet rule:

$$
\left[\ddot{O} = N - \ddot{O}: \right]^{-}
\qquad
\left[:\ddot{O} - N = \ddot{O} \right]^{-}
$$

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

2.53 (a) $:\ddot{Cl} - \dot{\ddot{O}}:$ (b) $:\ddot{Cl} - \ddot{O} - \ddot{O} - \ddot{Cl}:$

   radical   not a radical

(c) $\ddot{O} = \overset{\overset{\displaystyle O - \ddot{Cl}:}{|}}{N} - \ddot{O}:$ (d) $:\ddot{Cl} - \ddot{O} - \dot{\ddot{O}}$
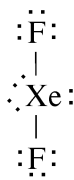
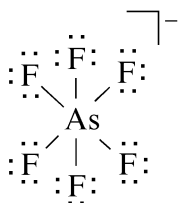   not a radical   radical
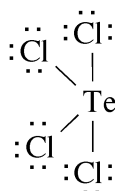
2.55 (a)

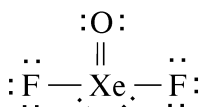12 electrons

(b)

10 electrons
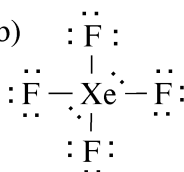
(c)

12 electrons

(d)

10 electrons

2.57 (a)

2 lone pairs

(b)

2 lone pairs

(c)
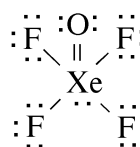
1 lone pair

2.59 I (2.7) < Br (3.0) < Cl (3.2) < F (4.0)

2.61 In (1.8) < Sn (2.0) < Sb (2.1) < Se (2.6)

2.63 (a) Iodide is more polarizable than Cl^-, so HI would be more covalent than HCl.

(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.

2.65 $Rb^+ < Sr^{2+} < Be^{2+}$; smaller, more highly charged cations have greater polarizing power. The ionic radii are 149 pm, 116 pm, 27 pm, respectively.
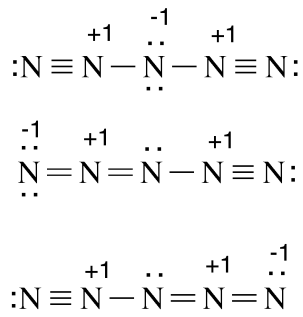
2.67 $O^{2-} < N^{3-} < Cl^- < Br^-$; the polarizability increases as the ion gets larger and less electronegative. The ionic radii for these species are 140 pm, 171 pm, 181 pm, 196 pm, respectively.

2.69   (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 0 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) $CH_3NH_2 > CH_2NH > HCN$

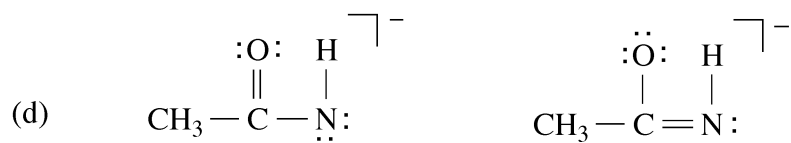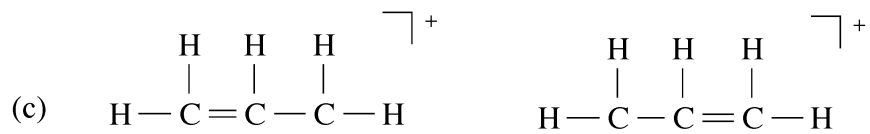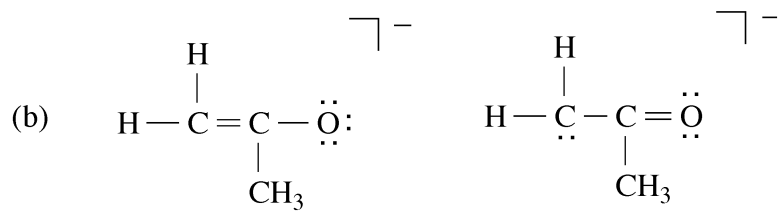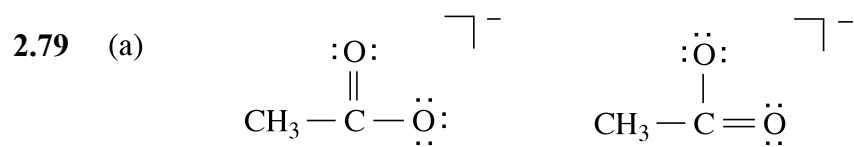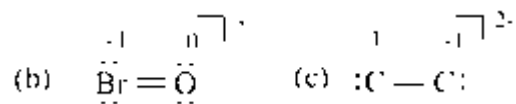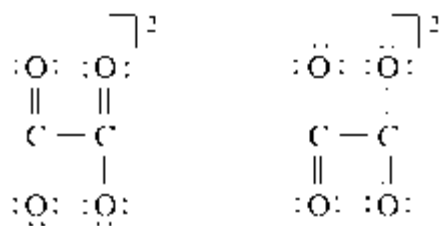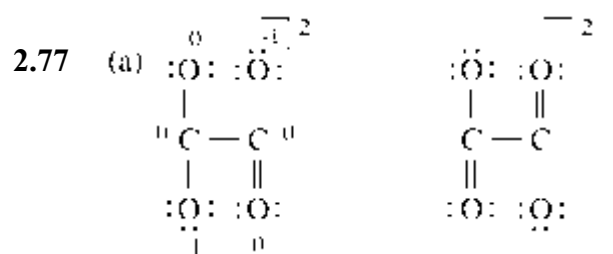The C—N bond in HCN is a triple bond, in CH_2NH it is a double bond, and in CH_3NH_2 it is a single bond. The C—N bond in the last molecule would, therefore, be expected to be the longest.

2.71 (a) The covalent radius of N is 75 pm, so the N—N single bond in hydrazine would be expected to be ca. 150 pm. The experimental value is 145 pm.   (b) 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 CRO in CO_2 to be ca. 127 pm. The experimental bond length is 116.3 pm.   (c) The C—O bond is a double bond so it would be expected to be the same as in (b), 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 132 pm, which is close to the experimental value of 133 pm.   (d) The N—N bond is a double bond so we expect the bond distance to be two times the double bond covalent radius of N, which is 2 × (60 pm) or 120 pm. The experimental value is 123.0 pm.

2.73 (a) 77 pm + 72 pm = 149 pm   (b) 111 pm + 72 pm = 183 pm
(c) 141 pm + 72 pm = 213 pm. Bond distance increases with size going down Group 14/IV.

2.75

$$:N \equiv N - \overset{-1}{\underset{..}{\overset{..}{N}}} - N \equiv N:$$
$$\overset{+1}{} \qquad \overset{+1}{}$$

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

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

2.77 (a)

$$\begin{bmatrix} \ddot{O} & \ddot{O} \\ \,|\, & \,|\, \\ :\ddot{O}: & :\ddot{O}: \\ C - C \\ :\ddot{O}: & :\ddot{O}: \end{bmatrix}^{2-} \qquad \begin{bmatrix} :\ddot{O}: & :O: \\ \,|\, & \,\|\, \\ C - C \\ :O: & :\ddot{O}: \end{bmatrix}^{2-}$$

$$\begin{bmatrix} :O: & :O: \\ \,\|\, & \,\|\, \\ C - C \\ \,|\, \\ :\ddot{O}: & :\ddot{O}: \end{bmatrix}^{2-} \qquad \begin{bmatrix} :\ddot{O}: & :\ddot{O}: \\ C - C \\ \,\|\, & \,|\, \\ :O: & :O: \end{bmatrix}^{2-}$$

(b) $\begin{bmatrix} \ddot{B}r = \ddot{O} \end{bmatrix}^{-}$ (c) $\begin{bmatrix} :C - C: \end{bmatrix}^{2-}$

2.79 (a)

$$\begin{bmatrix} :O: \\ \,\|\, \\ CH_3 - C - \ddot{O}: \end{bmatrix}^{-} \qquad \begin{bmatrix} :\ddot{O}: \\ \,|\, \\ CH_3 - C = \ddot{O} \end{bmatrix}^{-}$$

(b)

$$\begin{bmatrix} H \\ \,|\, \\ H - C = C - \ddot{O}: \\ \,|\, \\ CH_3 \end{bmatrix}^{-} \qquad \begin{bmatrix} H \\ \,|\, \\ H - C - C = \ddot{O} \\ \,|\, \\ CH_3 \end{bmatrix}^{-}$$

(c)

$$\begin{bmatrix} H & H & H \\ \,|\, & \,|\, & \,|\, \\ H - C = C - C - H \end{bmatrix}^{+} \qquad \begin{bmatrix} H & H & H \\ \,|\, & \,|\, & \,|\, \\ H - C - C = C - H \end{bmatrix}^{+}$$

(d)

$$\begin{bmatrix} :O: & H \\ \,\|\, & \,|\, \\ CH_3 - C - \ddot{N}: \end{bmatrix}^{-} \qquad \begin{bmatrix} :\ddot{O}: & H \\ \,|\, & \,|\, \\ CH_3 - C = \ddot{N}: \end{bmatrix}^{-}$$
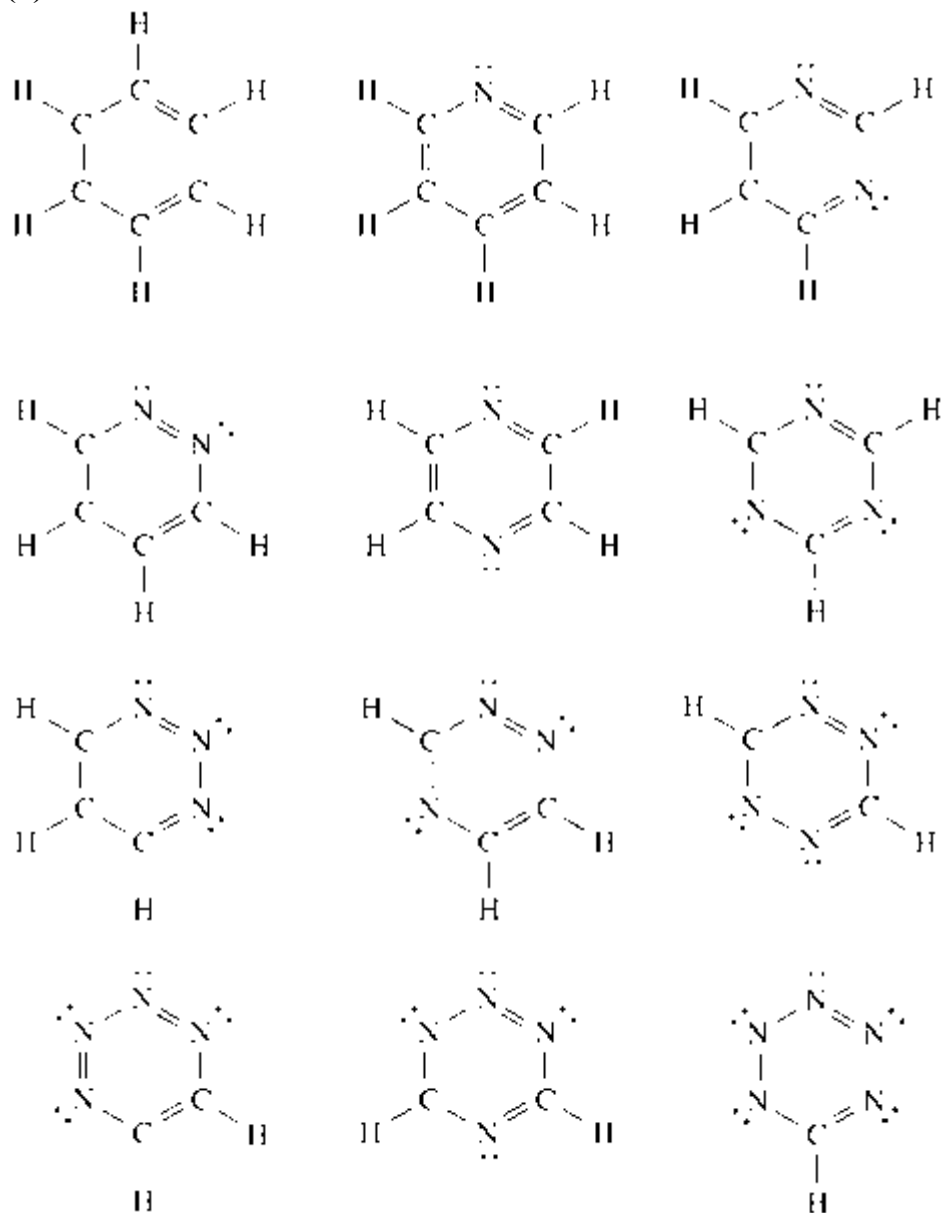
2.81 P and S are larger atoms that are less able to form multiple bonds to themselves, unlike the small N and O atoms. All bonds in P_4 and S_8 are single bonds, whereas N_2 has a triple bond and O_2 a double bond.
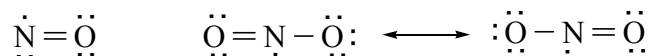
2.83 **(a)**

H—C≡C—H   H—C≡Si—H

H—Si—Si—H   H—C—N: :N≡N:
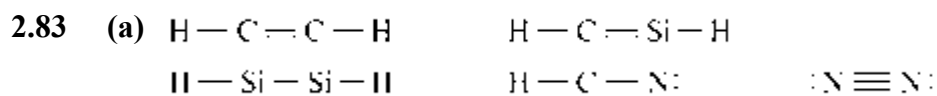
(b)

+ suitable resonance forms

2.85 The Lewis structures for NO and NO_2 are

$$\dot{N} = \ddot{O} \qquad \ddot{O} = \dot{N} - \ddot{O}: \longleftrightarrow :\ddot{O} - \dot{N} = \ddot{O}$$

Both compounds are radicals.

(a) NO has a double bond, but NO_2 has N-O bonds that are the average of a single bond and a double bond. Thus, NO would be expected to have a shorter, stronger bond, and this fact is indicated by the bond energies.

(b) The fact that the two N-O bonds in NO_2 are equal is a result of the two available resonance forms.

2.87 (a)

Metal Iodide	d(M – I), pm	Lattice Energy, kJ/mol
LiI	278	761
NaI	322	705
KI	358	649
RbI	369	632
CsI	390	601
AgI	353	886

Alkali Metal Iodide Lattice Energies vs d(M-I)

$y = -1.4399x + 1164.0$ $R^2 = 0.998$
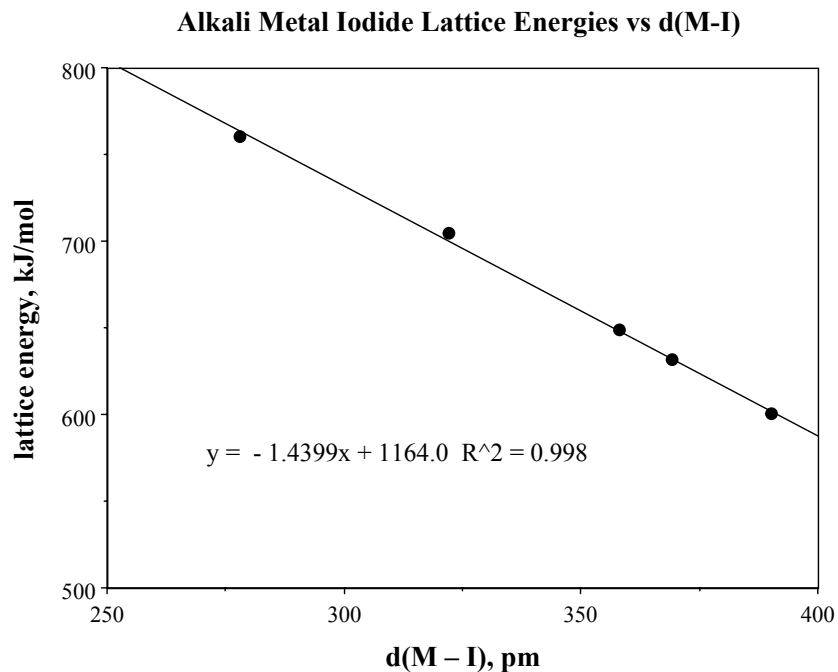
The correlation is excellent with an agreement coefficient of greater than 99%.

(b) From the equation of this line

Lattice Energy $= -1.440\, d_{M-X} + 1164$

and the Ag-I distance of 353 pm, we can estimate the AgI lattice energy to be $656\ \text{kJ}\cdot\text{mol}^{-1}$. This is not very good agreement with the experimental value of $886\ \text{kJ}\cdot\text{mol}^{-1}$. One possible explanation is that the structure of silver iodide is different from that of the alkali metal iodides and therefore would have a different Madelung constant. This is the case as AgI crystallizes in a type of lattice known as the Wurtzite structure. However, the Madelung constant for the Wurtzite structure is 1.641 versus 1.748 for the rock salt structure of all the alkali metal iodides (except CsI, which adopts the CsCl structure with a very similar Madelung constant of 1.763). One would therefore predict that the lattice energy of AgI would be less than the calculated value based upon the alkali metal series, rather than greater. A better explanation is that the Ag^+ ion is much more polarizable

than the alkali metal cations of similar size and therefore the bonding in AgI is much more covalent.

2.89   (a)
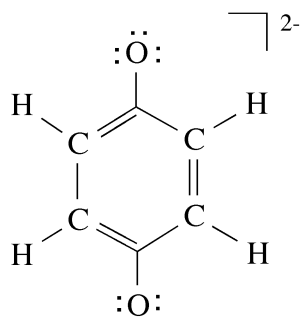
(b) All the atoms have formal charge 0 except the two oxygen atoms, which are -1. The negative charge is most likely to be concentrated at the oxygen atoms.
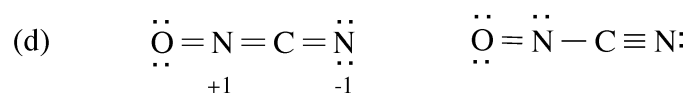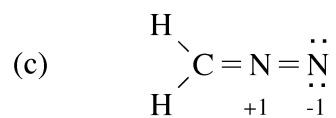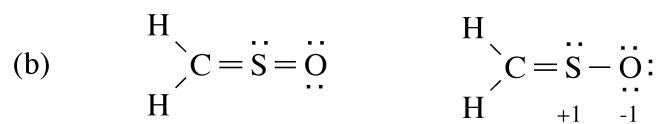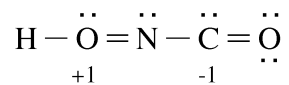
(c) Because the oxygen atoms are the most negative sites and the lone pairs on the oxygen atoms are good Lewis bases, the protons will bond to the oxygen atoms. This compound is known as hydroquinone.

Hydroquinone
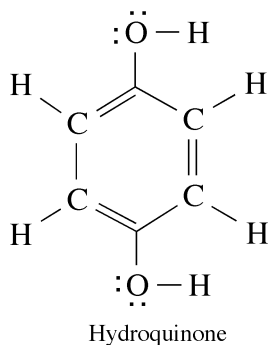
2.91

Z	Configuration	Number of unpaired e^-	Element	Charge	Energy state
26	$[Ar]3d^6$	4	Fe	2+	ground
52	$[Kr]5s^24d^{10}5p^56s^1$	2	Te	2-	excited
16	$[Ne]3s^23p^6$	0	S	2-	ground
39	$[Kr]4d^1$	1	Y	2+	ground
30	$[Ar]4s^23d^8$	2	Zn	2+	excited

2.93 (a)

$$H-\overset{..}{\underset{..}{O}}-\overset{..}{N}=C=\overset{..}{\underset{..}{O}}$$

$$H-\overset{..}{\underset{..}{O}}-N\equiv C-\overset{..}{\underset{..}{O}}:$$
$$\underset{+1}{}\underset{-1}{}$$

$$H-\overset{..}{O}=\overset{..}{N}-\overset{..}{C}=\overset{..}{\underset{..}{O}}$$
$$\underset{+1}{}\underset{-1}{}$$

(b)

$$\underset{H}{\overset{H}{>}}C=\overset{..}{S}=\overset{..}{\underset{..}{O}} \qquad \underset{H}{\overset{H}{>}}C=\overset{..}{S}-\overset{..}{\underset{..}{O}}:$$
$$\underset{+1}{}\underset{-1}{}$$

(c)

$$\underset{H}{\overset{H}{>}}C=N=\overset{..}{\underset{..}{N}}$$
$$\underset{+1}{}\underset{-1}{}$$

(d)

$$\overset{..}{\underset{..}{O}}=N=C=\overset{..}{\underset{..}{N}} \qquad \overset{..}{\underset{..}{O}}=\overset{..}{N}-C\equiv N:$$
$$\underset{+1}{}\underset{-1}{}$$

2.95

$$\underset{H-C=C-\overset{.}{C}-C=C-H}{\overset{R\ \ \ H\ \ \ H\ \ \ H\ \ \ R'}{\mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid}}$$

$$\underset{H-\overset{.}{C}-C=C-C=C-H}{\overset{R\ \ \ H\ \ \ H\ \ \ H\ \ \ R'}{\mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid}}$$

$$\underset{H-C=C-C=C-\overset{.}{C}-H}{\overset{R\ \ \ H\ \ \ H\ \ \ H\ \ \ R'}{\mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid\ \ \ \ \mid}}$$

2.97
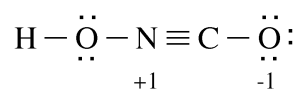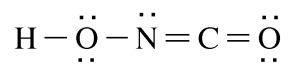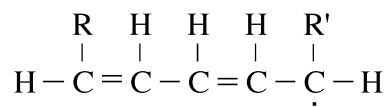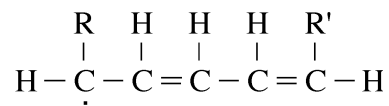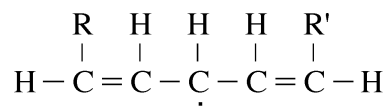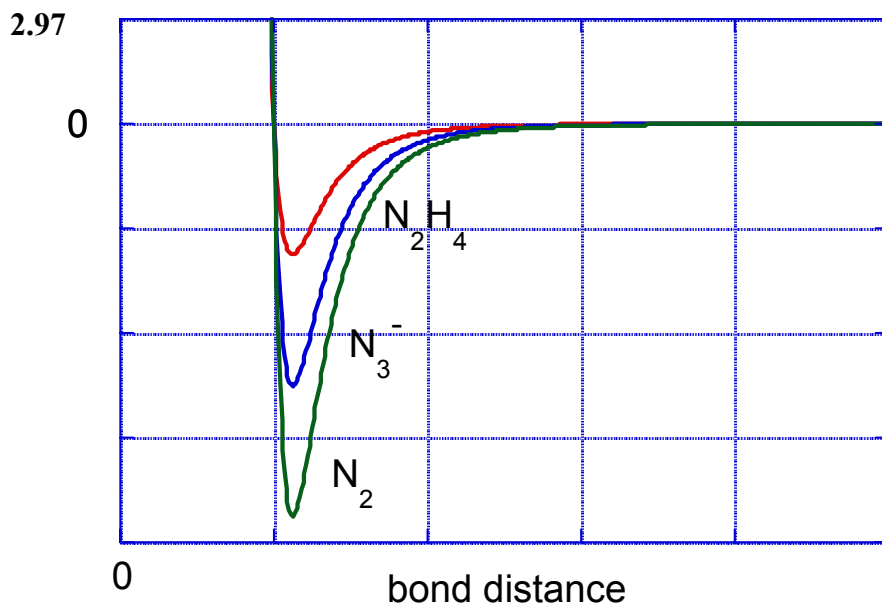
The potential energy well is deepest for N_2 ($N\equiv N$), then N_3^- ($N=N$), then N_2H_4 (N-N).

2.99 (a) I: Tl_2O_3; II: Tl_2O; (b) 3^+; 1^+; (c) $[Xe]4f^{14}5d^{10}$; $[Xe]\,4f^{14}5d^{10}6s^2$; (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.

2.101 The alkyne group has the stiffer C—H bond because a large force constant, k, results in a higher-frequency absorption.

2.103 (a)
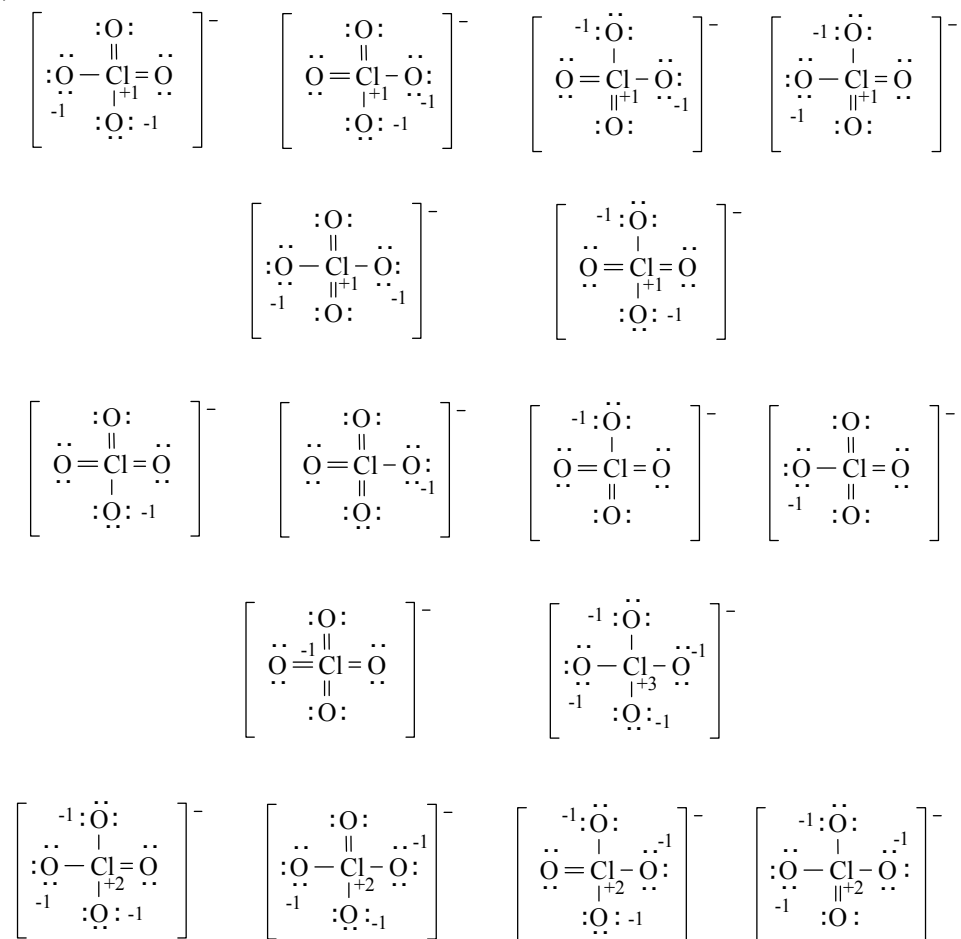
The four structures with three double bonds (third row) and the one with four double bonds are the most plausible Lewis structures according to formal charge arguments because these five structures minimize the formal charges. (b) The structure with four double bonds fits these observations best since 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

$\frac{1}{4}(170 \text{ pm}) + \frac{3}{4}(140 \text{ pm}) = 147.5$ 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.