

CHAPTER 2

CHEMICAL BONDS

- 2.2** The coulombic attraction is inversely proportional to the distance between the two oppositely charged ions (Equation 1) so the ions with the shorter radii will give the greater coulombic attraction. The answer is therefore (c) Mg^{2+} , O^{2-} .
- 2.4** The Br^- ion is smaller than the I^- ion (196 vs 220 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 iodide ion will have the lower lattice energy for a given cation.
- 2.6** (a) 7; (b) 10; (c) 7; (d) 2
- 2.8** (a) $[\text{Kr}]4d^{10}5s^25p^6$; (b) $[\text{Ar}]3d^8$; (c) $[\text{Xe}]4f^{14}5d^3$; (d) $[\text{Kr}]$
- 2.10** (a) $[\text{Ne}]$; (b) $[\text{Kr}]4d^3$; (c) $[\text{Rn}]$; (d) $[\text{Xe}]$
- 2.12** (a) Ca: $[\text{Ar}]4s^2$, Ti^{2+} : $[\text{Ar}]3d^2$; V^{3+} : $[\text{Ar}]3d^2$ In the d block, the energies of the $n-1$ d -orbitals lie below those of the ns -orbitals. Therefore, when V and Ti form ions they lose their $3s$ electrons before losing their $4d$ electrons.
(b) Ca: no unpaired electrons; Ti^{2+} : two unpaired electrons; V^{3+} : two unpaired electrons. (c) Ti^{3+} : $[\text{Ar}]3d^1$ no neutral atom has this electron configuration.

2.14 (a) Au^{3+} ; (b) Os^{3+} ; (c) I^{3+} ; (d) As^{3+}

2.16 (a) Co^{2+} ; (b) Rh^{2+} ; (c) Sn^{2+} ; (d) Hg^{2+}

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

2.20 (a) +2; (b) +2 due to the inert pair effect, but 4+ is also possible;
(c) +3; (d) -1; (e) -2

2.22 (a) 2; (b) 5; (c) 3; (d) 6

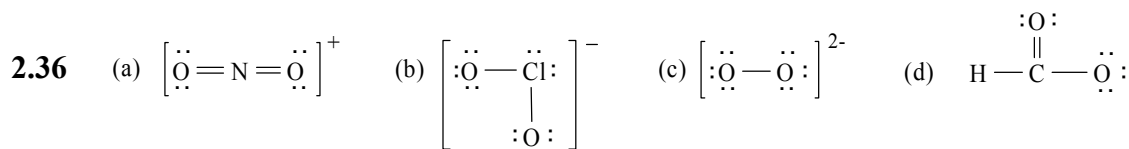
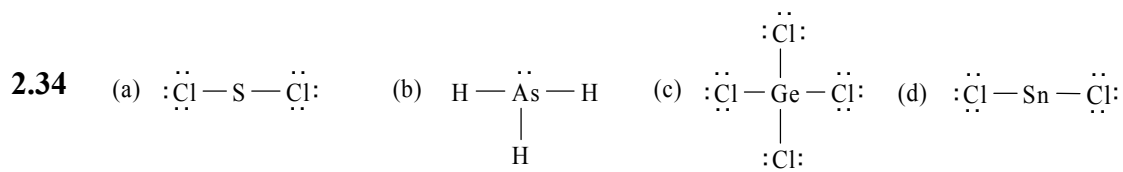
2.24 (a) $[\text{Ar}]3d^{10}4s^2$; no unpaired electrons; (b) $[\text{Ar}]3d^9$; one unpaired electron; (c) $[\text{Xe}]5d^{10}6s^2$; no unpaired electrons; (d) $[\text{Kr}]$; no unpaired electrons

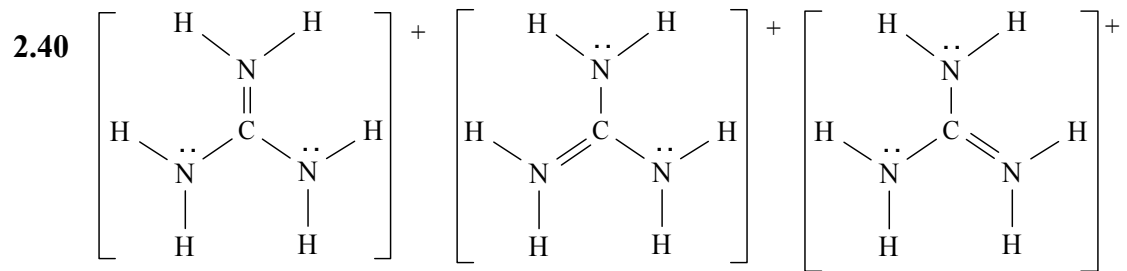
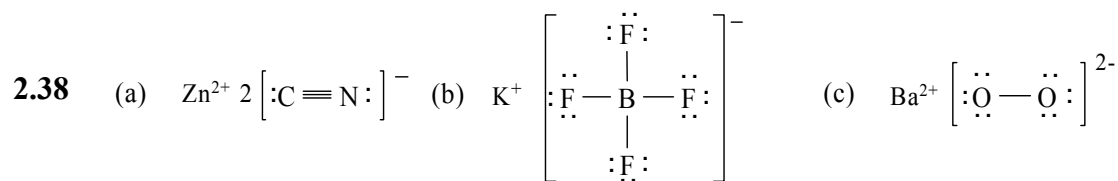
2.26 (a) $3d$; (b) $6s$; (c) $2p$; (d) $4p$

2.28 (a) +6; (b) -2; (c) $[\text{Ne}]$ for +6, $[\text{Ar}]$ for -2; (d) Electrons are lost or added to give noble gas configuration.

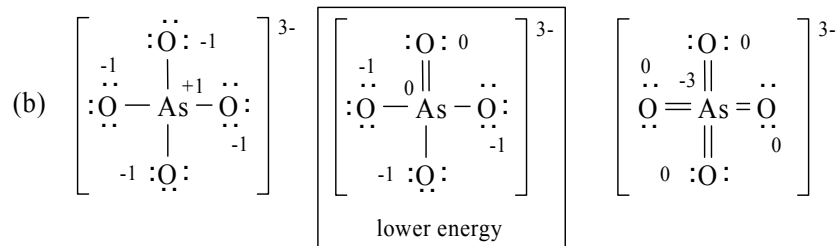
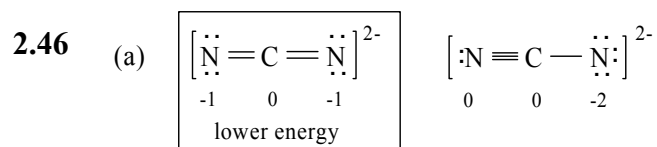
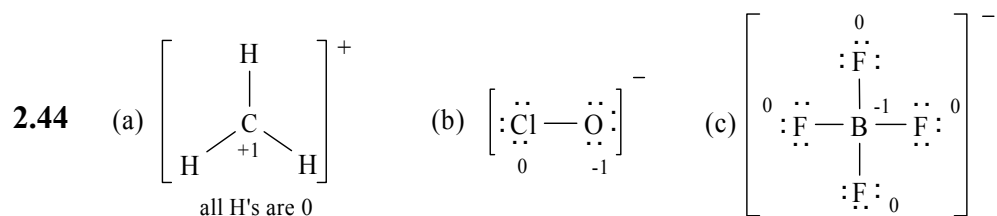
2.30 (a) MnTe ; (b) Ba_3As_2 ; (c) Si_3N_4 ; (d) Li_3Bi ; (e) ZrCl_4

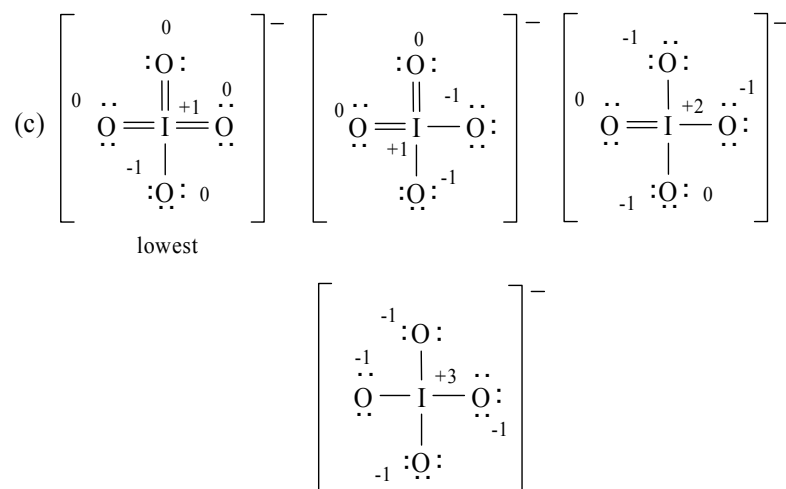
2.32 (a) FeS ; (b) CoCl_3 ; (c) Mg_3P_2





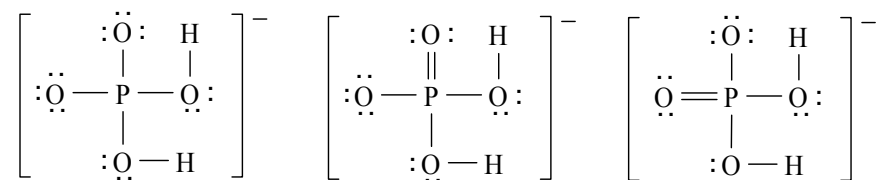
2.42 No. In order to have resonance structures, only the electrons are allowed to be rearranged. When atoms are in different relationship to each other, the result is *isomers*, not resonance forms.



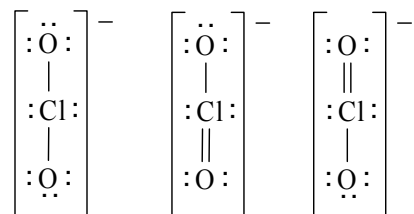


- 2.48** (a) The formal charge distribution is similar for both structures. In the first, the end nitrogen atom is -1 , the central N atom is $+1$, and O atom is 0 . For the second structure, the end N atom is 0 , the central N atom is still $+1$, but the O atom is -1 . The second is preferred because it places the negative formal charge on the most electronegative atom. (b) In the first structure, there are three O atoms with formal charges of -1 and one O atom with a formal charge of 0 . The formal charge on the P atom is 0 . In the second structure, the P atom has a formal charge of -1 ; there are two oxygen atoms with formal charges of -1 and two with formal charges of 0 . The first structure is preferred because it places the negative formal charge at the more electronegative atom, in this case O.

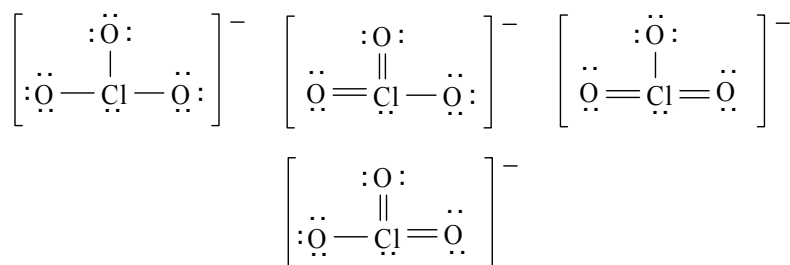
- 2.50** (a) The dihydrogen phosphate ion has one Lewis structure that obeys the octet rule. Including one double bond to oxygen lowers the formal charge at P. There are two resonance forms that include this contribution.



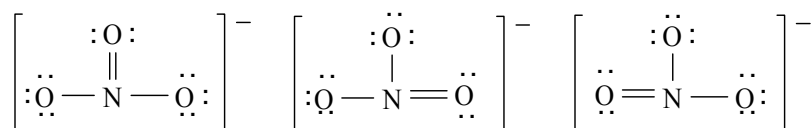
(b) There is one Lewis structure that obeys the octet rule shown below at the left. The formal charge at chlorine can be reduced to 0 by including one double bond contribution. This gives rise to two expanded octet structures.



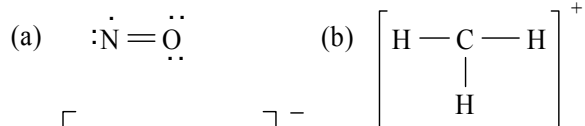
(c) As with the two preceding examples, there is one Lewis structure for the chlorate ion that obeys the octet rule. The formal charge at Cl can be reduced to 0 by including two double bond contributions, giving rise to three resonance forms.



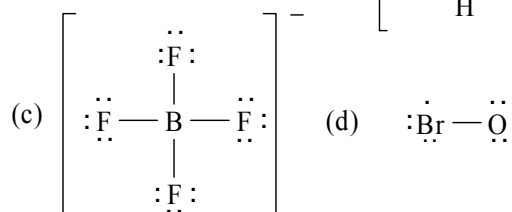
(d) For the nitrate ion, there are three resonance forms that all obey the octet rule.

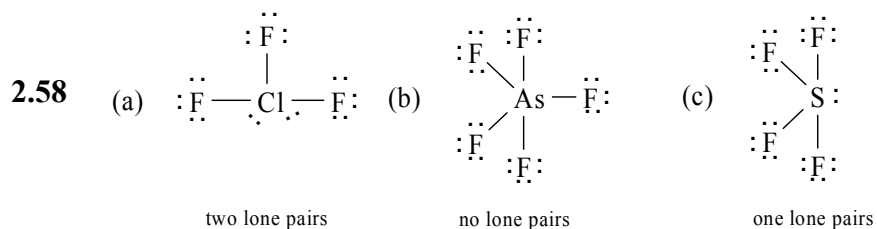
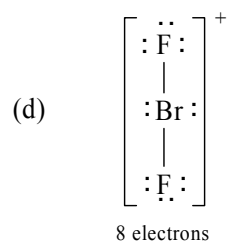
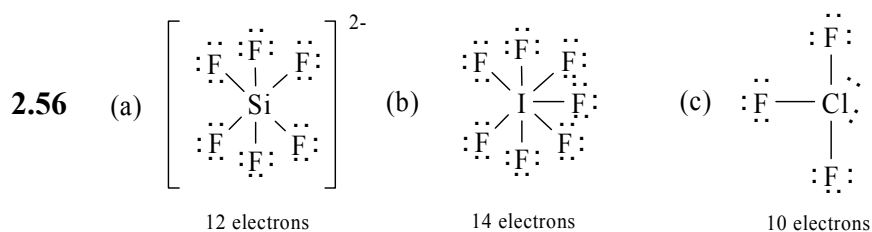
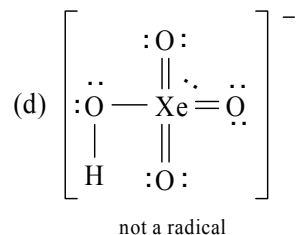
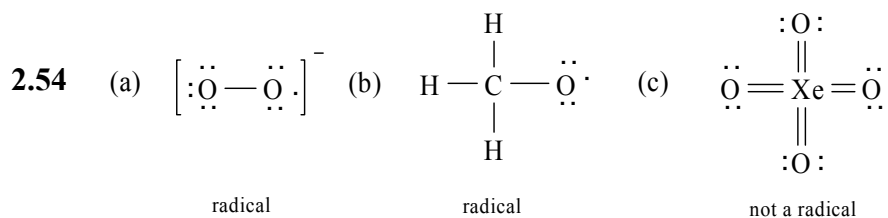


2.52 The Lewis structures are



Radicals are species with an unpaired electron, therefore (a) and (d) are radicals.





2.60 Electronegativity decreases with increased mass, so the heavier alkali metals and alkaline earth metals are the most electropositive. In order of increasing *electropositive* character: Li (1.0) < Na (0.93) < K (0.82) ~ Rb (0.82) < Cs (0.79); Be (1.6) < Mg (1.3) ~ Ca (1.3) < Sr (0.95) < Ba (0.89) ~ Ra (0.9)

2.62 $\text{Si} (1.9) < \text{P} (2.2) < \text{S} (2.6) \sim \text{C} (2.6) < \text{N} (3.0) < \text{O} (3.4) < \text{F} (4.0)$.

Generally electronegativity increases as one goes from left to right across the periodic table and as one goes from heavier to lighter elements within a group.

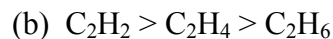
2.64 (a) The N—H bond in NH_3 would be more ionic; the electronegativity difference between N and H (3.0 versus 2.2) is greater than between P and H (2.2 versus 2.2). (b) N and O have similar electronegativities (3.0 versus 3.4), leading us to expect that the N—O bonds in NO_2 would be fairly covalent. The electronegativity difference between S and O is greater, so S—O bonds would be expected to be more ionic (2.6 versus 3.4). (c) Difference between SF_6 and IF_5 would be small because S and I have very similar electronegativities (2.6 versus 2.7). Because I has an electronegativity closer to that of F, it may be expected that IF_5 would have more covalent bond character, but probably only slightly more, than SF_6 .

2.66 $\text{Cs}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$: the smaller, more highly charged cations will be the more polarizing. The ionic radii are 170 pm, 138 pm, 72 pm, and 53 pm, respectively.

2.68 $\text{N}^{3-} < \text{P}^{3-} < \text{I}^- < \text{At}^-$: the polarizability should increase as the ion gets larger and less electronegative.

2.70 (a) $\text{NO} > \text{NO}_2 > \text{NO}_3^-$

NO_3^- . In NO the bond is a double bond, in NO_2 it is the average of a double and single bond (approximately 1.5), and in NO_3^- it is the average of three structures in which it is a single bond twice and a double bond once (approximately 1.33). The nitrate ion would, therefore, be expected to have the longest N—O bond length.



The bond would be longest in C_2H_6 in which it is a single bond. In C_2H_4 it is a double bond; in C_2H_2 it is a triple bond.

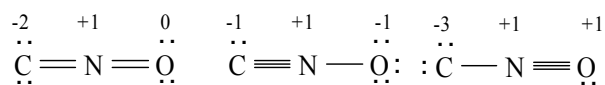


All the C—O bonds in CH_3OH and CH_3OCH_3 are single bonds and would be expected to be about the same length. The bond in formaldehyde H_2CO is a double bond and should be considerably shorter.

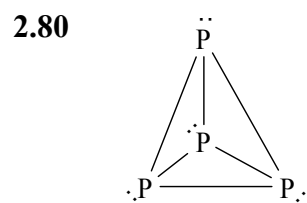
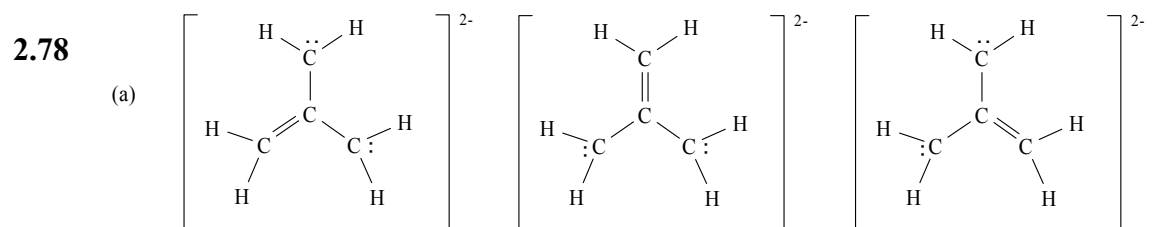
- 2.72** (a) The C—O bond in formaldehyde is a double bond, so the expected bond length will be 67 pm (double bond covalent radius of C) + 60 pm (double bond covalent radius of O) = 127 pm. The experimental value is 120.9 pm. (b) and (c) The C—O bonds in dimethyl ether and methanol are single bonds. The sum of the covalent single bond radii is 77 + 74 pm = 151 pm. The experimental value in methanol is 142.7 pm. (d) The C—S bond in methanethiol is a single bond. The sum of the covalent single bond radii is thus 77 + 102 pm = 179 pm. The experimental value is 181 pm.

- 2.74** The bond orders as determined by drawing the Lewis structures are 2 for (a), 1 for (b), and 3 for (c). Therefore, (c) HCN will have the greatest bond strength.

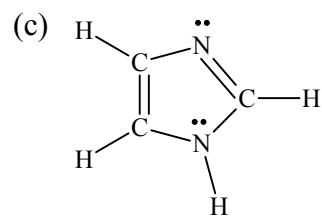
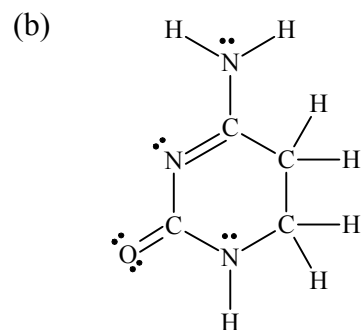
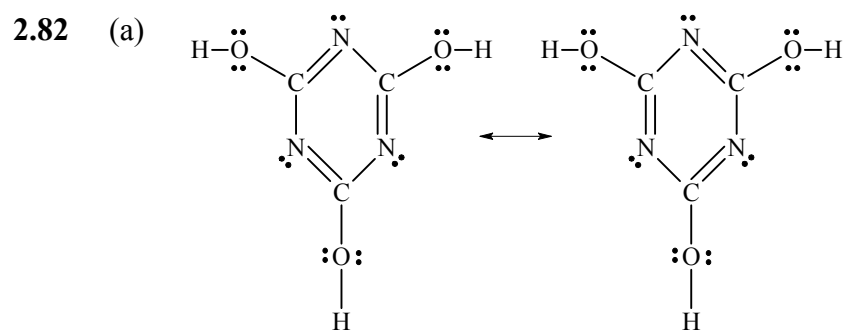
- 2.76** The Lewis structures are:



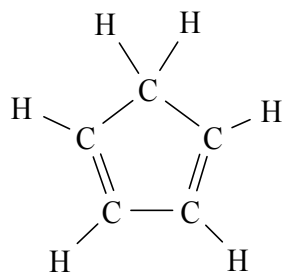
The Lewis structure in the center is probably the most important as it is the structure with the formal charges of the individual atoms closest to zero.



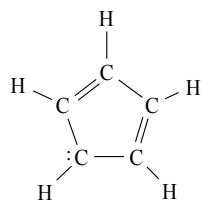
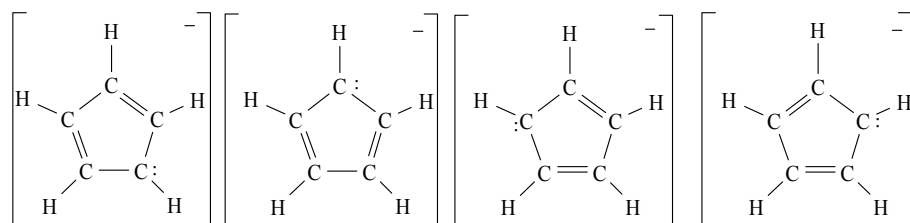
Yes, the molecule obeys the octet rule.



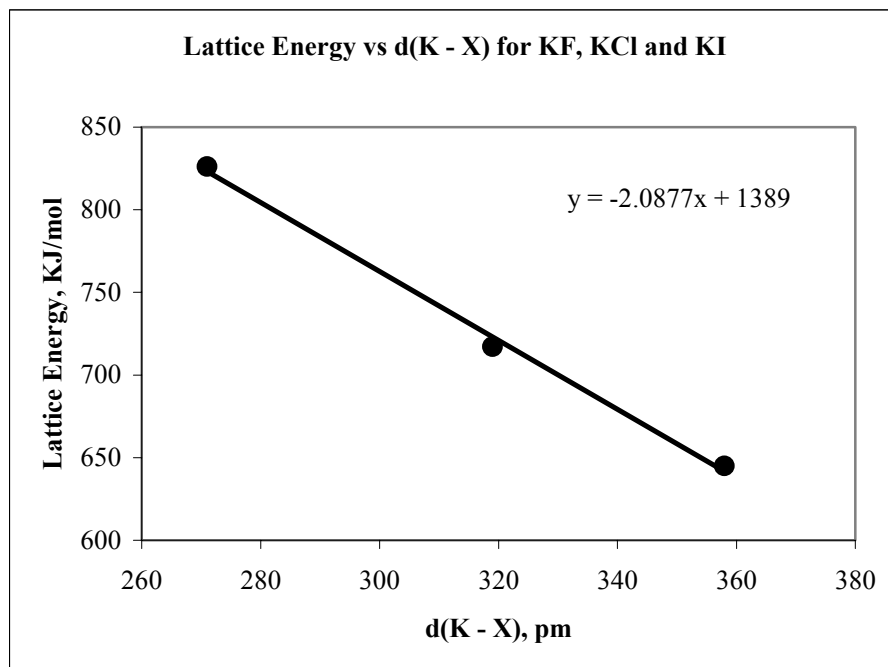
2.84 Cyclopentadiene has two C—C double bonds as shown. There are no resonance forms possible:



For the $[\text{C}_5\text{H}_5]^-$ ion, however, there are five resonance forms possible, as shown



2.86	$d(K - X)$	Lattice Energy, kJ/mol
Fluoride	271	826
Chloride	319	717
Iodide	358	645



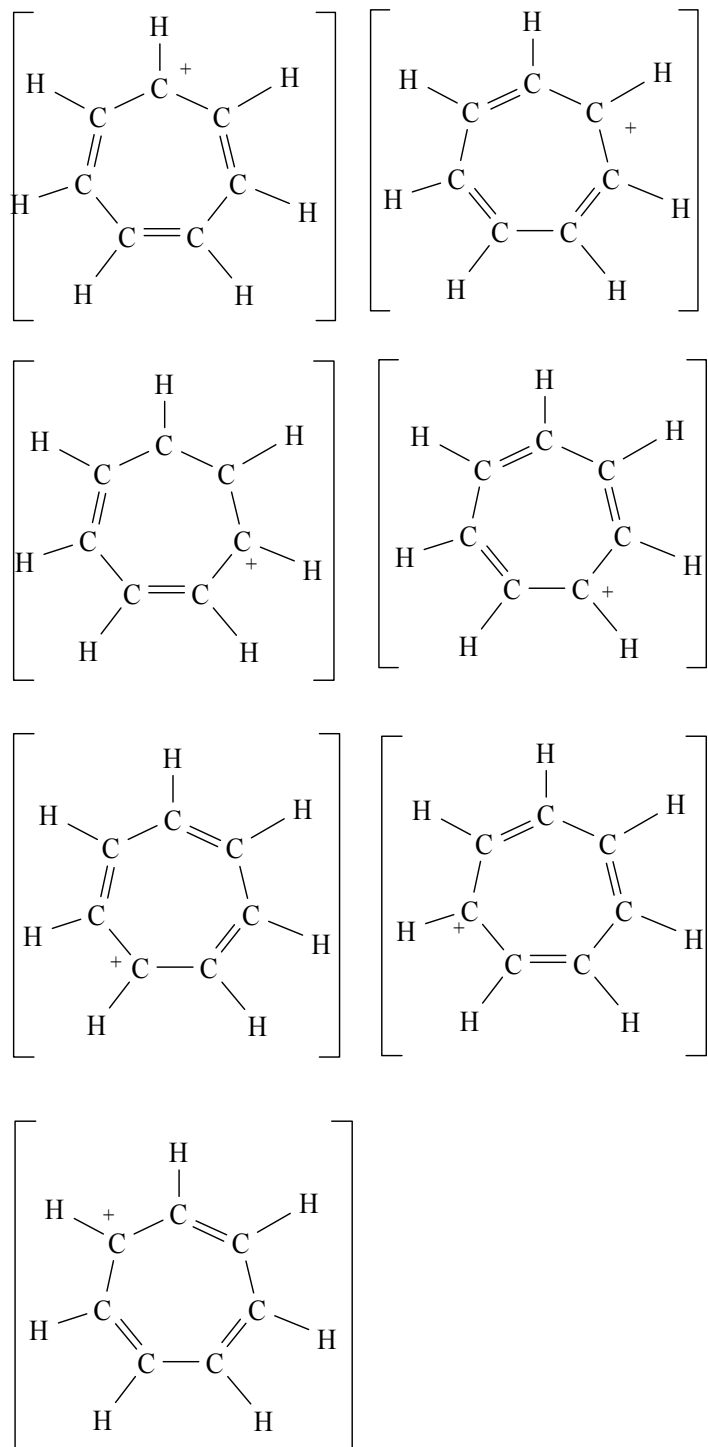
The data fit a straight line with a correlation coefficient of greater than 99%. (b) From the equation derived for the straight line relationship

$$\text{Lattice Energy} = -1.984 d_{M-X} + 1356$$

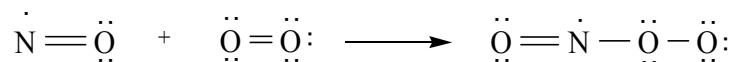
and the value of $d_{K-Br} = 338$ pm, we can estimate the lattice energy of KBr to be $693 \text{ kJ} \cdot \text{mol}^{-1}$.

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

2.88 There are seven resonance structures for the tropyllium cation. All the C—C bonds will have the same bond order, which will be the average of 4 single bonds and 3 double bonds to give 1.43.



2.90 The most likely way for these to react is for the molecules to join at the atoms that possess the unpaired electrons, forming a bond that will pair the two originally unpaired electrons:

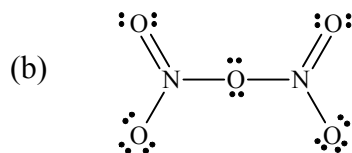
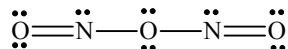


2.92

Z	Configuration	Number of unpaired e ⁻	Element	Charge	Energy state
38	[Kr]5p ¹	1	Sr	+1	excited
45	[Kr]4d ⁷	3	Rh	+2	ground
43	[Kr]5s ¹ 4d ⁵	6	Tc	+1	ground
8	[Ne]	0	O	-2	ground
21	[Ar]4s ¹ 3d ¹	2	Sc	+1	excited

2.94 (a) C: -1, N: 0; (b) C: -2, N: +1, O: 0; (c) terminal N's: -1, middle N: +1

2.96 (a) The structure with the lowest formal charges will be the most likely structure. All of the formal charges on the structure below are zero:



(c) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$. The secondary pollutant is nitric acid.

2.98 The energy of the O–O bond is given in Table 2.3 as 157 kJ/mol. The frequency of a photon that would deliver this minimum energy needed to break the bond is given by:

$$\nu = \frac{E}{h} = \frac{\left(\frac{157 \text{ kJ/mol}}{6.02214 \times 10^{23} \text{ mol}^{-1}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{6.62608 \times 10^{-34} \text{ J} \cdot \text{s}} = 3.39 \times 10^{14} \text{ Hz}$$

2.100 The C—H bond, because the effective mass is lower and the C—H bond is stiffer than the C—Cl bond.

2.102 This question can be answered by examining the equation that relates the reduced mass μ to the vibrational frequency:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

We will assume that the force constant k is essentially the same for the Fe—H and Fe—D bonds and set up the proportionality between the frequencies of the two vibrations:

$$\begin{aligned} \frac{\nu_{\text{Fe-D}}}{\nu_{\text{Fe-H}}} &= \frac{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{Fe-D}}}}}{\frac{1}{2\pi} \sqrt{\frac{k}{\mu_{\text{Fe-H}}}}} \\ \nu_{\text{Fe-D}} &= (\nu_{\text{Fe-H}}) \sqrt{\frac{\mu_{\text{Fe-H}}}{\mu_{\text{Fe-D}}}} \\ &= (1950 \text{ cm}^{-1}) \sqrt{\frac{\frac{m_{\text{Fe}} m_{\text{H}}}{m_{\text{Fe}} + m_{\text{H}}}}{\frac{m_{\text{Fe}} m_{\text{D}}}{m_{\text{Fe}} + m_{\text{D}}}}} \\ &= (1950 \text{ cm}^{-1}) \sqrt{\frac{(55.85)(1.01)}{55.85 + 1.01} \cdot \frac{55.85 + 2.01}{(55.85)(2.01)}} \\ &= (1950 \text{ cm}^{-1}) \sqrt{0.5113} \\ &= 1394 \text{ cm}^{-1} \end{aligned}$$

Note that we have also assumed the average mass for Fe to be 55.85 g · mol⁻¹. It would be more correct to use the mass of the particular isotope of Fe bonded to the H atom. Because that is not given, the average value has been used. The change in frequency due to the use of different isotopes of iron is very small compared to the change in frequency due to the substitution of D for H, because the percentage change is much greater

in the latter case. The mass essentially doubles upon replacing H with D; however, only a small percentage change is observed on going from one isotope of iron to another.