

**CHAPTER 6: ACID-BASE AND DONOR-ACCEPTOR CHEMISTRY**

6.1	Acid	Base	Definition
a.	$\text{AlBr}_3$	$\text{Br}^-$	Lewis
b.	$\text{HClO}_4$	$\text{CH}_3\text{CN}$	Lewis, Brønsted-Lowry
c.	$\text{Ni}^{2+}$	$\text{NH}_3$	Lewis
d.	$\text{ClF}$	$\text{NH}_3$	Lewis
e.	$\text{SO}_2$	$\text{ClO}_3^-$	Lewis
f.	$\text{HF}$	$\text{C}_3\text{H}_7\text{COOH}$	Lewis, Brønsted-Lowry

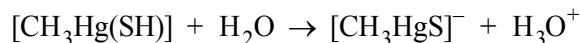
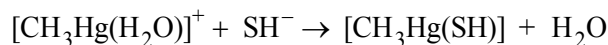
6.2	Acid	Base	Definition
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a.	$\text{XeO}_3$	$\text{OH}^-$	Lewis
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This is not a Brønsted-Lowry reaction since the product connectivity is  $[\text{XeO}_3(\text{OH})]^-$ .

b.	$\text{Pt}$	$\text{XeF}_4$	Lewis
c.	$\text{H}_2\text{SeO}_4$	$\text{C}_2\text{H}_5\text{OH}$	Lewis, Brønsted-Lowry
d.	$[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+$	$\text{SH}^-$	Lewis

This reaction likely occurs via the following steps:

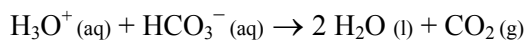


While a Brønsted-Lowry reaction occurs in the second step, the species listed in Problem 6.2d are involved in the initial Lewis acid-base reaction.

e.	$\text{CH}_3\text{COOH}$	$(\text{benzyl})_3\text{N}$	Lewis, Brønsted-Lowry
f.	$\text{HCl}$	$\text{SO}_2$	Lewis

6.3  $\text{Al}^{3+}$  is acidic:  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+$

The hydronium ions react with the basic bicarbonate to form  $\text{CO}_2$ :



With  $pK_a$  values of 5.0 for  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , 6.4 for  $\text{H}_2\text{CO}_3$ , and 2.0 for  $\text{HSO}_4^-$ , the pH is about 3, low enough to convert the bicarbonate to  $\text{CO}_2$ .

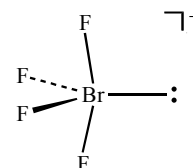
6.4 An increase in conductivity suggests that ions are formed:  $\text{BrF}_3 + \text{KF} \rightleftharpoons \text{BrF}_4^- + \text{K}^+$

6.5 a. The ions are  $[\text{BrF}_6]^-$  and  $[\text{BrF}_4]^+$ :  $2 \text{Cs}[\text{BrF}_6] + [\text{BrF}_4][\text{Sb}_2\text{F}_{11}] \longrightarrow 3 \text{BrF}_5 + 2 \text{CsSbF}_6$

b.  $[\text{BrF}_6]^-$ :  $O_h$  (this complex features a stereochemically inactive nonbonding pair on the central Br atom. See A. R. Mahjoub, X. Zhang, K. Seppelt, *Chem. Eur. J.* **1995**, *1*, 261.)

$[\text{BrF}_4]^+$ :  $C_{2v}$

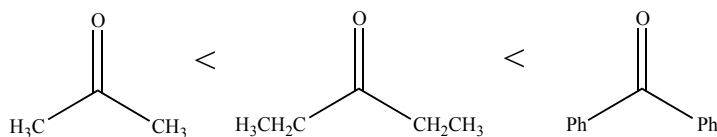
c.  $[\text{BrF}_4]^+$  acts as a Lewis acid, accepting  $\text{F}^-$ .



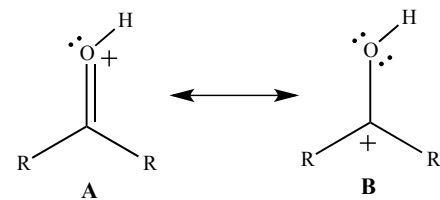
6.6  $2 \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$  and  $2 \text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_4\text{PO}_4^+ + \text{H}_2\text{PO}_4^-$   
form enough ions to allow conductance in the pure acids.

6.7 Gas-phase basicity is defined as  $\Delta G$  for  $\text{BH}^+(\text{g}) \rightarrow \text{B}(\text{g}) + \text{H}^+(\text{g})$ , while proton affinity is  $\Delta H$  for the same reaction. Since  $\Delta G = \Delta H - T\Delta S$ , and  $\Delta S$  is undoubtedly positive for these reactions (where one mole of gaseous reactant is converted to two moles of gaseous products), it makes sense that the gas-phase basicities in Table 6.6 are less positive than the corresponding proton affinities.

6.8 These data suggest the following basicity ranking for these ketones:



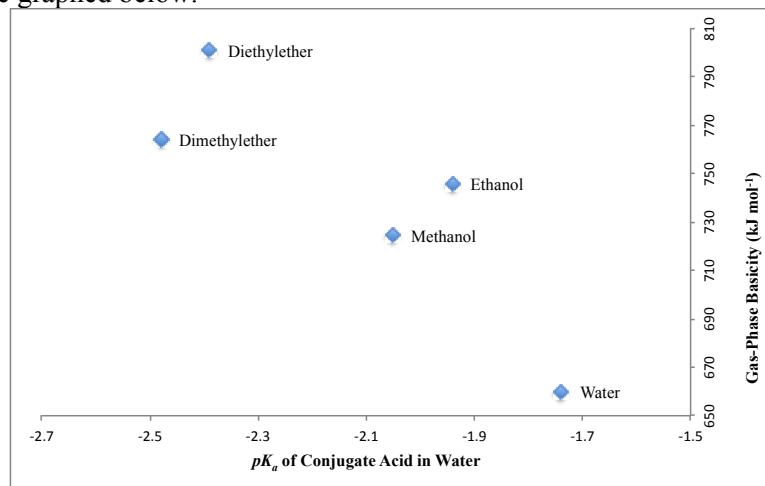
A convenient way to rationalize this basicity ranking is to examine the conjugate acids via resonance arguments. One resonance form features a positive charge on the carbonyl carbon (structure **B**, right). Since benzophenone can further delocalize this positive charge into its phenyl groups, the conjugate acid of benzophenone is the most stabilized of the three acids, leading to benzophenone being the strongest base. Since an ethyl group is slightly more electron-releasing than a methyl group, the conjugate acid of diethylketone is slightly more stabilized relative to the conjugate acid of acetone (structure **B** is more effectively stabilized in the conjugate acid of diethylketone relative to **A**, the conjugate acid of acetone). Acetone is consequently the weakest base among these ketones.



6.9 These data indicate that triphenylphosphine ( $\text{PPh}_3$ ) is more basic than triphenylamine ( $\text{NPh}_3$ ) in the gas phase. On the sole basis of electronics, triphenylamine would be expected to be more basic by virtue of the higher electronegativity of N relative to P, leading to the N center being more electron rich than the P center. However, the origin of the observed gas-phase basicity ranking must be the varying abilities of these atoms to accommodate the tetrahedral geometries of the conjugate acids. The larger covalent radius of P relative to N results in longer P—C(phenyl) bonds than N—C(phenyl) bonds, resulting in less steric strain between the phenyl rings in

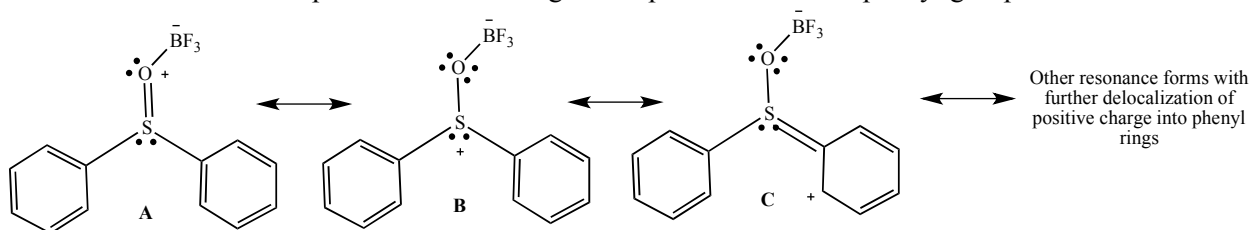
$[\text{HPPH}_3]^+$  relative to  $[\text{HNPh}_3]^+$ . The conjugate acid  $[\text{HPPH}_3]^+$  has less steric hindrance than  $[\text{HNPh}_3]^+$ , and  $\text{PPh}_3$  is more basic.

**6.10** The data are graphed below.



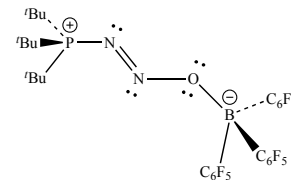
- The gas-phase and aqueous basicity data correlate poorly. The strongest base in aqueous solution ( $\text{H}_2\text{O}$ ) is the weakest base in the gas phase. While basicity in water increases as  $\text{Me}_2\text{O} < \text{Et}_2\text{O} < \text{MeOH} < \text{EtOH} < \text{H}_2\text{O}$ , the basicity in the gas-phase increases as  $\text{H}_2\text{O} < \text{MeOH} < \text{EtOH} < \text{Me}_2\text{O} < \text{Et}_2\text{O}$ .
- The ethers are the strongest gas-phase bases within this series on the basis of the electronic impact of two electron-releasing alkyl groups bound to the oxygen atom compared to one group ( $\text{ROH}$ ) or no alkyl groups ( $\text{H}_2\text{O}$ ). The oxygen atoms of these ethers are relatively electron rich as a result. However, the ethers are the weakest bases in water of this series; their conjugate acids have fewer sites for hydrogen bonding with  $\text{H}_2\text{O}$  relative to the conjugate acids of alcohols and water. The poorer ability of the conjugate acids of the ethers to be solvated by water renders these ethers very poor bases in aqueous solution.
- As shown in the graph and the basicity rankings above, the “ethyl” molecule is more basic than the “methyl” molecule in both the gas-phase and in aqueous solution. This is undoubtedly an inductive effect; the more electron-releasing ethyl group renders  $\text{Et}_2\text{O}$  and  $\text{EtOH}$  more basic than  $\text{Me}_2\text{O}$  and  $\text{MeOH}$ , respectively, in both phases.
- $\text{H}_2\text{O}$  is the strongest base in water of this series on the basis of the excellent ability of its conjugate acid ( $\text{H}_3\text{O}^+$ ) to be solvated by water via hydrogen bonding. It is the weakest gas-phase base within this series as a consequence of the relatively poor inductive effect of H compared to methyl and ethyl in increasing electron density at the oxygen atom.

- 6.11** This  $\text{BF}_3$  affinity trend is strongly correlated to the inductive ability of the groups bound to sulfur. These data suggest that the electron-releasing ability of substituents in sulfoxides ( $\text{R}_2\text{SO}$ ) increases as  $\text{R} = \text{Ph} < \text{Me} < {}^n\text{Bu} \approx \text{cyclo}-(\text{CH}_2)$ . A resonance argument can be employed to further rationalize the relatively low  $\text{BF}_3$  affinities of  $\text{Ph}_2\text{SO}$  and  $\text{PhSOMe}$ . The phenyl group permits delocalization of the formal positive charge at the oxygen in structure C (below), rendering this oxygen atom less Lewis basic than when alkyl groups—which cannot enable this attenuation of the positive formal charge—are present instead of phenyl groups.



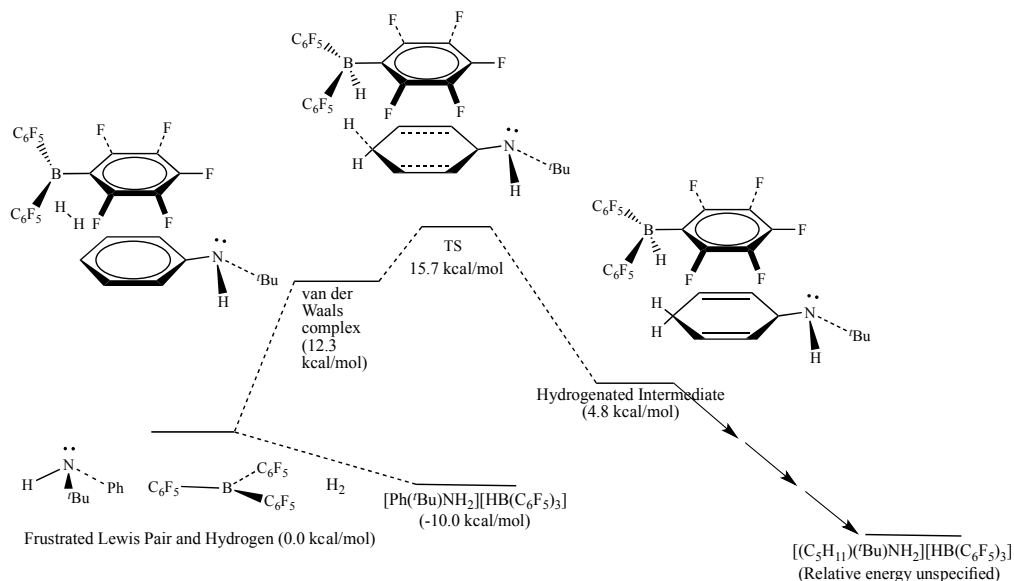
- 6.12**
- According to the authors, a reference acid should be a strong enough Lewis acid to react with most common bases; form 1:1 acid-base adducts; have spectroscopic characteristics that can be monitored to observe variations in the strength of Lewis bases when reactions are conducted; and should not undergo side reactions while acting as a Lewis acid.
  - Lewis basicity towards the zinc(II) reference is governed significantly by the steric hindrance created at the nitrogen upon complexation. The bases quinuclidine and pyridine, both of which feature insignificant geometric changes at nitrogen upon binding, were found more Lewis basic than all primary, secondary, and tertiary amines examined with the zinc(II) reference. This is not the case when assessing Lewis basicity via  $\text{BF}_3$  affinities. For example, the  $\text{BF}_3$  affinity for pyridine ( $128.08 \text{ kJ/mol}$ ) is less than for some tertiary amines (for example, the  $\text{BF}_3$  affinity of  $\text{Me}_3\text{N}$  is  $139.53 \text{ kJ/mol}$ ).
  - The importance of steric hindrance is reflected in the trends observed. When acyclic amines are considered, the less hindered primary amines were generally the strongest Lewis bases. A clear trend was not observed with secondary and tertiary amines, but secondary amines were found stronger bases than tertiary amines when bases with the same alkyl group were examined. Among alicyclic amines, the trend is opposite in that quinuclidine (tertiary) was found stronger than the secondary amine piperidine. The authors state the relative order of the Lewis basicity for acyclic amines as primary > secondary > tertiary, but an inverted order for alicyclic amines (tertiary > secondary  $\approx$  primary (acyclic)).

- 6.13**
- The frustrated Lewis pair of the sterically encumbered  $\text{P}(t\text{-C}_4\text{H}_9)_3$ , in combination with the highly Lewis acidic  $\text{B}(\text{C}_6\text{F}_5)_3$ , binds  $\text{N}_2\text{O}$  to give a PNNOB linkage.



- This complex has been characterized by single crystal X-ray crystallography (figure at right).

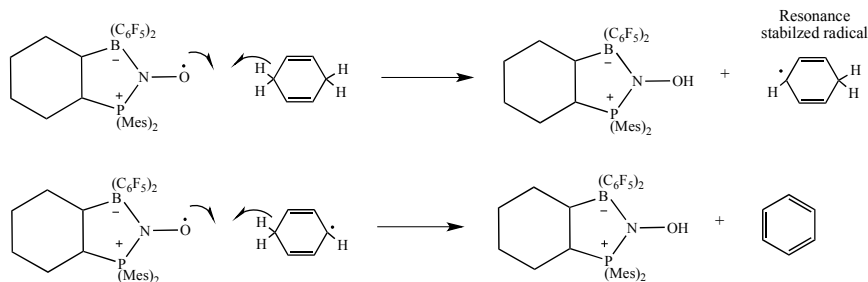
- 6.14 a. The reaction coordinate diagram is below. The van der Waals complex is hypothesized to be stabilized via significant pi-stacking between the aromatic rings of the borane and the secondary amine. In the transition state, the B—H bond has fully formed, and the proton is beginning to form a C—H bond with the previously aromatic ring of the amine. The formal positive charge of the hydrogenated intermediate (not shown on the *isop* carbon of the amine) is stabilized by resonance.



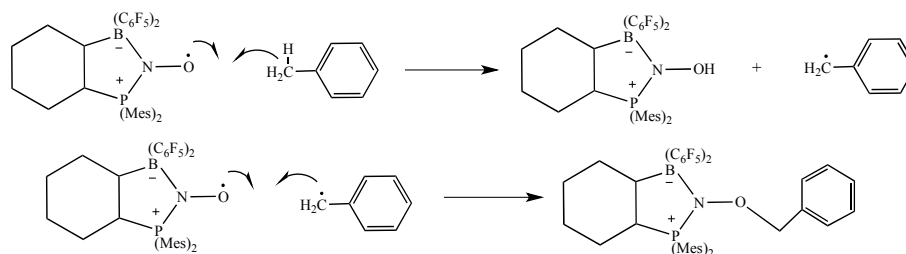
- b. As proposed in the reference, the phenyl ring of the amine in the van der Waals complex rotates towards the boron atom. The hydrogen molecule is then “split” in this cavity formed by the borane and the phenyl ring of the secondary amine. The hydride bonds to the boron, and the proton binds to the *para* carbon of the amine phenyl ring.
- c. The activation barrier for hydrogenation of the phenyl ring of the secondary amine is higher than that for formation of  $[Ph(tBu)NH_2][HB(C_6F_5)_3]$ , which is considered the resting state for this reaction. Therefore the rate of the hydrogenation reaction is exceedingly low in pentane at ambient temperature, but viable in refluxing toluene.
- d. The salt  $[{}^iPr_2NPh][HB(C_6F_5)_3]$  forms when the more basic  ${}^iPr_2NPh$  is employed. It is hypothesized that  ${}^iPr_2NPh$  is sufficiently basic to not allow formation of the arene-borane van der Waals complex necessary to permit hydrogenation of the aromatic ring of the amine.

6.15 The N—O distance in the complex **2b** is 129.6 pm, longer than the corresponding bond in free NO (115.1 pm). Bond lengthening is expected since NO likely uses its  $\pi^*$  orbital (its LUMO) to accept electron density from the phosphine. Population of an orbital that is antibonding with respect to the N—O bond will result in a longer bond distance. It is also noteworthy that the LUMO of NO features greater orbital contribution from the nitrogen atom relative to the oxygen atom, and the nitrogen atom binds to the phosphorous atom in **2b**.

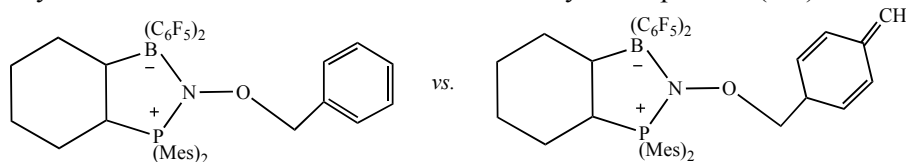
- a. Complex **2b** has strong radical character at oxygen, and reacts with 1,4-cyclohexadiene via a hydrogen-atom abstraction pathway to afford benzene.



Complex **2b** also reacts with the stronger C—H bond of toluene, with hydrogen-atom abstraction followed by radical coupling to form an O—C bond.



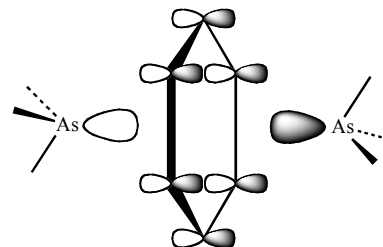
- b.** While the radical formed upon hydrogen-atom abstraction from the CH<sub>3</sub> group of toluene is resonance stabilized, C—O coupling involving a carbon atom in the ring would lead to a nonaromatic product (one such product is shown at right). Coupling at the primary carbon results in the retention of aromaticity in the product (left).



- 6.16**
- The  $\Delta pK_a$  for the water/HSCN pair is much smaller than for the water/HCN pair. The hydrogen bonding between water and HSCN is predicted as much stronger.
  - The hydrogen bond donors that have the smallest  $\Delta pK_a$  with nitriles are HClO<sub>4</sub> and HI.
  - (NC)<sub>3</sub>CH has the smallest  $\Delta pK_a$  with organic sulfides among the organic acids.
  - Classification on the basis of estimated  $\Delta pK_a$  values from the *Slide Rule* and the criteria in Section 6.5.1: Amines (medium strong), triphosphines (medium strong), sulfoxides (medium), ketones (medium/medium weak), and nitro compounds (medium weak).

6.17 a. The structure has the Br atoms in a staggered structure, resulting in  $S_6$  symmetry.

b. It is convenient to visualize this using tetrahedral,  $sp^3$  hybridized As. An  $sp^3$  orbital on each As points inward toward the benzene ring. If the hybrid lobes have opposite signs of their wave functions, they fit the symmetry of the  $\pi$  orbitals of the benzene ring to form bonding and antibonding molecular orbitals. The bonding interaction is shown.



6.18 a. The very high electronegativity of O in comparison with Al pulls the bonding pair very close to O. This increases the repulsion between the bonding pairs and causes the large angle. The steric bulk of the  $\text{AlCl}_3$  and  $\text{PCl}_3$  is not considered an important factor in dictating the large angle.

b. The dative bond between  $\text{OPCl}_3$  and  $\text{AlCl}_3$  likely employs a nonbonding donor orbital of  $\text{OPCl}_3$ . The donation of electron density from a nonbonding orbital of  $\text{OPCl}_3$  would not be expected to significantly impact the P—O bond order.

6.19 a. The methyl groups in  $(\text{CH}_3)_3\text{N—SO}_3$  donate electrons to the nitrogen, making  $(\text{CH}_3)_3\text{N}$  a stronger Lewis base and strengthening and shortening the N—S bond.

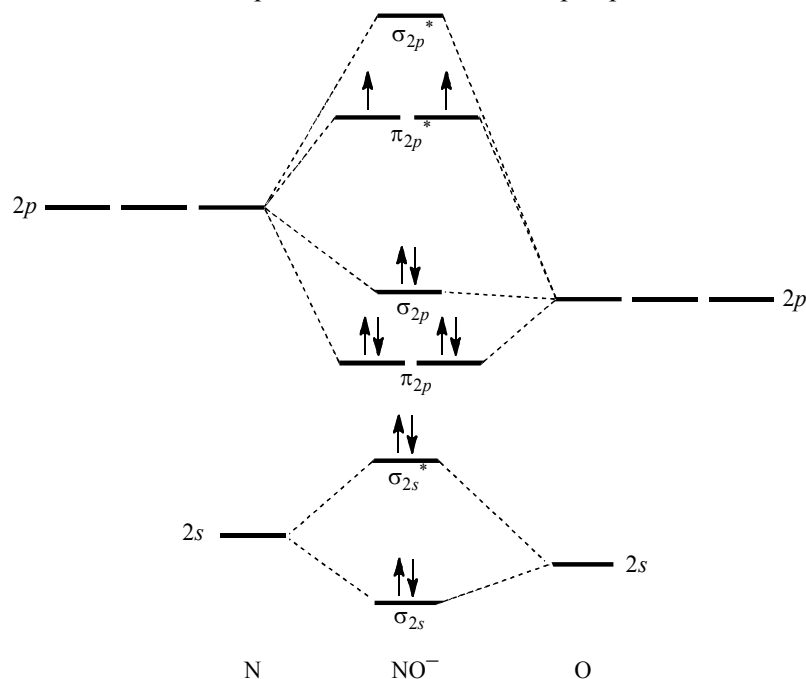
	$(\text{CH}_3)_3\text{N—SO}_3$	$\text{H}_3\text{N—SO}_3$
N—S	191.2 pm	195.7 pm
N—S—O	100.1°	97.6°

b. The greater concentration of electrons in the N—S bond of  $(\text{CH}_3)_3\text{N—SO}_3$  increases electron-electron ( $bp$ - $bp$ ) repulsions, opening up the N—S—O bond in comparison with  $\text{H}_3\text{N—SO}_3$ .

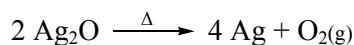
6.20 a. The polarity of the Xe—F bonds concentrates electrons on the fluorine atoms, which act as the centers of Lewis basicity. As shown in the reference, which provides the structure of  $[\text{Cd}(\text{XeF}_2)](\text{BF}_4)_2$ , the Xe—F—Cd bond is strongly bent at the fluorine and the geometry around xenon is nearly linear, with an F—Xe—F bond angle of 179.1°.

b. The  $\text{BF}_4^-$  ion is smaller than  $\text{AsF}_6^-$ , and the charge per fluorine is also greater in  $\text{BF}_4^-$ , making  $\text{BF}_4^-$  the stronger Lewis base. In addition, the higher oxidation state of cadmium(II) in  $[\text{Cd}(\text{XeF}_2)](\text{BF}_4)_2$  enables stronger interaction with the fluorines in  $\text{BF}_4^-$  than occurs between the silver(I) ion and  $\text{AsF}_6^-$  in  $[\text{Ag}(\text{XeF}_2)]\text{AsF}_6$ .

- 6.21** An energy level diagram for  $\text{NO}^-$  is below. The HOMO is the  $\pi^*$  orbital. Bonding with  $\text{H}^+$  depends on which end of the  $\pi^*$  orbital carries more electron density. Calculation shows slightly more electron density on N, making  $\text{HNO}$  the more likely (bent) molecule. This is consistent with the energy of the nitrogen  $2p$  subshell (-13.18 eV) relative that of the oxygen  $2p$  subshell (-15.85 eV); the nitrogen  $2p$  orbitals should contribute more to these  $\pi^*$  orbitals relative to the oxygen  $2p$  orbitals. Problem 6.43 asks for calculation of the molecular orbitals of both  $\text{HNO}$  and  $\text{HON}$  to address this question from an alternate perspective.



- 6.22** a. This is similar to the effects described in Section 6.4.2 for  $\text{I}_2$ .  $\text{Br}_2$  forms charge-transfer complexes with donor solvents such as methanol.
- b. The 500 nm band ( $\pi^* \rightarrow \sigma^*$ ) should shift to shorter wavelength (higher energy) because the difference in energy between the  $\pi^*$  and  $\sigma^*$  orbitals is greater in  $\text{Br}_2 \cdot \text{CH}_3\text{OH}$  than in  $\text{Br}_2$ .
- 6.23**  $\text{AlF}_3 + \text{F}^- \rightarrow \text{AlF}_4^-$ . The  $\text{Na}^+$ ,  $\text{AlF}_4^-$  salt can dissolve in  $\text{HF}$ . When  $\text{BF}_3$  is added, it has a stronger attraction for the fluoride ions, with the reaction  $\text{AlF}_4^- + \text{BF}_3 \rightarrow \text{AlF}_3 \downarrow + \text{BF}_4^-$ .
- 6.24** Soft metal ions do not combine with oxygen as strongly as hard metal ions, so reactions such as



are more easily carried out. Reduction of some of the softer metals can be carried out with relatively low temperatures (campfires); some think use of rocks containing ores could have led to accidental reduction to the metals and discovery of the smelting process. Harder metals such as iron require much higher temperatures for the reduction process.



**6.25** Hg is a much softer metal, and combines with the soft sulfide ion more strongly. Zinc and cadmium are more borderline metals, and combine with all the anions with more nearly equal facility.

**6.26** When any of these salts vaporize, the vapor phase consists of molecules. When they are in the solid state, they are ionic, with some covalent properties. The liquid state is between the two, and can be made up of ions, covalent molecules, or something between these two extremes. If the liquid is molecular, vaporization should be easier (molecules in the liquid phase being converted to molecules in the vapor phase). If the liquid is mostly ionic, vaporization is more difficult. Using this criterion, the most ionic liquids should be  $\text{ZnF}_2$  and  $\text{CdF}_2$ , and the most molecular liquids should be  $\text{HgF}_2$  and  $\text{HgCl}_2$ . On a more general view, mercury, as the softest metal in the series, forms the more molecular compounds and zinc, as the hardest, forms the more ionic compounds. Cadmium forms the most molecular compound with the borderline bromide.

**6.27 a.** pyridine +  $\text{BF}_3$ :

$$\begin{aligned}\Delta H &= -\left(E_{\text{py}}E_{\text{BF}_3} + C_{\text{py}}C_{\text{BF}_3}\right) \\ &= -[(1.17)(9.88) + (6.40)(1.62)] = -21.9 \text{ kcal/mol or } -91.6 \text{ kJ/mol. This predicted value is roughly 13\% less exothermic than the experimental value of } -105 \text{ kJ/mol.}\end{aligned}$$

pyridine +  $\text{B}(\text{CH}_3)_3$ :

$$\begin{aligned}\Delta H &= -\left(E_{\text{py}}E_{\text{B}(\text{CH}_3)_3} + C_{\text{py}}C_{\text{B}(\text{CH}_3)_3}\right) \\ &= -[(1.17)(6.14) + (6.40)(1.70)] = -18.1 \text{ kcal/mol, or } -75.7 \text{ kJ/mol. This predicted value is more exothermic than the experimental values of } -64 \text{ and } -71.1 \text{ kJ/mol, respectively.}\end{aligned}$$

**b.** Fluorine is electron-withdrawing, and  $\text{CH}_3$  electron-releasing. Therefore, B in  $\text{BF}_3$  carries a greater positive charge and interacts more strongly with Lewis bases such as pyridine.

**c.** The harder acid  $\text{BF}_3$  interacts more strongly with the borderline base pyridine.

**6.28**  $\text{NH}_3 + \text{BF}_3$ :

$$\begin{aligned}\Delta H &= -\left(E_{\text{NH}_3}E_{\text{BF}_3} + C_{\text{NH}_3}C_{\text{BF}_3}\right) \\ &= -[(1.36)(9.88) + (3.46)(1.62)] = -19.0 \text{ kcal/mol, or } -79.5 \text{ kJ/mol}\end{aligned}$$

$\text{NH}_3 + \text{B}(\text{CH}_3)_3$ :

$$\begin{aligned}\Delta H &= -\left(E_{\text{NH}_3}E_{\text{B}(\text{CH}_3)_3} + C_{\text{NH}_3}C_{\text{B}(\text{CH}_3)_3}\right) \\ &= [(1.36)(6.14) + (3.46)(1.70)] = -14.2 \text{ kcal/mol, or } -59.4 \text{ kJ/mol}\end{aligned}$$

The order is  $\text{pyridine} + \text{BF}_3 > \text{NH}_3 + \text{BF}_3 > \text{pyridine} + \text{B}(\text{CH}_3)_3 > \text{NH}_3 + \text{B}(\text{CH}_3)_3$ . The change from  $\text{BF}_3$  to  $\text{B}(\text{CH}_3)_3$  is larger than the change from pyridine to  $\text{NH}_3$ .

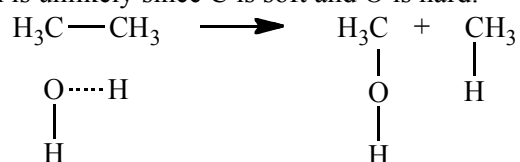
## 6.29 Absolute hardness parameters:

	<i>I</i>	<i>A</i>	$\eta$
BF <sub>3</sub>	15.81	-3.5	9.7
NH <sub>3</sub>	10.7	-5.6	8.2
C <sub>5</sub> H <sub>5</sub> N	9.3	-0.6	5.0
N(CH <sub>3</sub> ) <sub>3</sub>	7.8	-4.8	6.3

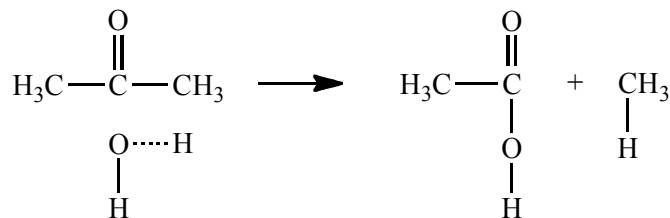
The difference between the HOMO of pyridine (9.3) and the LUMO of BF<sub>3</sub> (-3.5) is smaller than the other possible interaction, so this pair has the largest  $-\Delta H$ , in spite of the difference in hardness. By comparison with the nitrogen compounds, B(CH<sub>3</sub>)<sub>3</sub> is expected to have an absolute hardness lower than that of BF<sub>3</sub>, approximately 7.5–8.

6.30 CsI and LiF fit Basalo's principle that ions of similar size and equal (but opposite) charge form the least soluble salts. CsF and LiI have ionic sizes that are very different, and they do not fit as well into an ionic lattice. In addition, CsI and LiF are soft–soft and hard–hard combinations, which combine better than the hard–soft LiI and soft–hard CsF.

6.31 The following reaction is unlikely since C is soft and O is hard.



The second reaction is more likely. Adding the carbonyl oxygen makes C harder, and C in CH<sub>3</sub> and the H atom are soft.



- 6.32 a. Solubilities: MgSO<sub>4</sub> > CaSO<sub>4</sub> > SrSO<sub>4</sub> > BaSO<sub>4</sub>  
 Electrostatic forces predict the reverse order due to cation sizes (the charge density of Mg<sup>2+</sup> is greater than that of the larger Ba<sup>2+</sup>), but the larger cations fit better with the large sulfate anion in the crystals. Hydration of the cations is the strongest for Mg<sup>2+</sup>, weakest for Ba<sup>2+</sup>, agreeing with the solubility order.
- b. Solubilities: PbCl<sub>2</sub> > PbBr<sub>2</sub> > PbI<sub>2</sub> > PbS  
 As a moderately soft cation, Pb<sup>2+</sup> has stronger interactions with the softer anions (hardness order: Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> > S<sup>2-</sup>). In addition, hydration of the anions is largest for the chloride, smallest for sulfide, based on size.
- 6.33 The order is Al–OC–W (see Figure 13.17). The oxygen of CO is the “harder” end of this molecule and bonds with the harder Al atom; carbon and W engage in a soft–soft interaction.

- 6.34**
- TeH<sub>2</sub> is the strongest acid, because Te is more electronegative than either Sn or Sb. Therefore, the hydrogen is more positive and acidic.
  - NH<sub>3</sub> is the strongest base because N is more electronegative than either P or Sb.
  - (CH<sub>3</sub>)<sub>3</sub>N is the strongest base in the gas phase because the methyl groups contribute electron density to the nitrogen. In solution, the order is scrambled, probably due to solvation (Section 6.3.6).
  - 4-Methylpyridine > pyridine > 2-methylpyridine. Again, the methyl group adds electron density to the N. However, with methyl in the 2 position, steric hindrance makes bonding to BMe<sub>3</sub> more difficult.
- 6.35** In general, oxide ion reacts with water to form hydroxide:  $O^{2-} + H_2O \rightarrow 2 OH^-$ . In B<sub>2</sub>O<sub>3</sub>, the small, hard B<sup>3+</sup> holds on to the oxide ions strongly. As a result,  $B_2O_3 + 3 H_2O \rightarrow 2B(OH)_3 \rightleftharpoons H^+ + H_2BO_3^-$ , and the solution is very weakly acidic ( $pK_a = 9.25$ ). In Al<sub>2</sub>O<sub>3</sub>, the Al<sup>3+</sup> ion is larger and softer. It can form either [Al(OH)<sub>4</sub>]<sup>-</sup> (acting as an acid) or [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (acting as a base), depending on the other species in solution. Sc<sup>3+</sup> is still larger and softer, so it combines better with water than with hydroxide ion. The result is the reaction  $Sc_2O_3 + 15 H_2O \rightarrow 2[Sc(H_2O)_6]^{3+} + 6 OH^-$ .
- 6.36**
- $CaH_2 + 2 H_2O \rightarrow Ca^{2+} + 2 H_2\uparrow + 2 OH^-$  Calcium has a lower electronegativity than hydrogen, so CaH<sub>2</sub> is Ca<sup>2+</sup>(H<sup>-</sup>)<sub>2</sub> and the hydride ions react with water.
  - HBr + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + Br<sup>-</sup> Bromine is more electronegative than hydrogen, so the hydrogen is strongly positive and is readily transferred to the lone pair of water.
  - H<sub>2</sub>S + H<sub>2</sub>O  $\rightleftharpoons$  H<sub>3</sub>O<sup>+</sup> + HS<sup>-</sup> Sulfur is slightly more electronegative than hydrogen, and the positive hydrogen in H<sub>2</sub>S can dissociate to a small extent.
  - CH<sub>4</sub> + H<sub>2</sub>O → no reaction. The C–H bond is almost nonpolar; the interaction between the oxygen atom of water and this C–H bond required for hydrogen ion transfer is exceedingly weak.
- 6.37** BF<sub>3</sub> > B(CH<sub>3</sub>)<sub>3</sub> > B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> > B(C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> Alkyl groups are electron-donating and increase the electron density on B and reduce the attraction for the lone pair of NH<sub>3</sub>. The bulky mesityl groups render B(C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> less Lewis acidic on the basis of the steric hindrance introduced when these boron centers adopt the required tetrahedral geometry upon complexation of NH<sub>3</sub>.
- 6.38**
- CH<sub>3</sub>NH<sub>2</sub> is a stronger base on the basis of the electron-releasing ability of the methyl group.
  - Although 2-methylpyridine is the stronger base with smaller acid molecules, the methyl group interferes with adduct formation with trimethylboron (F-strain) and the pyridine-trimethylboron dative bond is stronger.

- c. Trimethylboron forms a stronger adduct with ammonia because the three phenyl rings of triphenylboron cannot bend back readily to allow the boron to become tetrahedral (B-strain).

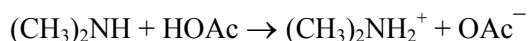
- 6.39 a. With the acids listed in order of increasing acidity:

	H <sub>3</sub> AsO <sub>4</sub>	H <sub>2</sub> SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HMnO <sub>4</sub>
<i>pK<sub>a</sub></i> (9-7 <i>n</i> )	2	2	-5	-12
<i>pK<sub>a</sub></i> (8-5 <i>n</i> )	3	3	-2	-7
<i>pK<sub>a</sub></i> (exp)	9.2	2.2	1.8	-11

- b. With the acids listed in order of increasing acidity:

	HClO	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>
<i>pK<sub>a</sub></i> (9-7 <i>n</i> )	9	2	-5	-12
<i>pK<sub>a</sub></i> (8-5 <i>n</i> )	8	3	-2	-7
<i>pK<sub>a</sub></i> (exp)	7.4	2	-1	-10

- 6.40 Dimethylamine acts as weak base in water, with a very small amount of OH<sup>-</sup> provided by the reaction (CH<sub>3</sub>)<sub>2</sub>NH + H<sub>2</sub>O  $\rightleftharpoons$  (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> + OH<sup>-</sup>. Acetic acid is a stronger acid than water, so dimethylamine acts as a stronger base, and the reaction



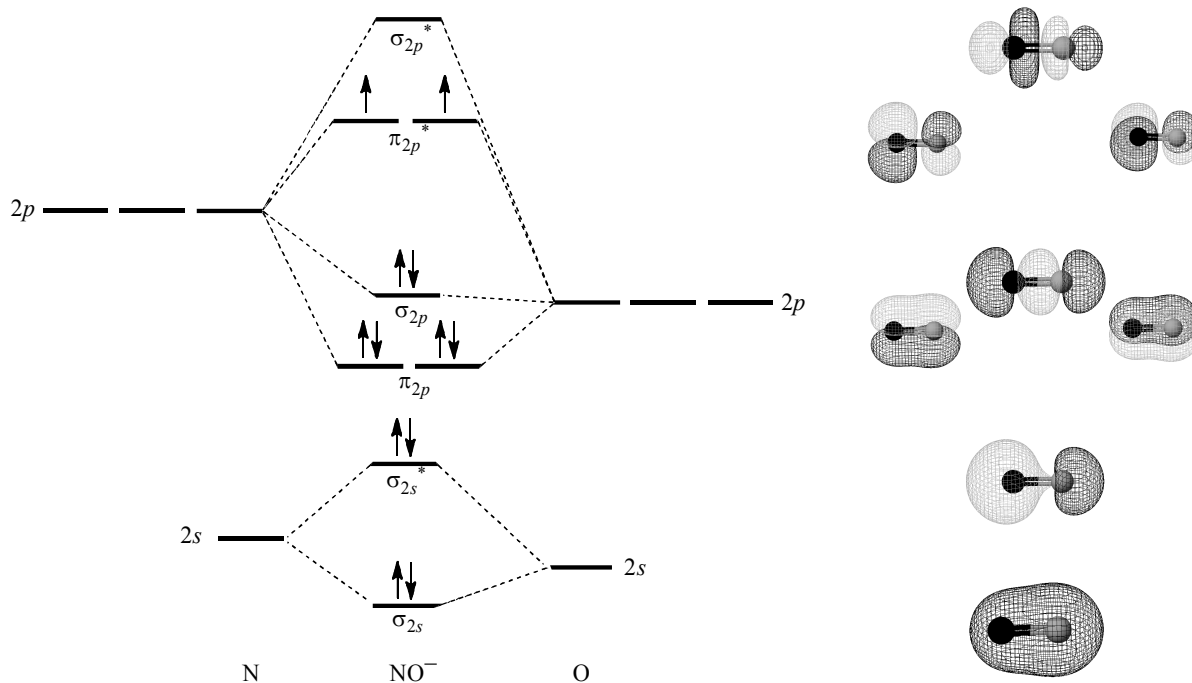
goes to completion. 2-Butanone is a neutral solvent; there is no significant acid-base reaction with dimethylamine.

- 6.41 SbF<sub>5</sub> in HF reacts to increase the H<sup>+</sup> concentration and decrease *H*<sub>0</sub>:



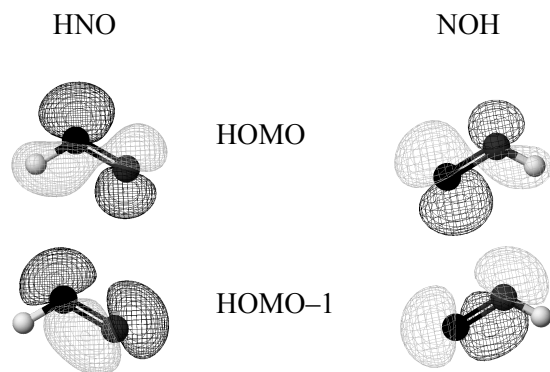
- 6.42 a. As the Lewis acids BF<sub>3</sub> and BCl<sub>3</sub> interact with NH<sub>3</sub>, the geometry around boron changes from planar to trigonal pyramidal; however, in accord with the LCP model the nonbonded F...F and Cl...Cl distances are nearly constant, suggesting that these atoms remain in contact with each other. Because these nonbonded distances remain essentially constant, the boron-halogen distance must increase as the distortion from trigonal geometry occurs. Because of the strength of the B-F bond, a consequence of the large electronegativity difference between B and F and the small size of the fluorine atom, more energy is required to distort BF<sub>3</sub> from planarity than to similarly distort BCl<sub>3</sub>. (Calculations in support of this argument are presented in the reference.) The consequence of this energy requirement is that BF<sub>3</sub> is a weaker Lewis base than BCl<sub>3</sub> toward NH<sub>3</sub>. The article does not address the relative Lewis basicity of BBr<sub>3</sub>, but a similar argument could apply for this compound.
- b. This article does not consider the LCP model but focuses on ab initio calculations on the adducts X<sub>3</sub>B-NH<sub>3</sub>. These calculations show a higher B-N bond dissociation energy in the BCl<sub>3</sub> adduct than in the BF<sub>3</sub> adduct. Although many factors are involved, an important issue is that BCl<sub>3</sub> has a lower energy LUMO that is able to interact more strongly with the donor orbital of NH<sub>3</sub>, giving a stronger covalent interaction (and stronger B-N bond) in Cl<sub>3</sub>B-NH<sub>3</sub>.

6.43 a. The energy diagram and the orbitals are shown below.

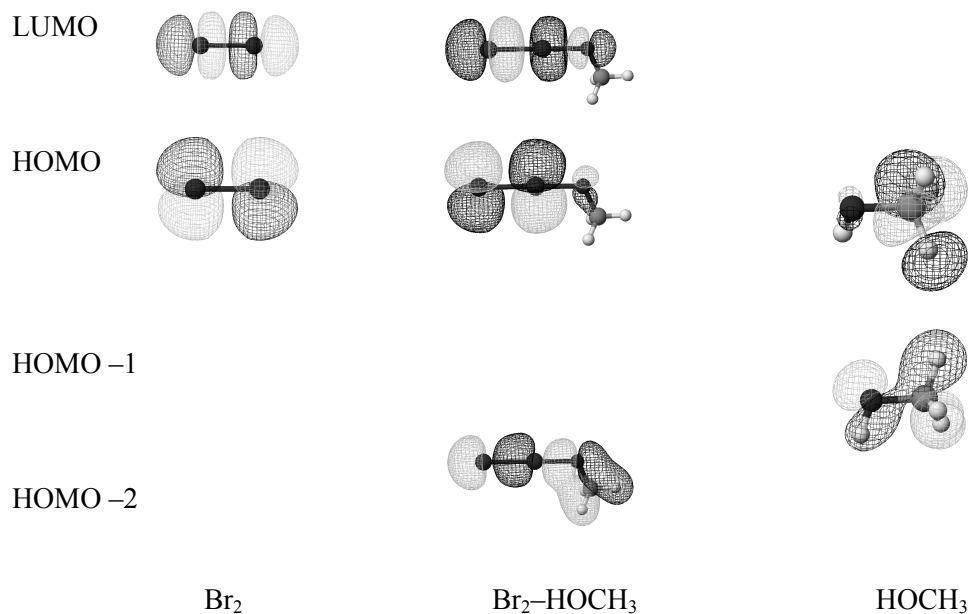


The HOMO is the  $\pi^*$ , with greater concentration of electron density on N. This orbital can overlap with the empty  $\text{H}^+$   $1s$  orbital, forming  $\text{HNO}$ , a bent molecule.

b. Calculations predict that  $\text{HNO}$  is more stable than  $\text{NOH}$ , with the energy of the  $\text{HNO}$  HOMO lower than the energy of the  $\text{NOH}$  HOMO. The HOMO and HOMO-1 of  $\text{HNO}$  and  $\text{NOH}$ , respectively, two of the nine molecular orbitals of these species arising from the valence orbitals, are shown below.

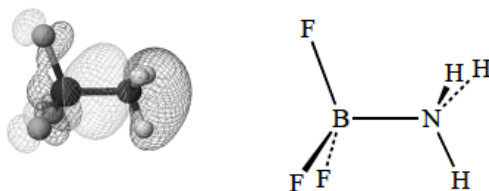


## 6.44

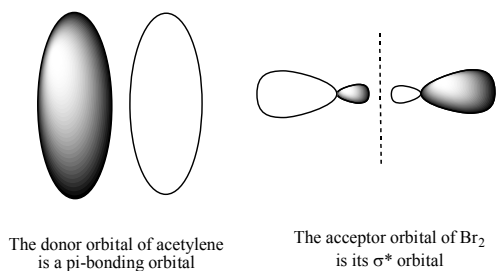


The interaction of the HOMO of the methanol and the LUMO of the  $\text{Br}_2$  results in the adduct LUMO and HOMO-2 orbitals, respectively. The geometry shown features the  $\text{Br}_2$  at approximately a trigonal angle ( $\text{H-O-Br}$  is  $113^\circ$  and  $\text{C-O-Br}$  is  $106^\circ$  in a PM3 calculation).

- 6.45** a. For orbitals of  $\text{BF}_3$  and  $\text{NH}_3$ , see Figures 5.32 and 5.30, respectively.
- b. The B-N bonding molecular orbital, shown below, is polarized toward the more electronegative nitrogen; the matching antibonding orbital, which has a node between the boron and nitrogen atoms, is polarized toward the boron.



- 6.46** a. The sketch below is a first approximation of the postulated interaction responsible for the halogen bond with acetylene.



- b.** A key orbital to look for is one in which the adjacent lobes of the pi-bonding orbital of acetylene, shown as **a**, and the  $\sigma^*$  orbital of Br<sub>2</sub> have merged into a larger lobe (occupied by an electron pair) that links the two molecules. This bonding orbital should have a matching antibonding orbital (empty) at higher energy.