Chapter 6
Acid-Base and Donor-Acceptor Chemistry

6-1

	Acid	Base	Definition
a.	BF_3	ClF	Lewis, solvent system
b.	$HClO_4$	CH_3CN	Lewis, Brønsted-Lowry
c.	ICl	PCl_5	Lewis, solvent system
d.	ClF_3	NOF	Lewis, solvent system
e.	SO_2	ClO_3^-	Lewis
f.	Pt	XeF_4	Lewis
g.	XeO_3	OH^-	Lewis
h.	SbF_5	HF	Lewis, solvent system
i.	Sn	NOCl	Lewis
j.	PtF_5	ClF_3	Lewis, solvent system
k.	CH_3COOH	$(benzyl)_3N$	Lewis, Brønsted-Lowry
l.	H_2O	BH_4^-	Lewis

6-2 Al^{3+} is acidic: $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$
The hydronium ions react with the basic bicarbonate to form CO_2:
$H_3O^+ + HCO_3^- \longrightarrow 2\ H_2O + CO_2\uparrow$ With pK_a values of 5.0 for $[Al(H_2O)_6]^{3+}$, 6.4 for H_2 and 2.0 for HSO_4^-, the pH is about 3, low enough to convert the bicarbonate to CO_2.

6-3 An increase in conductivity suggests that ions are formed:

$BrF_3 + AgF \rightleftharpoons BrF_4^- + Ag^+$

$BrF_3 + SnF_4 \rightleftharpoons BrF_2^+ + SnF_5^-$ or

$2\ BrF_3 + SnF_4 \rightleftharpoons 2\ BrF_2^+ + SnF_6^{2-}$

6-4 **a.** $3\ ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$ (see Greenwood and Earnshaw, *Chemistry of the Elements*, 2nd ed., p. 827)

b. Both solutes increase the concentration of ions:

$NaCl + ICl \longrightarrow Na^+ + ICl_2^-$
(NaCl acts as a base)

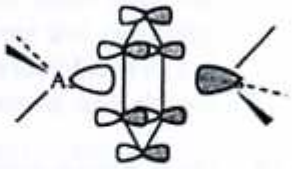
$AlCl_3 + 2\ ICl \longrightarrow I_2Cl^+ + AlCl_4^-$ ($AlCl_3$ acts as an acid)

6-5 $SnCl_4 + 2\ Cl^- \longrightarrow SnCl_6^{2-}$ is the primary reaction. NH_4Cl in ICl forms NH_4^+ and ICl_2^-, and the chloride ions are then transferred to $SnCl_4$.

6-6 $KF + IF_5 \rightleftharpoons K^+ + IF_6^-$, and the ions conduct electricity.

6-7 $2\ H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$ and $2\ H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$ form enough ions to allow conductance in the pure acids.

6-8 **a.** The structure has the Br atoms in a staggered structure, resulting in an S_6 symmetry.



b. It may be easier to visualize this by using tetrahedral As. The fourth sp^3 orbitals point inward toward the benzene ring. If one is added and one is subtracted, they fit the symmetry of the π orbitals of the benzene ring to form bonding and antibonding orbitals. An essentially nonbonding orbital can be made from the two lobes with the same sign; one side has a bonding interaction with the benzene orbitals and the other has an antibonding interaction.

6-9 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.

6-10 **a.** The methyl groups in $(CH_3)_3N—SO_3$ donate electrons to the nitrogen, making $(CH_3)_3N$ a stronger Lewis base and strengthening and shortening the N—S bond. the greater concentration of electrons in the N—S bond of $(CH_3)_3N—SO_3$ increases electron-electron (*bp-bp*) repulsions, opening up the N—S—O bond in comparison with $H_3N—SO_3$.

	$(CH_3)_3N—SO_3$	$H_3N—SO_3$
N—S	191.2 pm	195.7 pm
N—S—O	100.1°	97.6°

6-11 NO^- is isoelectronic with O_2 and has the electronic structure $\sigma^2\ \pi^2\ \pi^2\ \pi^{*1}\ \pi^{*1}$. Bonding with H^+ depends on which end of the π* orbital carries more electron density. Calculation shows slightly more electron density on N, making HNO the more likely (bent) molecule. NO^- readily dimerizes to $N_2O_2^{2-}$, with a *trans* configuration and a combination of π* orbitals from each of the monomers.

6-12 **a.** This is similar to the effects described in Section 6-2-8 for I_2. Br_2 forms charge-transfer complexes with donor solvents such as methanol.

6-27. **a.** CH_3NH_2 is a stronger base. The methyl group pushes electron density onto the nitrogen.

b. 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 formation 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).

6-28. **a.** With the acids listed in order of increasing acidity:

	H_3AsO_4	H_2SO_3	H_2SO_4	$HMnO_4$
pK_a (9-7*n*)	2	2	-5	-12
pK_a (8-5*n*)	3	3	-2	-7
pK_a (exptl)	9.2	2.2	1.8	-11

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

	HClO	$HClO_2$	$HClO_3$	$HClO_4$
pK_a (9-7*n*)	9	2	-5	-12
pK_a (8-5*n*)	8	3	-2	-7
pK_a (exptl)	7.4	2	-1	-10

6-29 Dimethylamine acts as a weak base in water, with a very small amount of OH^- provided by the reaction $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$. Acetic acid is a stronger acid than water, so dimethylamine acts as a stronger base and the reaction $(CH_3)_2NH$ + HOAc $\longrightarrow (CH_3)_2NH_2^+ + OAc^-$ goes to completion. 2-Butanone is a neutral solvent; there is no significant acid-base reaction with dimethylamine.

6-30. SbF_5 in HF reacts to increase the H^+ concentration and decrease H_0:

$SbF_5 + HF \rightleftharpoons H^+ + SbF_6^-$ These ions then can react with alkenes.