# CHAPTER

# 6

# Acid-Base and Donor-Acceptor Chemistry

## 6-1
## ACID-BASE CONCEPTS AS ORGANIZING CONCEPTS

The concept of acids and bases has been important since ancient times. It has been used to correlate large amounts of data and to predict trends. Jensen[1] has described a useful approach in the preface to his book on the Lewis acid-base concept:

> ...acid-base concepts occupy a somewhat nebulous position in the logical structure of chemistry. They are, strictly speaking, neither facts nor theories and are, therefore, never really "right" or "wrong." Rather they are classificatory definitions or organizational analogies. They are useful or not useful ... acid-base definitions are always a reflection of the facts and theories current in chemistry at the time of their formulation and ... they must, necessarily, evolve and change as the facts and theories themselves evolve and change ...

The changing definitions described in this chapter have generally led to a more inclusive and useful approach to acid-base concepts. Most of this chapter is concerned with the Lewis definition, its more recent explanation in terms of molecular orbitals, and its application to inorganic chemistry.

### 6-1-1 HISTORY

Practical acid-base chemistry was known in ancient times and developed gradually during the time of the alchemists. During the early development of acid-base theory, experimental observations included the sour taste of acids and the bitter taste of bases, color changes in indicators caused by acids and bases, and the reaction of acids with bases to form salts. Partial explanations included the idea that all acids contained oxygen (oxides of nitrogen, phosphorus, sulfur, and the halogens all form acids in water), but by the early 19th century, many acids that do not contain oxygen were known. By 1838, Liebig defined acids as "compounds containing hydrogen, in which the hydrogen can be replaced by a metal,"[2] a definition that still works well in many instances.

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[1] W. B. Jensen, *The Lewis Acid-Base Concepts*, Wiley-Interscience, New York, 1980, p. vii.
[2] R. P. Bell, *The Proton in Chemistry*, 2nd ed., Cornell University Press, Ithaca, NY, 1973, p. 9.

**TABLE 6-1**
**Comparison of Acid-Base Definitions**

| | | Definitions | | Examples | |
|---|---|---|---|---|---|
| Description | Date | Acid | Base | Acid | Base |
| Lavoisier | ~1776 | Oxide of N, P, S | Reacts with acid | $SO_3$ | NaOH |
| Liebig | 1838 | H replaceable by metal | Reacts with acid | $HNO_3$ | NaOH |
| Arrhenius | 1894 | Forms hydronium ion | Forms hydroxide ion | $H^+$ | $OH^-$ |
| Brønsted-Lowry | 1923 | Hydrogen ion donor | Hydrogen ion acceptor | $H_3O^+$ | $H_2O$ |
| | | | | $H_2O$ | $OH^-$ |
| | | | | $NH_4^+$ | $NH_3$ |
| Lewis | 1923 | Electron pair acceptor | Electron pair donor | $Ag^+$ | $NH_3$ |
| Ingold-Robinson | 1932 | Electrophile (electron pair acceptor) | Nucleophile (electron pair donor) | $BF_3$ | $NH_3$ |
| Lux-Flood | 1939 | Oxide ion acceptor | Oxide ion donor | $SiO_2$ | CaO |
| Usanovich | 1939 | Electron acceptor | Electron donor | $Cl_2$ | Na |
| Solvent system | 1950s | Solvent cation | Solvent anion | $BrF_2^+$ | $BrF_4^-$ |
| Frontier orbitals | 1960s | LUMO of acceptor | HOMO of donor | $BF_3$ | $NH_3$ |

Although many other acid-base definitions have been proposed and have been useful in particular types of reactions, only a few have been widely adopted for general use. Among these are the ones attributed to Arrhenius (based on hydrogen and hydroxide ion formation), Brønsted-Lowry (hydrogen ion donors and acceptors), and Lewis (electron pair donors and acceptors). Others have received less attention or are useful only in a narrow range of situations. For example, the Lux-Flood definition[3] is based on oxide ion, $O^{2-}$, as the unit transferred between acids (oxide ion acceptors) and bases (oxide ion donors). The Usanovich definition[4] proposes that any reaction leading to a salt (including oxidation-reduction reactions) should be considered an acid-base reaction. This definition could include nearly all reactions, and has been criticized for this all-inclusive approach. The Usanovich definition is rarely used today, but it fits the frontier orbital approach described in Section 6-2-5. The electrophile-nucleophile approach of Ingold[5] and Robinson,[6] widely used in organic chemistry, is essentially the Lewis theory with terminology related to reactivity (electrophilic reagents are acids, nucleophilic reagents are bases). Another approach that is described later in this chapter is an extension of the Lewis theory in terms of frontier orbitals. Table 6-1 summarizes these acid-base definitions.

**6-2**
**MAJOR ACID-BASE CONCEPTS**

## 6-2-1 ARRHENIUS CONCEPT

Acid-base chemistry was first satisfactorily explained in molecular terms after Ostwald and Arrhenius established the existence of ions in aqueous solution in 1880–1890 (after much controversy and professional difficulties, Arrhenius received the 1903 Nobel Prize in Chemistry for this theory). As defined at that time, **Arrhenius acids form**

[3]H. Lux, Z. Electrochem., **1939**, 45, 303; H. Flood and T. Förland, Acta Chem. Scand., **1947**, 1, 592, 718; W. B. Jensen, The Lewis Acid-Base Concepts, Wiley-Interscience, New York, 1980, pp. 54–55.

[4]M. Usanovich, Zh. Obshch. Khim., **1939**, 9, 182; H. Gehlen, Z. Phys. Chem., **1954**, 203, 125; H. L. Finston and A. C. Rychtman, A New View of Current Acid-Base Theories, John Wiley & Sons, New York, 1982, pp. 140–146.
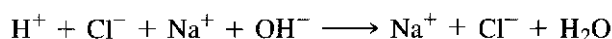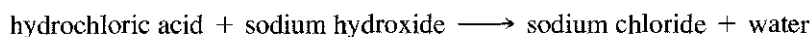
[5]C. K. Ingold, J. Chem. Soc., **1933**, 1120; Chem. Rev., **1934**, 15, 225; Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, NY, 1953, Chapter V; W. B. Jensen, The Lewis Acid-Base Concepts, Wiley-Interscience, New York, 1980, pp. 58–59.

[6]R. Robinson, Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions, Institute of Chemistry, London, 1932, pp. 12–15; W. B. Jensen, The Lewis Acid-Base Concepts, Wiley-Interscience, New York, 1980, pp. 58–59.

hydrogen ions (now frequently called hydronium or oxonium[7] ions, $H_3O^+$) in aqueous solution, Arrhenius bases form hydroxide ions in aqueous solution, and the reaction of hydrogen ions and hydroxide ions to form water is the universal aqueous acid-base reaction. The ions accompanying the hydrogen and hydroxide ions form a salt, so the overall Arrhenius acid-base reaction can be written

$$acid + base \longrightarrow salt + water$$

For example,

$$hydrochloric\ acid + sodium\ hydroxide \longrightarrow sodium\ chloride + water$$

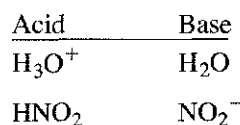$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

This explanation works well in aqueous solution, but it is inadequate for nonaqueous solutions and for gas and solid phase reactions in which $H^+$ and $OH^-$ may not exist. Definitions by Brønsted and Lewis are more appropriate for general use.
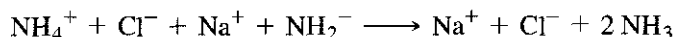
## 6-2-2 BRØNSTED-LOWRY CONCEPT

In 1923, Brønsted[8] and Lowry[9] defined an **acid as a species with a tendency to lose a hydrogen ion and a base as a species with a tendency to gain a hydrogen ion.**[7] This definition expanded the Arrhenius list of acids and bases to include the gases HCl and $NH_3$, along with many other compounds. This definition also introduced the concept of **conjugate acids and bases,** differing only in the presence or absence of a proton, and described all reactions as occurring between a stronger acid and base to form a weaker acid and base:
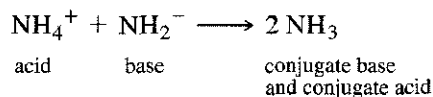
$$H_3O^+ + NO_2^- \longrightarrow H_2O + HNO_2$$

acid 1     base 2     base 1     acid 2

Conjugate acid-base pairs:
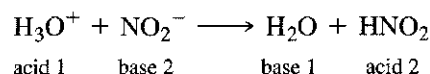
| Acid | Base |
|------|------|
| $H_3O^+$ | $H_2O$ |
| $HNO_2$ | $NO_2^-$ |

In water, HCl and NaOH react as the acid $H_3O^+$ and the base $OH^-$ to form water, which is the conjugate base of $H_3O^+$ and the conjugate acid of $OH^-$. Reactions in nonaqueous solvents having ionizable hydrogens parallel those in water. An example of such a solvent is liquid ammonia, in which $NH_4Cl$ and $NaNH_2$ react as the acid $NH_4^+$ and the base $NH_2^-$ to form $NH_3$, which is both a conjugate base and a conjugate acid:

$$NH_4^+ + Cl^- + Na^+ + NH_2^- \longrightarrow Na^+ + Cl^- + 2\ NH_3$$

with the net reaction

$$NH_4^+ + NH_2^- \longrightarrow 2\ NH_3$$

acid     base     conjugate base
and conjugate acid

[7]In American practice, $H_3O^+$ is frequently called the hydronium ion. The International Union of Pure and Applied Chemistry (IUPAC) now recommends oxonium for this species. In many equations, the shorthand $H^+$ notation is used, for which the IUPAC recommends the terms hydron or hydrogen ion, rather than proton.

[8]J. N. Brønsted, *Rec. Trav. Chem.,* **1923,** *42,* 718.

[9]T. M. Lowry, *Chem. Ind. (London),* **1923,** *42,* 43.

In any solvent, the direction of the reaction always favors the formation of weaker acids or bases than the reactants. In the two examples above, $H_3O^+$ is a stronger acid than $HNO_2$ and the amide ion is a stronger base than ammonia (and ammonium ion is a stronger acid than ammonia), so the reactions favor formation of $HNO_2$ and ammonia.
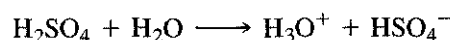
### 6-2-3 SOLVENT SYSTEM CONCEPT

Aprotic nonaqueous solutions require a similar approach, but with a different definition of acid and base. The solvent system definition applies to any solvent that can dissociate into a cation and an anion (autodissociation), where **the cation resulting from autodissociation of the solvent is the acid and the anion is the base. Solutes that increase the concentration of the cation of the solvent are considered acids and solutes that increase the concentration of the anion are considered bases.**

The classic solvent system is water, which undergoes autodissociation:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$
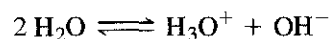
By the solvent system definition, the cation, $H_3O^+$, is the acid and the anion, $OH^-$, is the base. For example, in the reaction

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$$

sulfuric acid increases the concentration of the hydronium ion and is an acid by any of the three definitions given.

The solvent system approach can also be used with solvents that do not contain hydrogen. For example, $BrF_3$ also undergoes autodissociation:
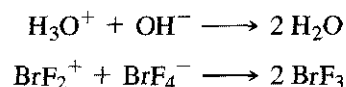
$$2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$
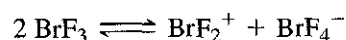
Solutes that increase the concentration of the acid, $BrF_2^+$, are considered acids. For example, $SbF_5$ is an acid in $BrF_3$:
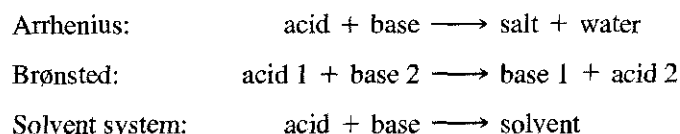
$$SbF_5 + BrF_3 \longrightarrow BrF_2^+ + SbF_6^-$$
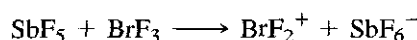
and solutes such as KF that increase the concentration of $BrF_4^-$ are considered bases:

$$F^- + BrF_3 \longrightarrow BrF_4^-$$
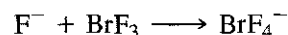
Acid-base reactions in the solvent system concept are the reverse of autodissociation:

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O$$
$$BrF_2^+ + BrF_4^- \longrightarrow 2\,BrF_3$$

The Arrhenius, Brønsted-Lowry, and solvent system neutralization reactions can be compared as follows:

Arrhenius:            acid + base $\longrightarrow$ salt + water

Brønsted:            acid 1 + base 2 $\longrightarrow$ base 1 + acid 2

Solvent system:      acid + base $\longrightarrow$ solvent

**EXERCISE 6-1**

$IF_5$ undergoes autodissociation into $IF_4^+$ + $IF_6^-$. $SbF_5$ acts as an acid and KF acts as a base when dissolved in $IF_5$. Write balanced chemical equations for these reactions.

Table 6-2 gives some properties of common solvents. The $pK_{ion}$ is the autodissociation constant for the pure solvent, indicating that, among these acids, sulfuric acid dissociates much more readily than any of the others, and that acetonitrile is least likely to autodissociate. The boiling points are given to provide an estimate of the conditions under which each solvent might be used.

Caution is needed in interpreting these reactions. For example, $SOCl_2$ and $SO_3^{2-}$ react as acid and base in $SO_2$ solvent, with the reaction apparently occurring as

$$SOCl_2 + SO_3^{2-} \rightleftharpoons 2\,SO_2 + 2\,Cl^-$$

It was at first believed that $SOCl_2$ dissociated and that the resulting $SO^{2+}$ reacted with $SO_3^{2-}$:

$$SOCl_2 \rightleftharpoons SO^{2+} + 2\,Cl^-$$
$$SO^{2+} + SO_3^{2-} \rightleftharpoons 2\,SO_2$$
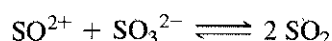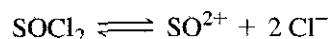
However, the reverse reactions should lead to the exchange of oxygen atoms between $SO_2$ and $SOCl_2$, but none is observed.[10] The details of the $SOCl_2$ + $SO_3^{2-}$ reaction are still uncertain, but may involve dissociation of only one chloride, as in
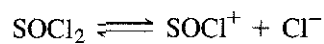
$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

**TABLE 6-2**
**Properties of Solvents**

| *Protic Solvents* | | | | |
| --- | --- | --- | --- | --- |
| *Solvent* | *Acid Cation* | *Base Anion* | *$pK_{ion}$ (25° C)* | *Boiling point (° C)* |
| Sulfuric acid, $H_2SO_4$ | $H_3SO_4^+$ | $HSO_4^-$ | 3.4 (10°) | 330 |
| Hydrogen fluoride, HF | $H_2F^+$ | $HF_2^-$ | ~12 (0°) | 19.5 |
| Water, $H_2O$ | $H_3O^+$ | $OH^-$ | 14 | 100 |
| Acetic acid, $CH_3COOH$ | $CH_3COOH_2^+$ | $CH_3COO^-$ | 14.45 | 118.2 |
| Methanol, $CH_3OH$ | $CH_3OH_2^+$ | $CH_3O^-$ | 18.9 | 64.7 |
| Ammonia, $NH_3$ | $NH_4^+$ | $NH_2^-$ | 27 | −33.4 |
| Acetonitrile, $CH_3CN$ | $CH_3CNH^+$ | $CH_2CN^-$ | 28.6 | 81 |

| *Aprotic Solvents* | |
| --- | --- |
| *Solvent* | *Boiling Point (° C)* |
| Sulfur dioxide, $SO_2$ | −10.2 |
| Dinitrogen tetroxide, $N_2O_4$ | 21.2 |
| Pyridine, $C_5H_5N$ | 115.5 |
| Bromine trifluoride, $BrF_3$ | 127.6 |
| Diglyme, $CH_3(OCH_2CH_2)_2OCH_3$ | 162 |

SOURCE: Data from W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice Hall, Englewood Cliffs, NJ, 1970, pp. 99–101. Data for many other solvents are also given by Jolly.

[10]W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice Hall, Englewood Cliffs. NJ, 1970, pp. 108–109; R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Am. Chem. Soc.*, **1951**, *73*, 3052.

**EXERCISE 6-2**

Show that the reverse of the reactions

$$SOCl_2 \rightleftharpoons SO^{2+} + 2\,Cl^-$$

$$SO^{2+} + SO_3{}^{2-} \rightleftharpoons 2\,SO_2$$
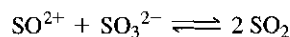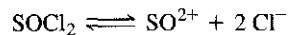
should lead to oxygen atom exchange between $SO_2$ and $SOCl_2$, if one of them initially contains $^{18}O$.

## 6-2-4 LEWIS CONCEPT

Lewis[11] defined **a base as an electron-pair donor and an acid as an electron-pair acceptor**. This definition further expands the list to include metal ions and other electron pair acceptors as acids and provides a handy framework for nonaqueous reactions. Most of the acid-base descriptions in this book will use the Lewis definition, which encompasses the Brønsted-Lowry and solvent system definitions. In addition to all the reactions discussed previously, the Lewis definition includes reactions such as

$$Ag^+ + 2\,:NH_3 \longrightarrow [H_3N:Ag:NH_3]^+$$
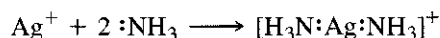
with silver ion (or other cation) as an acid and ammonia (or other electron-pair donor) as a base. In reactions such as this one, the product is often called an **adduct**, a product of the reaction of a Lewis acid and base to form a new combination. Another example is the boron trifluoride–ammonia adduct, $BF_3 \cdot NH_3$. The $BF_3$ molecule described in Sections 3-1-4, 3-2-3, and 5-4-5 has a planar triangular structure with some double bond character in each B — F bond. Because fluorine is the most electronegative element, the boron atom in $BF_3$ is quite positive, and the boron is frequently described as electron-deficient. The lone pair in the HOMO of the ammonia molecule combines with the empty LUMO of the $BF_3$, which has very large, empty orbital lobes on boron, to form the adduct. The molecular orbitals involved are depicted in Figure 6-1 and the energy levels of these orbitals are shown in Figure 6-2. The B — F bonds in the product
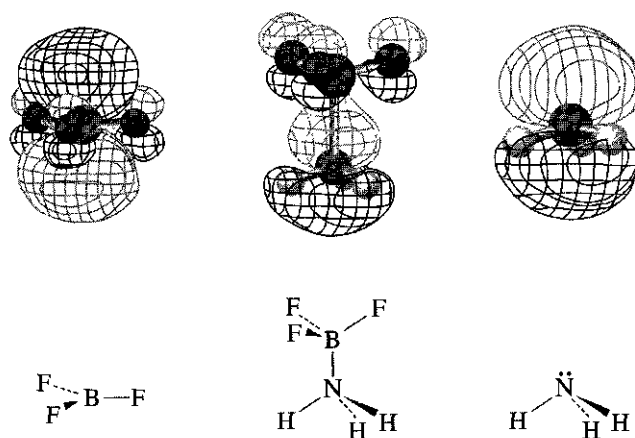


**FIGURE 6-1** Donor-Acceptor Bonding in $BF_3 \cdot NH_3$.

[11]G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog, New York, 1923, pp. 141–142; *J. Franklin Inst.*, **1938**, *226*, 293.
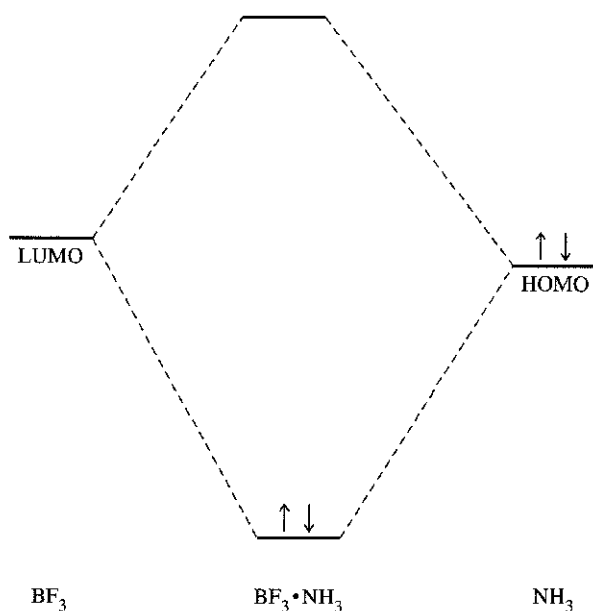
**FIGURE 6-2** Energy Levels for the $BF_3 \cdot NH_3$ Adduct.

are bent away from the ammonia into a nearly tetrahedral geometry around the boron. Similar interactions in which electrons are donated or accepted completely (oxidation-reduction reactions) or shared, as in this reaction, are described in more detail in Sections 6-2-5 through 6-2-8.

Another common adduct, the boron trifluoride-diethyl ether adduct, $BF_3 \cdot O(C_2H_5)_2$, is frequently used in synthesis. Lone pairs on the oxygen of the diethyl ether are attracted to the boron; the result is that one of the lone pairs bonds to boron, changing the geometry around B from planar to nearly tetrahedral, as shown in Figure 6-3. As a result, $BF_3$, with a boiling point of $-99.9°$ C, and diethyl ether, with a boiling point of $34.5°$ C, form an adduct with a boiling point of $125°$ to $126°$ C (at which temperature it decomposes into its two components). The formation of the adduct raises the boiling point enormously, a common result of such reactions.

Lewis acid-base adducts involving metal ions are called **coordination compounds** (bonds formed with both electrons from one atom are called coordinate bonds); their chemistry will be discussed in Chapters 9 through 14.
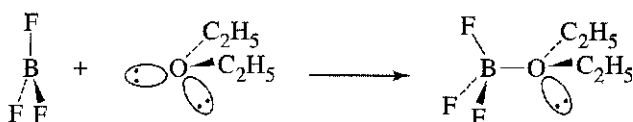


**FIGURE 6-3** Boron Trifluoride-Ether Adduct.

## 6-2-5 FRONTIER ORBITALS AND ACID-BASE REACTIONS[12]

The molecular orbital description of acid-base reactions mentioned in Section 6-2-4 uses **frontier molecular orbitals** (those at the occupied-unoccupied frontier), and can be illustrated by the simple reaction $NH_3 + H^+ \longrightarrow NH_4^+$. In this reaction, the $a_1$ orbital containing the lone pair electrons of the ammonia molecule (see Figure 5-31)

[12]W. B. Jensen, *The Lewis Acid-base Concepts*, Wiley-Interscience, New York, 1980, pp. 112–155.

New antibonding
orbital $(t_2)$

New bonding
orbital $(t_2)$

**FIGURE 6-4**
$NH_3 + H^+ \longrightarrow NH_4^+$ Molecular
Energy Levels.

$H^+$      $NH_4^+$      $NH_3$

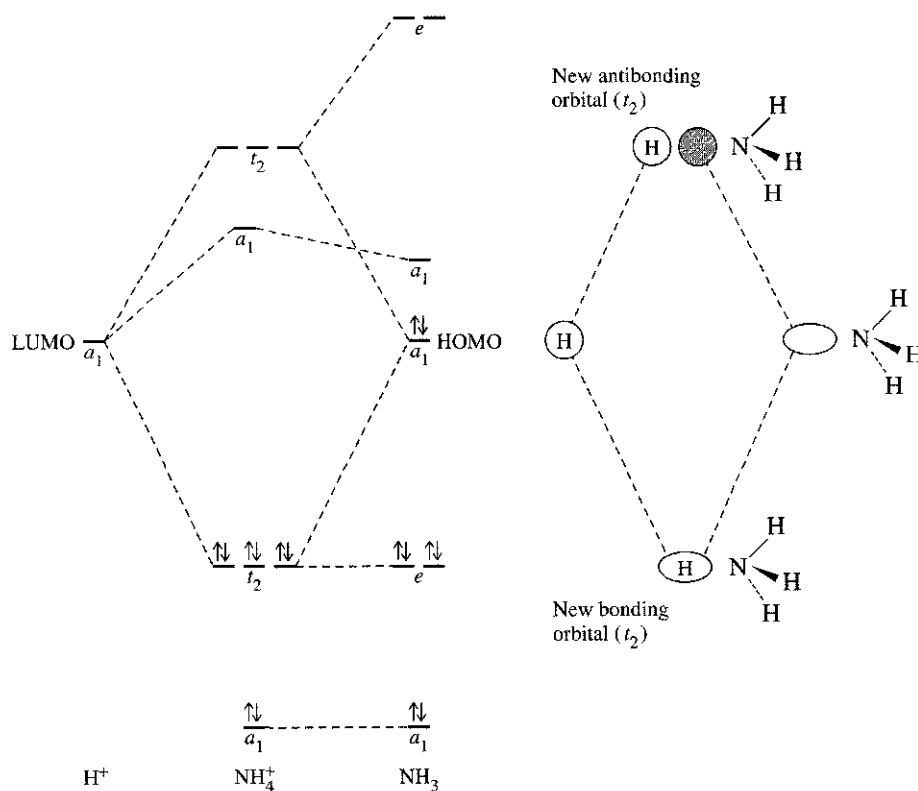combines with the empty $1s$ orbital of the hydrogen ion to form bonding and antibonding orbitals. The lone pair in the $a_1$ orbital of $NH_3$ is stabilized by this interaction, as shown in Figure 6-4. The $NH_4^+$ ion has the same molecular orbital structure as methane, $CH_4$, with four bonding orbitals ($a_1$ and $t_2$) and four antibonding orbitals (also $a_1$ and $t_2$). Combining the seven $NH_3$ orbitals and the one $H^+$ orbital, with the change in symmetry from $C_{3v}$ to $T_d$, gives the eight orbitals of the $NH_4^+$. When the eight valence electrons are placed in these orbitals, one pair enters the bonding $a_1$ orbital and three pairs enter bonding $t_2$ orbitals. The net result is a lowering of energy as the nonbonding $a_1$ becomes a bonding $t_2$, making the combined $NH_4^+$ more stable than the separated $NH_3 + H^+$. This is an example of the combination of the HOMO of the base $NH_3$ and the LUMO of the acid $H^+$ accompanied by a change in symmetry to make the new sets of orbitals, one bonding and one antibonding.

In most acid-base reactions, **a HOMO-LUMO combination forms new HOMO and LUMO orbitals of the product**. We can see that orbitals whose shapes allow significant overlap and whose energies are similar form useful bonding and antibonding orbitals. On the other hand, if the orbital combinations have no useful overlap, no net bonding is possible (as shown in Chapter 5) and they cannot form acid-base products.[13]

Even when the orbital shapes match, several reactions may be possible, depending on the relative energies. A single species can act as an oxidant, an acid, a base, or a reductant, depending on the other reactant. These possibilities are shown in Figure 6-5. Although predictions on the basis of these arguments may be difficult when the orbital energies are not known, they still provide a useful background to these reactions.

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[13]In a few cases, the orbitals with the required geometry and energy do not include the HOMO; this possibility should be kept in mind. When this happens, the HOMO is usually a lone pair that does not have the geometry needed for bonding with the acid.
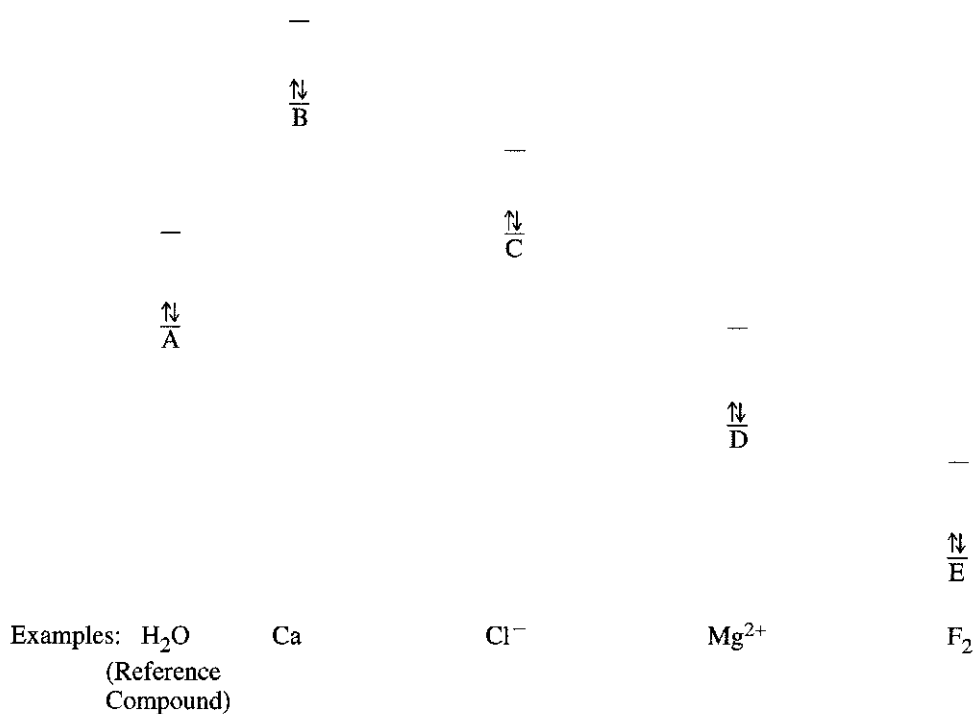
⥮
B

⥮
C

⥮
A

—

⥮
D

—

⥮
E

Examples:  $H_2O$      Ca          $Cl^-$          $Mg^{2+}$        $F_2$
(Reference
Compound)

Reactant A is taken as a reference; water is a good example. The first combination of reactants, A + B, has all the B orbitals at a much higher energy than those of water (Ca, for example; the alkali metals react similarly but have only one electron in their highest $s$ orbital). The energies are so different that no adduct can form, but a transfer of electrons can take place from B to A. From simple electron transfer, we might expect formation of $H_2O^-$, but reduction of water yields hydrogen gas instead. As a result, water is reduced to $H_2$ and $OH^-$, Ca is oxidized to $Ca^{2+}$:

$$2 H_2O + Ca \longrightarrow Ca^{2+} + 2 OH^- + H_2 \qquad \text{(water as oxidant)}$$

If orbitals with matching shapes have similar energies, the resulting bonding orbitals will have lower energy than the reactant HOMOs, and a net decrease in energy (stabilization of electrons in the new HOMOs) results. An adduct is formed, with its stability dependent on the difference between the total energy of the product and the total energy of the reactants.

An example with water as acceptor (with lower energy orbitals) is the reaction with chloride ion (C in Figure 6-5):

$$n H_2O + Cl^- \longrightarrow [Cl(H_2O)_n]^- \qquad \text{(water as acid)}$$
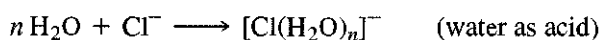
In this reaction, water is the acceptor, and the LUMO used is an antibonding orbital centered primarily on the hydrogen atoms (the chloride HOMO is one of its lone pairs from a $3p$ orbital).

A reactant with orbitals lower in energy than those of water (for example, $Mg^{2+}$, D in Figure 6-5) allows water to act as a donor:

$$6 H_2O + Mg^{2+} \longrightarrow [Mg(H_2O)_6]^{2+} \qquad \text{(water as base)}$$
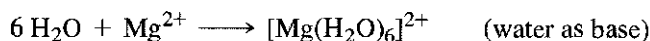
Here, water is the donor, contributing a lone pair primarily from the HOMO, which has a large contribution from the $p_x$ orbital on the oxygen atom (the magnesium ion LUMO is the vacant $3s$ orbital). The molecular orbital levels that result from reactions with B or C are similar to those in Figures 6-7 and 6-8 for hydrogen bonding.

Finally, if the reactant has orbitals much lower than the water orbitals ($F_2$, for example, E in Figure 6-5), water can act as a reductant and transfer electrons to the other reactant. The product is not the simple result of electron transfer ($H_2O^+$), but the result of the breakup of the water molecule to molecular oxygen and hydrogen ions:

$$2\,H_2O + 2\,F_2 \longrightarrow 4\,F^- + 4\,H^+ + O_2 \qquad \text{(water as reductant)}$$
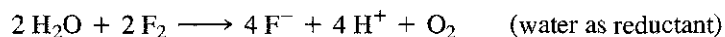
Similar reactions can be described for other species, and the adducts formed in the acid-base reactions can be quite stable or very unstable, depending on the exact relationship between the orbital energies.

We are now in a position to reformulate the Lewis definition of acids and bases in terms of frontier orbitals: **A base has an electron pair in a HOMO of suitable symmetry to interact with the LUMO of the acid** (although lone pair orbitals with the wrong geometry may need to be ignored). The better the energy match between the base's HOMO and the acid's LUMO, the stronger the interaction.

## 6-2-6 HYDROGEN BONDING

The effects of hydrogen bonding were described in Section 3-4. In this section, the molecular orbital basis for hydrogen bonding is described as an introduction to the frontier molecular orbital approach to acid-base behavior.

The molecular orbitals for the symmetric $FHF^-$ ion were described in Chapter 5 (Figure 5-18) as combinations of the atomic orbitals. They may also be generated by combining the molecular orbitals (MOs) of HF with $F^-$, as shown in Figure 6-6. The $p_x$ and $p_y$ lone pair orbitals on the fluorines of both $F^-$ and HF can be ignored, because there are no matching orbitals on the H atom. The shapes of the other orbitals are appropriate for bonding; overlap of the $\sigma\,F^-$ orbital with the $\sigma$ and $\sigma^*$ HF orbitals forms the three product orbitals. These three orbitals are all symmetric about the central H nucleus. The lowest orbital is distinctly bonding, with all three component orbitals contributing and no nodes between the atoms. The middle (HOMO) orbital is essentially nonbonding, with nodes through each of the nuclei. The highest energy orbital (LUMO) is antibonding, with nodes between each pair of atoms. The symmetry of the molecule dictates the nodal pattern, increasing from two to three to four nodes with increasing energy. In general, orbitals with nodes between adjacent atoms are antibonding; orbitals with nodes through atoms may be either bonding or nonbonding, depending on the orbitals involved. When three atomic orbitals are used ($2p$ orbitals from each $F^-$ and the $1s$ orbital from $H^+$), the resulting pattern is one low-energy molecular orbital, one high-energy molecular orbital, and one intermediate-energy molecular orbital. The intermediate orbital may be slightly bonding, slightly antibonding, or nonbonding; we describe such orbitals as essentially nonbonding. The two lowest energy orbitals of Figure 5-18 are essentially nonbonding; the fluorine $2s$ orbitals are the major contributors. The energy of the hydrogen $1s$ orbital is too high to participate significantly in these molecular orbitals.

For unsymmetrical hydrogen bonding, such as that of B + HA $\rightleftharpoons$ BHA shown in Figure 6-7, the pattern is similar. The two electron pairs in the lower orbitals have a lower total energy than the total for the electrons in the two reactants.

Regardless of the exact energies and location of the nodes, the general pattern is the same. The resulting $FHF^-$ or BHA structure has a total energy lower than the sum of the energies of the reactants. For the general case of B + HA, three possibilities exist, but with a difference from the earlier HOMO-LUMO illustration (see Figure 6-5) created by the possibility of hydrogen ion transfer. These possibilities are illustrated in
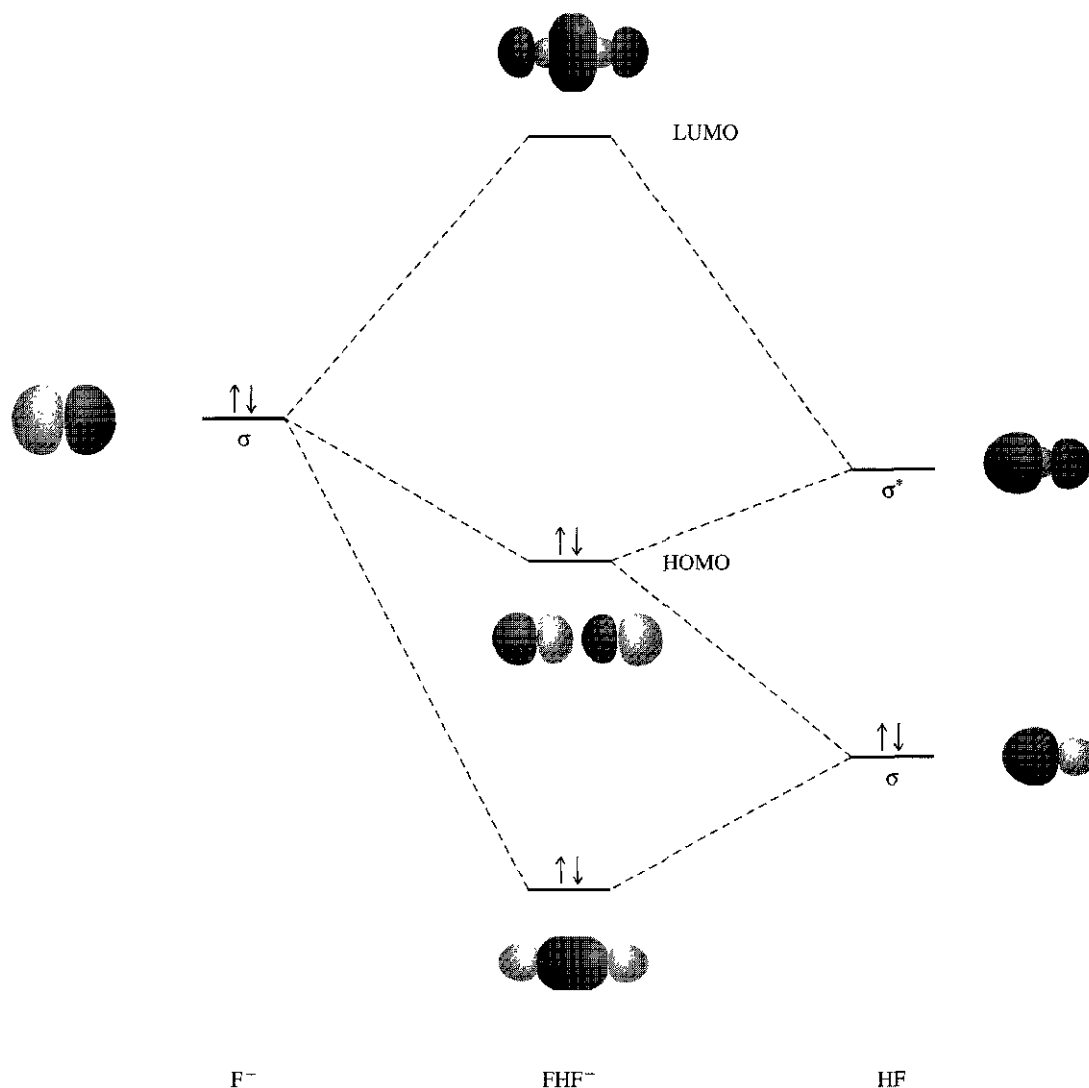
LUMO

σ

σ*

HOMO

σ

F⁻                    FHF⁻                    HF

**FIGURE 6-6** Molecular Orbitals for Hydrogen Bonding in FHF⁻. The $1s$ and the $2p$ nonbonding orbitals of F⁻ are omitted. Figure 5-18 shows the full set of molecular orbitals.

Figure 6-8. First, for a poor match of energies when the occupied reactant orbitals are lower in total energy than those of the possible hydrogen-bonded product, no new product will be formed; there will be no hydrogen bonding. Second, for a good match of energies, the occupied product orbitals are lower in energy and a hydrogen-bonded product forms. The greater the lowering of energies of these orbitals, the stronger the hydrogen bonding. Finally, for a very poor match of energies, occupied orbitals of the species BH + A are lower than those of B + HA; in this case, complete hydrogen ion transfer occurs.

In Figure 6-8(a), the energy of the HOMO of B is well below that of the LUMO of HA. Because the lowest molecular orbital is only slightly lower than the HA orbital, and the middle orbital is higher than the B orbital, little or no reaction occurs. In aqueous solution, interactions between water and molecules with almost no acid-base character, such as $CH_4$, fit this group. Little or no interaction occurs between the hydrogens of the methane molecule and the lone pairs of surrounding water molecules.

In Figure 6-8(b), the LUMO of HA and the HOMO of B have similar energies, both occupied product orbitals are lower than the respective reactant orbitals, and a
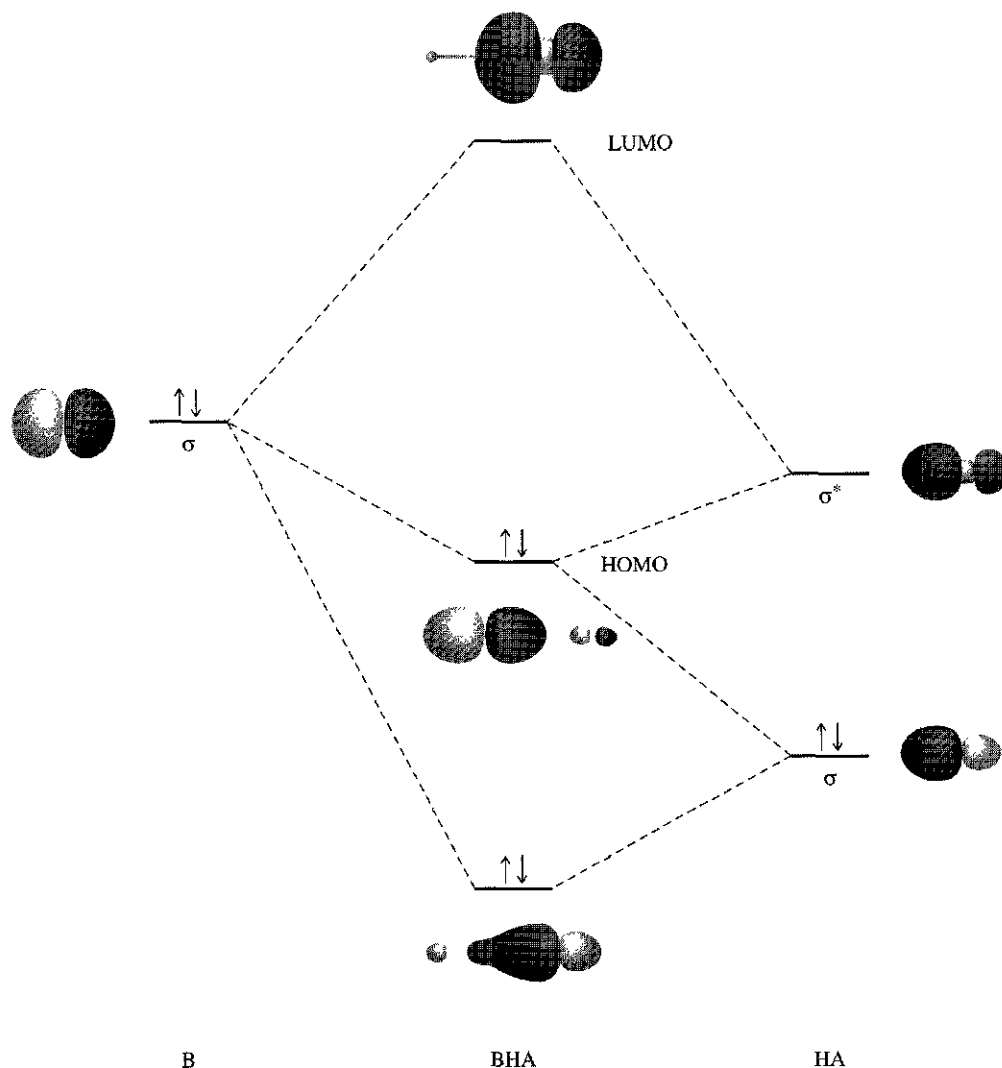
LUMO

σ

σ*

HOMO

σ

**FIGURE 6-7** Molecular Orbitals for Unsymmetrical Hydrogen Bonding.

B                    BHA                    HA

hydrogen-bonded product forms with a lower total energy than the reactants. The node of the product HOMO is near the H atom, and the hydrogen-bonded product has a B—H bond similar in strength to the H—A bond. If the B HOMO is slightly higher than the HA LUMO, as in the figure, the H—A portion of the hydrogen bond is stronger. If the B HOMO is lower than the HA LUMO, the B—H portion is stronger (the product HOMO consists of more B than A orbital). Weak acids such as acetic acid are examples of hydrogen-bonding solutes in water. Acetic acid hydrogen bonds strongly with water (and to some extent with other acetic acid molecules), with a small amount of hydrogen ion transfer to water to give hydronium and acetate ions.

In Figure 6-8(c), the HOMO-LUMO energy match is so poor that no useful adduct orbitals can be formed. The product MOs here are those of $A^-$ and $BH^+$, and the hydrogen ion is transferred from A to B. Strong acids such as HCl will donate their hydrogen ions completely to water, after which the $H_3O^+$ formed will hydrogen bond strongly with other water molecules.

In all these diagrams, either HA or BH (or both) may have a positive charge and either A or B (or both) may have a negative charge, depending on the circumstances.

When A is a highly electronegative element such as F, O, or N, the highest occupied orbital of A has lower energy than the hydrogen 1s orbital and the H—A bond is relatively weak, with most of the electron density near A and with H somewhat
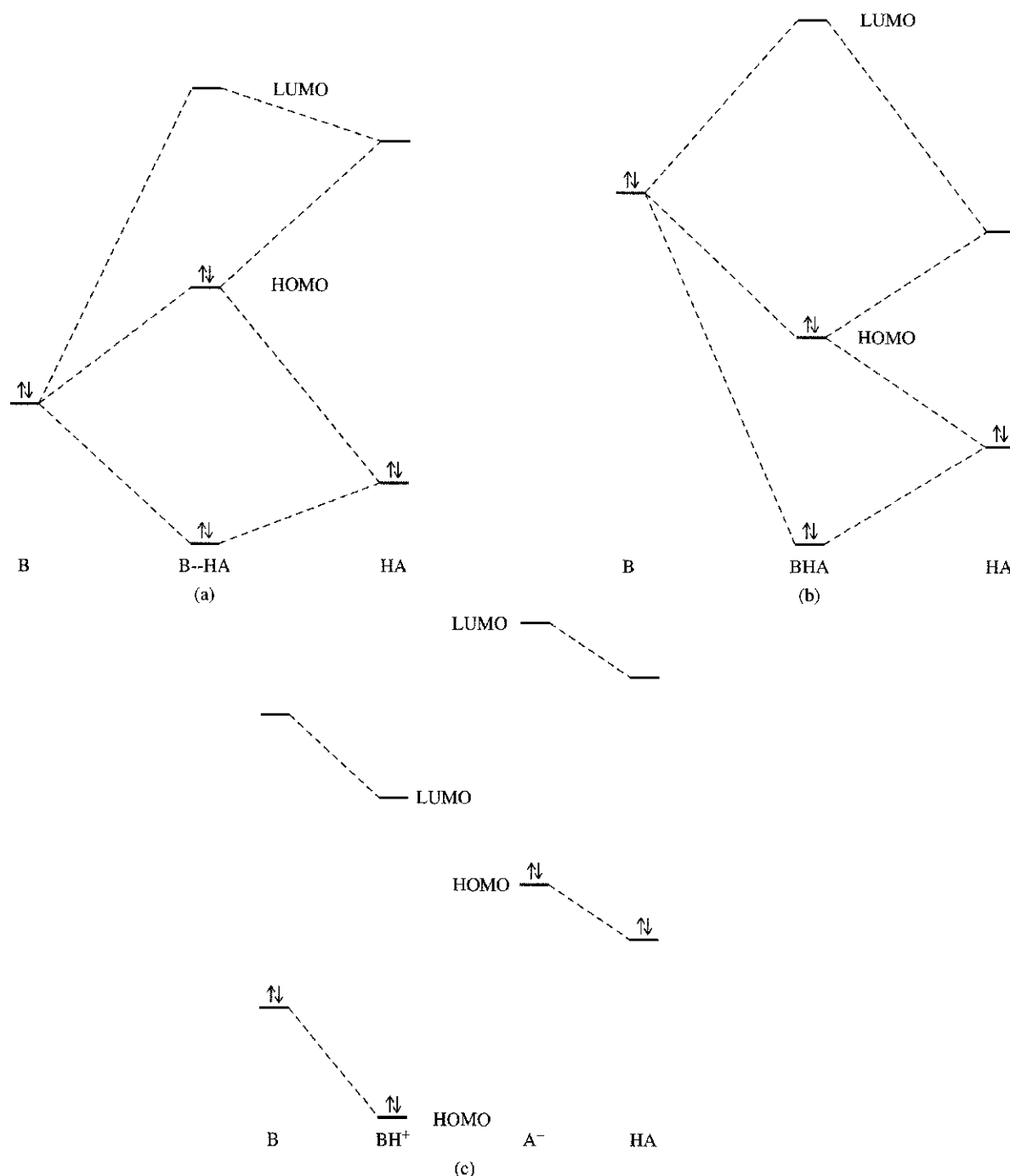
**FIGURE 6-8** Orbital Possibilities for Hydrogen Bonding. (a) Poor match of HOMO-LUMO energies, little or no hydrogen bonding (HOMO of B well below LUMO of HA; reactants' energy below that of BHA). (b) Good match of energies, good hydrogen bonding (HOMO of B at nearly the same energy as LUMO of HA; BHA energy lower than reactants). (c) Very poor match of energies, transfer of hydrogen ion (HOMO of B below both LUMO and HOMO of HA; $BH^+$ + $A^-$ energy lower than B + HA or BHA).

positively charged. This favors the hydrogen-bonding interaction by lowering the overall energy of the HA bonding orbital and improving overlap with the B orbital. In other words, when the reactant HA has a structure close to $H^+\cdots A^-$, hydrogen bonding is more likely. This explains the strong hydrogen bonding in cases with hydrogen bridging between F, O, and N atoms in molecules and the much weaker or nonexistent hydrogen

bonding between other atoms. The description above can be described as a three-center four-electron model,[14] which results in a bond angle at the hydrogen within 10° to 15° of a linear 180° angle.

## 6-2-7 ELECTRONIC SPECTRA (INCLUDING CHARGE TRANSFER)

One reaction that shows the effect of adduct formation dramatically is the reaction of $I_2$ as an acid with different solvents and ions that act as bases. The changes in spectra and visible color caused by changes in electronic energy levels (shown in Figures 6-9 and 6-10) are striking. The upper molecular orbitals of $I_2$ are shown on the left in Figure 6-9, with a net single bond due to the filled $9\sigma_g$ orbital and lone pairs in the $4\pi_u$ and $4\pi_g{}^*$ orbitals. In the gas phase, $I_2$ is violet, absorbing light near 500 nm because of promotion of an electron from the $4\pi_g{}^*$ level to the $9\sigma_u{}^*$ level (shown in Figure 6-9). This absorption removes the middle yellow, green, and blue parts of the visible spectrum, leaving red and violet at opposite ends of the spectrum to combine in the violet color that is seen.

In nondonor solvents such as hexane, the iodine color remains essentially the same violet, but in benzene and other $\pi$-electron solvents it becomes more red-violet, and in good donors such as ethers, alcohols, and amines the color becomes distinctly brown. The solubility of $I_2$ also increases with increasing donor character of the solvent. Interaction of the donor orbital of the solvent with the $9\sigma_u{}^*$ orbital results in a lower occupied bonding orbital and a higher unoccupied antibonding orbital. As a result, the $\pi_g{}^* \longrightarrow \sigma_u{}^*$ transition for $I_2$ + donor (Lewis base) has a higher energy and an absorbance peak shifted toward the blue. The transmitted color shifts toward brown (combined red, yellow, and green), as more of the yellow and green light passes through. Water is also a donor, but not a very good one; $I_2$ is only slightly soluble in water, and the solution is yellow-brown. Adding $I^-$ (a very good donor) results in the formation of $I_3^-$, which is brown and, being ionic, is very soluble in water. When the interaction between the donor and $I_2$ is strong, the LUMO of the adduct has a higher energy and the energy of the donor-acceptor transition $(\pi_g{}^* \longrightarrow \sigma_u{}^*)$ increases.

In addition to these shifts, a new charge-transfer band appears at the edge of the ultraviolet (230–400 nm, marked CT in Figure 6-10). This band is due to the transition $\sigma \longrightarrow \sigma^*$, between the two new orbitals formed by the interaction. Because the $\sigma$ orbital has a larger proportion of the donor (solvent or $I^-$) orbital and the $\sigma^*$ orbital has a larger proportion of the $I_2$ orbital, the transition transfers an electron from an orbital that is primarily of donor composition to one that is primarily of acceptor composition; hence, the name **charge transfer** for this transition. The energy of this transition is less predictable because it depends on the energy of the donor orbital. The transition may be shown schematically as

$$I_2 \cdot \text{Donor} \xrightarrow[CT]{h\nu} [I_2]^- \cdot [\text{Donor}]^+$$
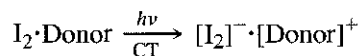
The charge-transfer phenomenon also appears in many other adducts. If the charge-transfer transition actually transfers the electron permanently, the result is an oxidation-reduction reaction—the donor is oxidized and the acceptor is reduced. The sequence of reactions of $[Fe(H_2O)_6]^{3+}$ (the acid) and aquated halide ions (the bases)

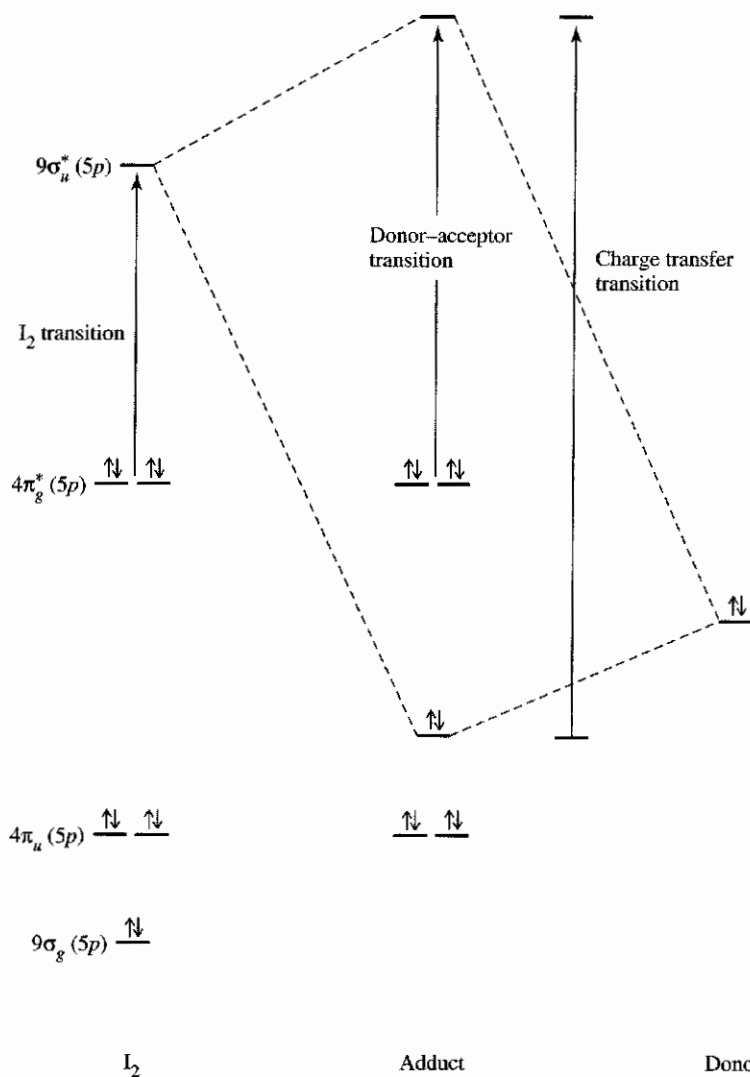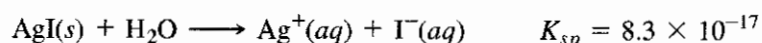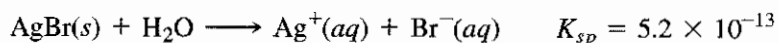[14]R. L. DeKock and W. B. Bosma, *J. Chem. Educ.*, **1988**, 65, 194.

**FIGURE 6-9** Electronic Transitions in $I_2$ Adducts.

forming $[Fe(H_2O)_5X]^{2+}$ illustrates the whole range of possibilities as the energy of the HOMO of the halide ion increases from $F^-$ to $I^-$. All of them show charge-transfer transitions. In concentrated iodide, there is complete transfer of the electron through the reaction $2\ Fe^{3+} + 2\ I^- \longrightarrow 2\ Fe^{2+} + I_2$.

**6-3**
**HARD AND SOFT**
**ACIDS AND BASES**

In addition to their intrinsic strength, acids and bases have other properties that determine the extent of reaction. For example, silver halides have a range of solubilities in aqueous solution. A simple series shows the trend:

$$AgF(s) + H_2O \longrightarrow Ag^+(aq) + F^-(aq) \qquad K_{sp} = 205$$

$$AgCl(s) + H_2O \longrightarrow Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$AgBr(s) + H_2O \longrightarrow Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.2 \times 10^{-13}$$

$$AgI(s) + H_2O \longrightarrow Ag^+(aq) + I^-(aq) \qquad K_{sp} = 8.3 \times 10^{-17}$$
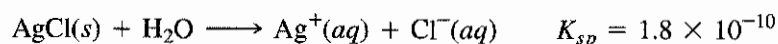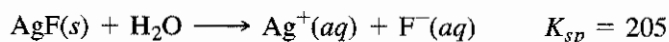
Solvation of the ions is certainly a factor in these reactions, with fluoride ion being much more strongly solvated than the other anions. However, the trend is also related to changes in the degree of interaction between the halides and the silver ions. The interactions can be expressed in terms of **hard and soft acids and bases** (HSAB), in which
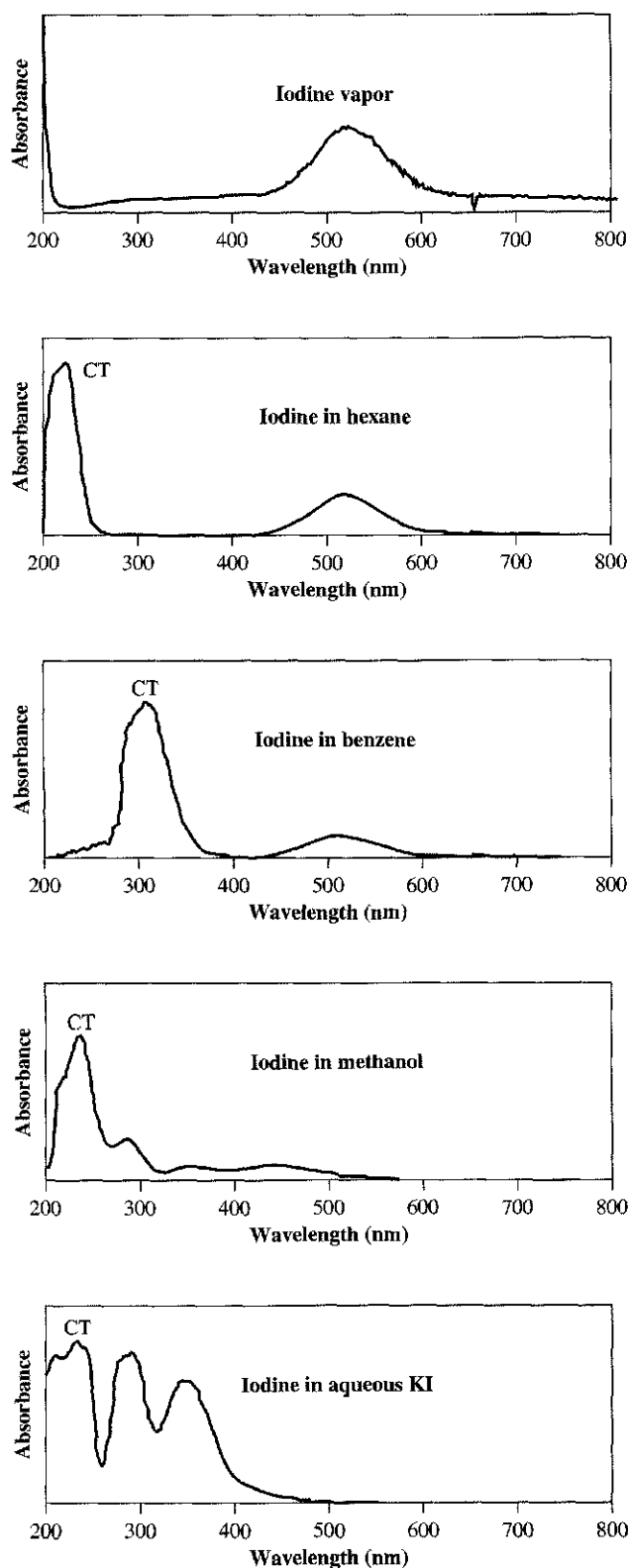
**FIGURE 6-10** Spectra of $I_2$ with Different Bases.

$I_2$ vapor is purple or violet, absorbing near 520 nm, with no charge-transfer bands.

$I_2$ in hexane is purple or violet, absorbing near 520 nm, with a charge-transfer band at about 225 nm.

$I_2$ in benzene is red-violet, absorbing near 500 nm, with a charge-transfer band at about 300 nm.

$I_2$ in methanol is yellow-brown, absorbing near 450 nm, with a charge-transfer band near 240 nm and a shoulder at 290 nm.

$I_2$ in aqueous KI is brown, absorbing near 360 nm, with charge-transfer bands at higher energy.

the metal cation is the Lewis acid and the halide anion is the Lewis base. Hard acids and bases are small and nonpolarizable, whereas soft acids and bases are larger and more polarizable; interactions between two hard or two soft species are stronger than those between one hard and one soft species. In the series of silver ion-halide reactions,

iodide ion is much softer (more polarizable) than the others, and interacts more strongly with silver ion, a soft cation. The result is a more covalent bond. The colors of the salts are also worth noting. Silver iodide is yellow, silver bromide is slightly yellow, and silver chloride and silver fluoride are white. Color depends on the difference in energy between occupied and unoccupied orbitals. A large difference results in absorption in the ultraviolet region of the spectrum; a smaller difference in energy levels moves the absorption into the visible region. Compounds absorbing violet appear to be yellow; as the absorption band moves toward lower energy, the color shifts and becomes more intense. Black indicates very broad and very strong absorption. Color and low solubility typically go with soft-soft interactions; colorless compounds and high solubility generally go with hard-hard interactions, although some hard-hard combinations have low solubility.

For example, the lithium halides have solubilities roughly in the reverse order: LiBr > LiCl > LiI > LiF. The solubilities show a strong hard-hard interaction in LiF that overcomes the solvation of water, but the weaker hard-soft interactions of the other halides are not strong enough to prevent solvation and these halides are more soluble than LiF. LiI is out of order, probably because of the poor solvation of the very large iodide ion, but it is still about 100 times as soluble as LiF on a molecular basis.

These reactions illustrate the general rules described by Fajans in 1923.[15] They can be summarized in four rules, in which increased covalent character means lower solubility, increased color, and shorter interionic distances:

1. For a given cation, covalent character increases with increase in size of the anion.
2. For a given anion, covalent character increases with decrease in size of the cation.
3. Covalent character increases with increasing charge on either ion.
4. Covalent character is greater for cations with nonnoble gas electronic configurations.

**EXAMPLE**

Explain each the following, using Fajan's rules:

a. $Ag_2S$ is much less soluble than $Ag_2O$.

Rule 1: $S^{2-}$ is much larger than $O^{2-}$.

b. $Fe(OH)_3$ is much less soluble than $Fe(OH)_2$.

Rule 3: $Fe^{3+}$ has a larger charge than $Fe^{2+}$.

**EXERCISE 6-3**

Explain each of the following:

a. FeS is much less soluble than $Fe(OH)_2$.

b. $Ag_2S$ is much less soluble than AgCl.

c. Salts of the transition metals are usually less soluble than the corresponding salts of the alkali and alkaline earth metals.

These rules are helpful in predicting behavior of specific cation-anion combinations in relation to others, although they are not enough to explain all such reactions. For example, the lithium series (omitting LiI) does not fit and requires a different explanation, which is provided by HSAB arguments. The solubilities of the alkaline earth carbonates are $MgCO_3$ > $CaCO_3$ > $SrCO_3$ > $BaCO_3$. Rule 2 predicts the reverse of this order. The difference appears to lie in the aquation of the metal ions. $Mg^{2+}$ (small,

[15]K. Fajans, *Naturwissenschaften*, **1923**, *11*, 165.

with higher charge density) attracts water molecules much more strongly than the others, with $Ba^{2+}$ (large, with smaller charge density) the least strongly solvated.

Ahrland, Chatt, and Davies[16] classified some of the same phenomena (as well as others) by dividing the metal ions into two classes:

| Class (a) ions | Class (b) ions |
|---|---|
| Most metals | $Cu^{2+}$, $Pd^{2+}$, $Ag^+$, $Pt^{2+}$, $Au^+$, $Hg_2^{2+}$, $Hg^{2+}$, $Tl^+$, $Tl^{3+}$, $Pb^{2+}$, and heavier transition metal ions |

The members of class (b) are located in a small region in the periodic table at the lower right-hand side of the transition metals. In the periodic table of Figure 6-11, the elements that are always in class (b) and those that are commonly in class (b) when they have low or zero oxidation states are identified. In addition, the transition metals have class (b) character in compounds in which their oxidation state is zero (organometallic compounds). The class (b) ions form halides whose solubility is in the order $F^- > Cl^- > Br^- > I^-$. The solubility of class (a) halides is in the reverse order. The class (b) metal ions also have a larger enthalpy of reaction with phosphorus donors than with nitrogen donors, again the reverse of the class (a) metal ion reactions.

Ahrland, Chatt, and Davies explained the class (b) metals as having $d$ electrons available for $\pi$ bonding (a discussion of metal-ligand bonding is included in Chapters 10 and 13). Therefore, high oxidation states of elements to the right of the transition metals have more class (b) character than low oxidation states. For example, thallium(III) and thallium(I) are both class (b) in their reactions with halides, but Tl(III) shows stronger class (b) character because Tl(I) has two $6s$ electrons that screen the $5d$ electrons and keep them from being fully available for $\pi$ bonding. Elements farther left in the table have more class (b) character in low or zero oxidation states, when more $d$ electrons are present.

Donor molecules or ions that have the most favorable enthalpies of reaction with class (b) metals are those that are readily polarizable and have vacant $d$ or $\pi^*$ orbitals available for $\pi$ bonding.



**FIGURE 6-11** Location of Class (b) Metals in the Periodic Table. Those in the outlined region are always class (b) acceptors. Others indicated by their symbols are borderline elements, whose behavior depends on their oxidation state and the donor. The remainder (blank) are class (a) acceptors. (Adapted with permission from S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev. Chem. Soc.*, **1958**, *12*, 265.)

[16]S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev. Chem. Soc.*, **1958**, *12*, 265.

## 6-3-1 THEORY OF HARD AND SOFT ACIDS AND BASES

Pearson[17] designated the class (a) ions **hard acids** and class (b) ions **soft acids**. Bases are also classified as hard or soft. The halide ions range from $F^-$, a very hard base, through less hard $Cl^-$ and $Br^-$ to $I^-$, a soft base. Reactions are more favorable for hard-hard and soft-soft interactions than for a mix of hard and soft in the reactants. For example, in aqueous solution:

$Ag^+ + I^- \longrightarrow$ $AgI(s)$ is a very favorable soft-soft reaction; AgI is very insoluble.

$Li^+ + F^- \longrightarrow$ $LiF(s)$ is a very favorable hard-hard reaction; LiF is only slightly soluble.

$Ag^+ + F^- \longrightarrow$ $AgF(s)$ is a soft-hard reaction that is not favored; AgF is moderately soluble.

$Li^+ + I^- \longrightarrow$ $LiI(s)$ is a hard-soft reaction that is not favored; LiI is soluble
(although it is something of a special case, as mentioned earlier).
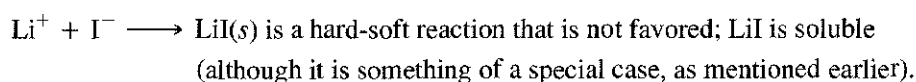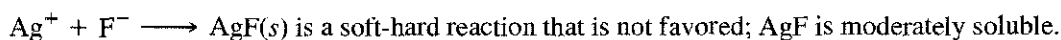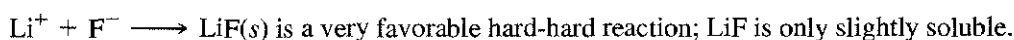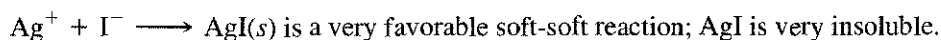
Much of the hard-soft distinction depends on polarizability, the degree to which a molecule or ion is easily distorted by interaction with other molecules or ions. Electrons in polarizable molecules can be attracted or repelled by charges on other molecules, forming slightly polar species that can then interact with the other molecules. Hard acids and bases are relatively small, compact, and nonpolarizable; soft acids and bases are larger and more polarizable (therefore "softer"). The hard acids are therefore any cations with large positive charge (3+ or larger) or those whose $d$ electrons are relatively unavailable for $\pi$ bonding (e.g., alkaline earth ions, $Al^{3+}$). Other hard acid cations that do not fit this description are $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, and $Co^{3+}$. Soft acids are those whose $d$ electrons or orbitals are readily available for $\pi$ bonding (+1 cations, heavier +2 cations). In addition, the larger and more massive the atom, the softer it is likely to be, because the large numbers of inner electrons shield the outer ones and make the atom more polarizable. This description fits the class (b) ions well because they are primarily 1+ and 2+ ions with filled or nearly filled $d$ orbitals, and most are in the second and third rows of the transition elements, with 45 or more electrons. Tables 6-3 and 6-4 list bases and acids in terms of their hardness or softness.

**TABLE 6-3**
**Hard and Soft Bases**

| Hard Bases | Borderline Bases | Soft Bases |
|---|---|---|
| | | $H^-$ |
| $F^-, Cl^-$ | $Br^-$ | $I^-$ |
| $H_2O, OH^-, O^{2-}$ | | $H_2S, HS^-, S^{2-}$ |
| $ROH, RO^-, R_2O, CH_3COO^-$ | | $RSH, RS^-, R_2S$ |
| $NO_3^-, ClO_4^-$ | $NO_2^-, N_3^-$ | $SCN^-, CN^-, RNC, CO$ |
| $CO_3^{2-}, SO_4^{2-}, PO_4^{3-}$ | $SO_3^{2-}$ | $S_2O_3^{2-}$ |
| $NH_3, RNH_2, N_2H_4$ | $C_6H_5NH_2, C_5H_5N, N_2$ | $R_3P, (RO)_3P, R_3As\ C_2H_4, C_6H_6$ |

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

[17]R. G. Pearson, *J. Am. Chem. Soc.*, **1963**, *85*, 3533; *Chem. Br.*, **1967**, *3*, 103; R. G. Pearson, ed., *Hard and Soft Acids and Bases*, Dowden, Hutchinson & Ross, Stroudsburg, PA, 1973. The terms *hard* and *soft* are atributed to D. H. Busch in the first paper of this footnote.

**TABLE 6-4**
**Hard and Soft Acids**

| Hard Acids | Borderline Acids | Soft Acids |
|---|---|---|
| $H^+$, $Li^+$, $Na^+$, $K^+$ | | |
| $Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^2$ | | |
| $BF_3$, $BCl_3$, $B(OR)_3$ | $B(CH_3)_3$ | $BH_3$, $Tl^+$, $Tl(CH_3)_3$ |
| $Al^{3+}$, $Al(CH_3)_3$, $AlCl_3$, $AlH_3$ | | |
| $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{3+}$ | $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$ | $Cu^+$, $Ag^+$, $Au^+$, $Cd^{2+}$, $Hg_2^{2+}$, |
| | $Rh^{3+}$, $Ir^{3+}$, $Ru^{3+}$, $Os^{2+}$ | $Hg^{2+}$, $CH_3Hg^+$, $[Co(CN)_5]^{3-}$, |
| | | $Pd^{2+}$, $Pt^{2+}$, $Pt^{4+}$, |
| Ions with oxidation states of 4 or higher | | $Br_2$, $I_2$ |
| | | Metals with zero oxidation state |
| HX (hydrogen-bonding molecules) | | $\pi$ acceptors: e.g., trinitrobenzene, quinones, tetracyanoethylene |

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

The trends in bases are even easier to see, with fluoride hard and iodide soft. Again, more electrons and larger size lead to softer behavior. In another example, $S^{2-}$ is softer than $O^{2-}$ because it has more electrons spread over a slightly larger volume, making $S^{2-}$ more polarizable. Within a group, such comparisons are easy; as the electronic structure and size change, comparisons become more difficult but are still possible. Thus, $S^{2-}$ is softer than $Cl^-$, which has the same electronic structure, because $S^{2-}$ has a smaller nuclear charge and a slightly larger size. As a result, the negative charge is more available for polarization. Soft acids tend to react with soft bases and hard acids with hard bases, so the reactions produce hard-hard and soft-soft combinations. Quantitative measures of hard-soft parameters are described in Section 6-3-2.

**EXAMPLE**

Is $OH^-$ or $S^{2-}$ more likely to form insoluble salts with 3+ transition metal ions? Which is more likely to form insoluble salts with 2+ transition metal ions?

Because $OH^-$ is hard and $S^{2-}$ is soft, $OH^-$ is more likely to form insoluble salts with 3+ transition metal ions (hard) and $S^2$ is more likely to form insoluble salts with 2+ transition metal ions (borderline or soft).

**EXERCISE 6-4**

Some of the products of the following reactions will be insoluble and some form soluble adducts. Consider only the HSAB characteristics in your answers.

a. Will $Cu^{2+}$ react more strongly with $OH^-$ or $NH_3$? With $O^{2-}$ or $S^{2-}$?
b. Will $Fe^{3+}$ react more strongly with $OH^-$ or $NH_3$? With $O^{2-}$ or $S^{2-}$?
c. Will $Ag^+$ react more strongly with $NH_3$ or $PH_3$?
d. Will Fe, $Fe^{2+}$, or $Fe^{3+}$ react more strongly with CO?

More detailed comparisons are possible, but another factor, called the inherent acid-base strength, must also be kept in mind in these comparisons. An acid or a base may be either hard or soft and at the same time be either strong or weak. The strength of the acid or base may be more important than the hard-soft characteristics; both must be considered at the same time. If two soft bases are in competition for the same acid, the one with more inherent base strength may be favored unless there is considerable difference in softness. As an example, consider the following reaction. Two hard-soft

combinations react to give a hard-hard and a soft-soft combination, although ZnO is composed of the strongest acid ($Zn^{2+}$) and the strongest base ($O^{2-}$):

$$ZnO + 2\,LiC_4H_9 \rightleftharpoons Zn(C_4H_9)_2 + Li_2O$$

| soft-hard | hard-soft | soft-soft | hard-hard |

In this case, the HSAB parameters are more important than acid-base strength, because $Zn^{2+}$ is considerably softer than $Li^+$. As a general rule, hard-hard combinations are more favorable energetically than soft-soft combinations.
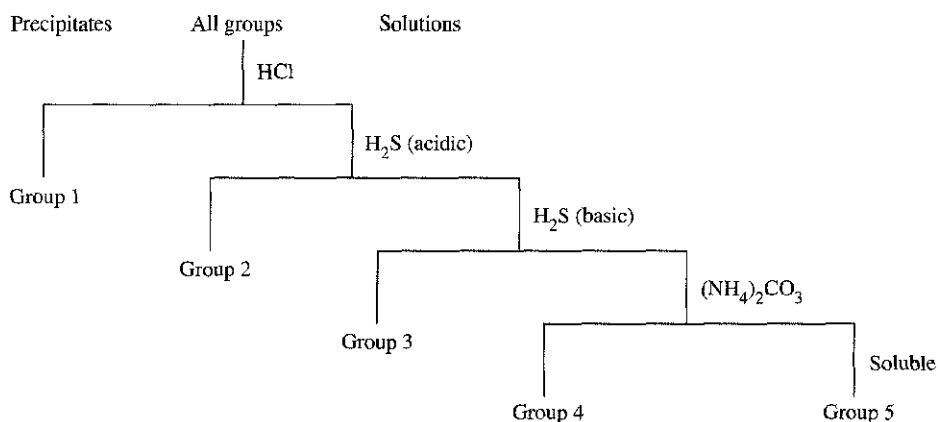
**EXAMPLE**

Qualitative Analysis

**TABLE 6-5**
**HSAB and Qualitative Analysis**

*Qualitative Analysis Separation*

|  | Group 1 | Group 2 | Group 3 | Group 4 | Group 5 |
|---|---|---|---|---|---|
| HSAB acids | Soft | Borderline and soft | Borderline | Hard | Hard |
| Reagent | HCl | $H_2S$ (acidic) | $H_2S$ (basic) | $(NH_4)_2CO_3$ | Soluble |
| Precipitates | AgCl | HgS | MnS | $CaCO_3$ | $Na^+$ |
|  | $PbCl_2$ | CdS | FeS | $SrCO_3$ | $K^+$ |
|  | $Hg_2Cl_2$ | CuS | CoS | $BaCO_3$ | $NH_4^+$ |
|  |  | SnS | NiS |  |  |
|  |  | $As_2S_3$ | ZnS |  |  |
|  |  | $Sb_2S_3$ | $Al(OH)_3$ |  |  |
|  |  | $Bi_2S_3$ | $Cr(OH)_3$ |  |  |

Precipitates    All groups        Solutions

| HCl

$H_2S$ (acidic)

Group 1

$H_2S$ (basic)

Group 2

$(NH_4)_2CO_3$

Group 3

Soluble

Group 4                                Group 5

The traditional qualitative analysis scheme can be used to show how the HSAB theory can be used to correlate solubility behavior; it also can show some of the difficulties with such correlations. In qualitative analysis for metal ions, the cations are successively separated into groups by precipitation for further detailed analysis. The details differ with the specific reagents used, but generally fall into the categories in Table 6-5. In the usual analysis, the reagents are used in the order given from left to right. The cations $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$ (Group 1) are the only metal ions that precipitate with chloride, even though they are considered soft acids and chloride is a marginally hard base. Apparently, the sizes of the ions permit strong bonding in the crystal lattice in spite of this mismatch, partly because their interaction with water (another hard base) is not strong enough to prevent precipitation. The reaction

$$M^{n+}(H_2O)_m + n\,Cl^-(H_2O)_p \longrightarrow MCl_n\!\downarrow + (m + p)\,H_2O$$
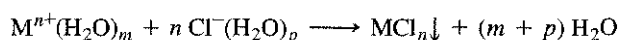
is favorable (although $PbCl_2$ is appreciably soluble in hot water).

Group 2 is made up of borderline and soft acids that are readily precipitated in acidic $H_2S$ solution, in which the $S^{2-}$ concentration is very low because the equilibrium

$$H_2S \rightleftharpoons 2\,H^+ + S^{2-}$$
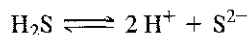
lies far to the left in acid solution. The metal ions in this group are soft enough that a low concentration of the soft sulfide is sufficient to precipitate them. Group 3 cleans up the remaining transition metals in the list, all of which are borderline acids. In the basic $H_2S$ solution, the equilibrium above lies far to the right and the high sulfide ion concentration precipitates even these cations. $Al^{3-}$ and $Cr^{3+}$ are hard enough that they prefer $OH^-$ over $S^{2-}$ and precipitate as hydroxides. Another hard acid could be $Fe^{3+}$, but it is reduced by $S^{2-}$, and iron precipitates as FeS. Group 4 is a clear-cut case of hard-hard interactions, and Group 5 cations are larger, with only a single electronic charge, and thus have small electrostatic attractions for anions. For this reason, they do not precipitate except with certain highly specific reagents, such as perchlorate, $ClO_4^-$, for potassium and tetraphenylborate, $[B(C_6H_5)_4]^-$, or zinc uranyl acetate, $[Zn(UO_2)_3(C_2H_3O_2)_9]^-$, for sodium.

This quick summary of the analysis scheme shows where hard-hard or soft-soft combinations lead to insoluble salts, but also shows that the rules have limitations. Some cations considered hard will precipitate under the same conditions as others that are clearly soft. For this reason, any solubility predictions based on HSAB must be considered tentative, and solvent and other interactions must be considered carefully.

HSAB arguments such as these explain the formation of some metallic ores described in Chapter 1 (soft and borderline metal ions form sulfide ores, hard metal ions form oxide ores, some ores such as bauxite result from the leaching away of soluble salts) and some of the reactions of ligands with metals (borderline acid cations of Co, Ni, Cu, and Zn tend to form —NCS complexes, whereas softer acid cations of Rh, Ir, Pd, Pt, Au, and Hg tend to form —SCN complexes). Few of these cases involve only this one factor, but it is important in explaining trends in many reactions. There are examples of both —SCN and —NCS bonding with the same metal (Section 9-3-7), along with compounds in which both types of bonding are found, with the thiocyanate bridging between two metal atoms.

A somewhat oversimplified way to look at the hard-soft question considers the hard-hard interactions as simple electrostatic interactions, with the LUMO of the acid far above the HOMO of the base and relatively little change in orbital energies on adduct formation.[18] A soft-soft interaction involves HOMO and LUMO energies that are much closer and give a large change in orbital energies on adduct formation. Diagrams of such interactions are shown in Figure 6-12, but they need to be used with caution. The small drop in energy in the hard-hard case that seems to indicate only small interactions is not necessarily the entire story. The hard-hard interaction depends on a longer range electrostatic force, and this interaction can be quite strong. Many comparisons of hard-hard and soft-soft interactions indicate that the hard-hard combination is stronger and is the primary driving force for the reaction. The contrast between the hard-hard product and the hard-soft reactants in such cases provides the net energy difference that leads to the products. One should also remember that many reactions to which the HSAB approach is applied involve competition between two different conjugate acid-base pairs; only in a limited number of cases is one interaction large enough to overwhelm the others and determine whether the reaction will proceed.

[18] Jensen, pp. 262-265; C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1966**, *1*, 234.
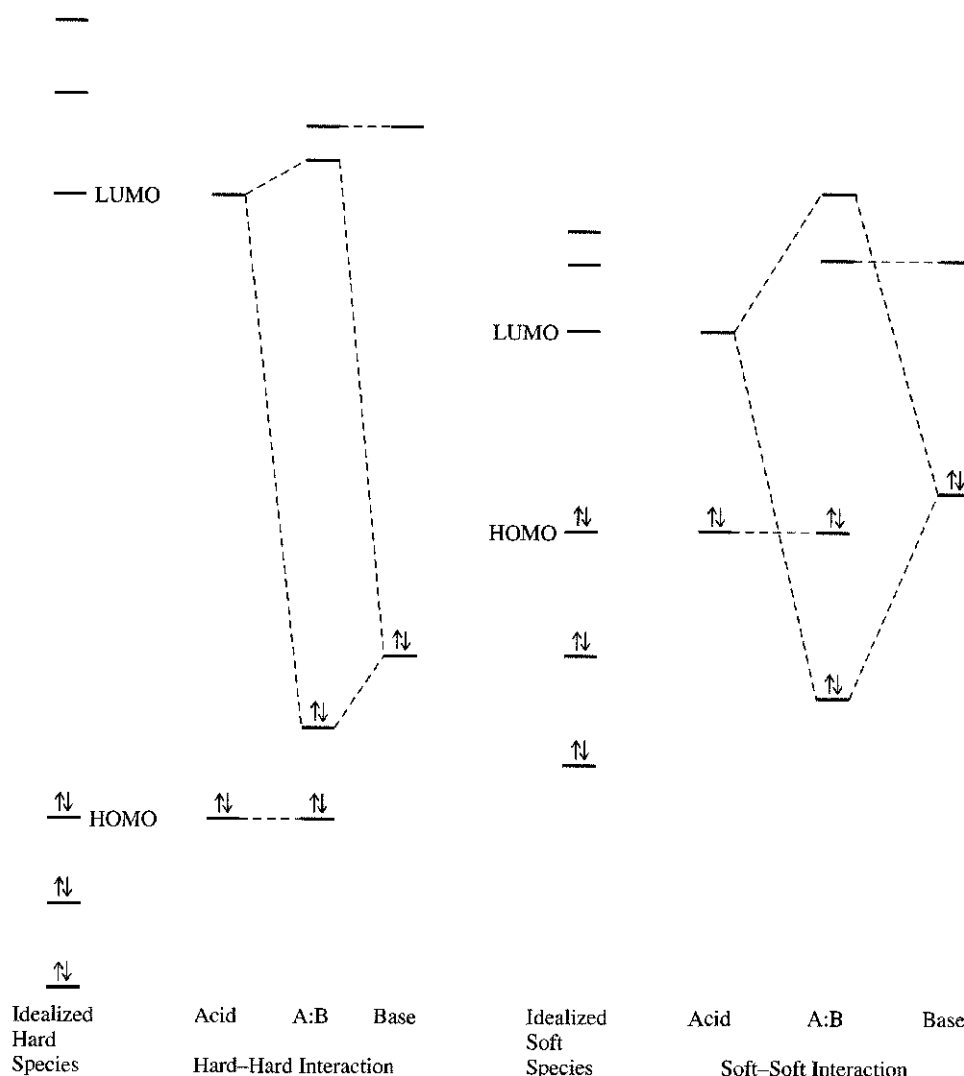
**FIGURE 6-12** HOMO-LUMO
Diagrams for Hard-Hard and Soft-
Soft Interactions. (Adapted with
permission from W. B. Jensen, *The
Lewis Acid-Base Concepts*, Wiley-
Interscience, New York, 1980,
pp. 262–263. Copyright © 1980,
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Sons, Inc.)

## 6-3-2 QUANTITATIVE MEASURES

There are two major approaches to quantitative measures of acid-base reactions. One, developed by Pearson,[19] uses the hard-soft terminology, and defines the **absolute hardness**, $\eta$, as one-half the difference between the ionization energy and the electron affinity (both in eV):

$$\eta = \frac{I - A}{2}$$

This definition of hardness is related to Mulliken's definition of electronegativity, called absolute electronegativity by Pearson:

$$\chi = \frac{I + A}{2}$$

This approach describes a hard acid or base as a species that has a large difference between its ionization energy and its electron affinity. Ionization energy is assumed to measure the energy of the HOMO and electron affinity is assumed to measure the

[19]R. G. Pearson, *Inorg. Chem.*, **1988**, *27*, 734.

LUMO for a given molecule: $E_{HOMO} = -I$, $E_{LUMO} = -A$. Softness is defined as the inverse of hardness, $\sigma = \dfrac{1}{\eta}$. Because there are no electron affinities for anions, Pearson uses the values for the atoms as approximate equivalents.

The halogen molecules offer good examples of the use of these orbital arguments to illustrate HSAB. For the halogens, the trend in $\eta$ parallels the change in HOMO energies because the LUMO energies are nearly the same, as shown in Figure 6-13. Fluorine is the most electronegative halogen. It is also the smallest and least polarizable halogen and is therefore the hardest. In orbital terms, the LUMOs of all the halogen molecules are nearly identical, and the HOMOs increase in energy from $F_2$ to $I_2$. The absolute electronegativities decrease in order $F_2 > Cl_2 > Br_2 > I_2$ as the HOMO energies increase. The hardness also decreases in the same order as the difference between the HOMO and LUMO decreases. Data for a number of other species are given in Table 6-6 and more are given in Appendix B-5.

---

### EXERCISE 6-5

Confirm the absolute electronegativity and absolute hardness values for the following species, using data from Table 6-6 and Appendix B-5:

a. $Al^{3+}$, $Fe^{3+}$, $Co^{3+}$

b. $OH^-$, $Cl^-$, $NO_2^-$

c. $H_2O$, $NH_3$, $PH_3$

---

The absolute hardness is not enough to fully describe reactivity (for example, some hard acids are weak acids and some are strong) and it deals only with gas phase
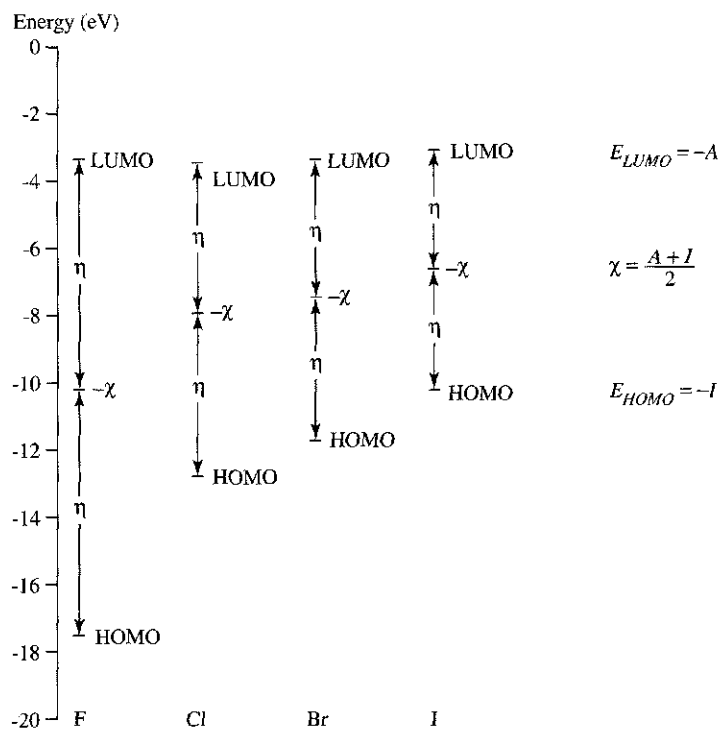


**FIGURE 6-13** Energy Levels for Halogens. Relationships between absolute electronegativity $(\chi)$, absolute hardness $(\eta)$, and HOMO and LUMO energies for the halogens.

**TABLE 6-6**
**Hardness Parameters (eV)**

| Ion | $I$ | $A$ | $\chi$ | $\eta$ |
|---|---|---|---|---|
| $Al^{3+}$ | 119.99 | 28.45 | 74.22 | 45.77 |
| $Li^+$ | 75.64 | 5.39 | 40.52 | 35.12 |
| $Mg^{2+}$ | 80.14 | 15.04 | 47.59 | 32.55 |
| $Na^+$ | 47.29 | 5.14 | 26.21 | 21.08 |
| $Ca^{2+}$ | 50.91 | 11.87 | 31.39 | 19.52 |
| $Sr^{2+}$ | 43.6 | 11.03 | 27.3 | 16.3 |
| $K^+$ | 31.63 | 4.34 | 17.99 | 13.64 |
| $Zn^{2+}$ | 39.72 | 17.96 | 28.84 | 10.88 |
| $Hg^{2+}$ | 34.2 | 18.76 | 26.5 | 7.7 |
| $Ag^+$ | 21.49 | 7.58 | 14.53 | 6.96 |
| $Pd^{2+}$ | 32.93 | 19.43 | 26.18 | 6.75 |
| $Rh^{2+}$ | 31.06 | 18.08 | 24.57 | 6.49 |
| $Cu^+$ | 20.29 | 7.73 | 14.01 | 6.28 |
| $Sc^{2+}$ | 24.76 | 12.80 | 18.78 | 5.98 |
| $Ru^{2+}$ | 28.47 | 16.76 | 22.62 | 5.86 |
| $Au^+$ | 20.5 | 9.23 | 14.90 | 5.6 |
| $BF_3$ | 15.81 | −3.5 | 6.2 | 9.7 |
| $H_2O$ | 12.6 | −6.4 | 3.1 | 9.5 |
| $NH_3$ | 10.7 | −5.6 | 2.6 | 8.2 |
| $PF_3$ | 12.3 | −1.0 | 5.7 | 6.7 |
| $(CH_3)_3N$ | 7.8 | −4.8 | 1.5 | 6.3 |
| $PH_3$ | 10.0 | −1.9 | 4.1 | 6.0 |
| $(CH_3)_3P$ | 8.6 | −3.1 | 2.8 | 5.9 |
| $SO_2$ | 12.3 | 1.1 | 6.7 | 5.6 |
| $C_6H_6$ | 9.3 | −1.2 | 4.1 | 5.3 |
| $C_5H_5N$ | 9.3 | −0.6 | 4.4 | 5.0 |
| $F^-$ | 17.42 | 3.40 | 10.41 | 7.01 |
| $OH^-$ | 13.17 | 1.83 | 7.50 | 5.67 |
| $CN^-$ | 14.02 | 3.82 | 8.92 | 5.10 |
| $Cl^-$ | 13.01 | 3.62 | 8.31 | 4.70 |
| $Br^-$ | 11.84 | 3.36 | 7.60 | 4.24 |
| $NO_2^-$ | >10.1 | 2.30 | >6.2 | >3.9 |
| $I^-$ | 10.45 | 3.06 | 6.76 | 3.70 |

SOURCE: Data from R. G. Pearson, *Inorg. Chem.*, **1988**, *27*, 734.

NOTE: The anion values are calculated from data for the radicals or atoms.

conditions. Drago and Wayland[20] have proposed a quantitative system of acid-base parameters to account more fully for reactivity by including electrostatic and covalent factors. This approach uses the equation

$$-\Delta H = E_A E_B + C_A C_B$$

where $\Delta H$ is the enthalpy of the reaction A + B $\longrightarrow$ AB in the gas phase or in an inert solvent, and $E$ and $C$ are parameters calculated from experimental data. $E$ is a measure of the capacity for electrostatic (ionic) interactions and $C$ is a measure of the

[20]R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **1965**, *87*, 3571; R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **1971**, *93*, 6014; R. S. Drago, *Struct. Bonding (Berlin)*, **1973**, *15*, 73; R. S. Drago, L. B. Parr, and C. S. Chamberlain, *J. Am. Chem. Soc.*, **1977**, *99*, 3203.

**TABLE 6-7**

$C_A$, $E_A$, $C_B$, and $E_B$ Values (kcal/mol)

| Acid | $C_A$ | $E_A$ |
|------|-------|-------|
| Trimethylboron, $B(CH_3)_3$ | 1.70 | 6.14 |
| Boron trifluoride (gas), $BF_3$ | 1.62 | 9.88 |
| Trimethylaluminum, $Al(CH_3)_3$ | 1.43 | 16.9 |
| Iodine (standard), $I_2$ | 1.00* | 1.00* |
| Trimethylgallium, $Ga(CH_3)_3$ | 0.881 | 13.3 |
| Iodine monochloride, ICl | 0.830 | 5.10 |
| Sulfur dioxide, $SO_2$ | 0.808 | 0.920 |
| Phenol, $C_6H_5OH$ | 0.442 | 4.33 |
| tert-butyl alcohol, $C_4H_9OH$ | 0.300 | 2.04 |
| Pyrrole, $C_4H_4NH$ | 0.295 | 2.54 |
| Chloroform, $CHCl_3$ | 0.159 | 3.02 |

| Base | $C_B$ | $E_B$ |
|------|-------|-------|
| 1-Azabicyclo[2.2.2] octane, $HC(C_2H_4)_3N$ (quinuclidine) | 13.2 | 0.704 |
| Trimethylamine, $(CH_3)_3N$ | 11.54 | 0.808 |
| Triethylamine, $(C_2H_5)_3N$ | 11.09 | 0.991 |
| Dimethylamine, $(CH_3)_2NH$ | 8.73 | 1.09 |
| Diethyl sulfide, $(C_2H_5)_2S$ | 7.40* | 0.399 |
| Pyridine, $C_5H_5N$ | 6.40 | 1.17 |
| Methylamine, $CH_3NH_2$ | 5.88 | 1.30 |
| Ammonia, $NH_3$ | 3.46 | 1.36 |
| Diethyl ether, $(C_2H_5)_2O$ | 3.25 | 0.963 |
| N,N-dimethylacetamide, $(CH_3)_2NCOCH_3$ | 2.58 | 1.32* |
| Benzene, $C_6H_6$ | 0.681 | 0.525 |

SOURCE: Data from R. S. Drago, *J. Chem. Educ.*, **1974**, *51*, 300.

NOTE: * Reference values.

tendency to form covalent bonds. The subscripts refer to values assigned to the acid and base, with $I_2$ chosen as the reference acid and N,N-dimethylacetamide and diethyl sulfide as reference bases. The defined values (in units of kcal/mol) are

| | $C_A$ | $E_A$ | $C_B$ | $E_B$ |
|---|-------|-------|-------|-------|
| $I_2$ | 1.00 | 1.00 | | |
| N,N-dimethylacetamide | | | | 1.32 |
| Diethyl sulfide | | | 7.40 | |

Values of $E_A$ and $C_A$ for selected acids and $E_B$ and $C_B$ for selected bases are given in Table 6-7, and a longer list is in Appendix B-6. Combining the values of these parameters for acid-base pairs gives the enthalpy of reaction in kcal/mol; multiplying by 4.184 J/cal converts to joules (although we use joules in this book, these numbers were originally derived for calories and we have chosen to leave them unchanged).

Examination of the data shows that most acids have lower $C_A$ values and higher $E_A$ values than $I_2$. Because $I_2$ has no permanent dipole, it has little electrostatic attraction for bases and has a low $E_A$. On the other hand, it has a strong tendency to bond with some other bases, indicated by a relatively large $C_A$. Because 1.00 was chosen as the reference value for both parameters for $I_2$, most $C_A$ values are below 1 and most $E_A$ values are above 1. For $C_B$ and $E_B$, this relationship is reversed.

The example of iodine and benzene shows how these tables can be used.

$$I_2 + C_6H_6 \longrightarrow I_2 \cdot C_6H_6$$
$$\text{acid} \quad \text{base}$$
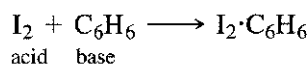
$$-\Delta H = E_A E_B + C_A C_B \quad \text{or} \quad \Delta H = -(E_A E_B + C_A C_B)$$

$$\Delta H = -([1.00 \times 0.681] + [1.00 \times 0.525]) = -1.206 \, \text{kcal/mol, or} -5.046 \, \text{kJ/mol}$$

The experimental value of $\Delta H$ is $-1.3$ kcal/mol, or $-5.5$ kJ/mol, 10% larger.[21] This is a weak adduct (other bases combining with $I_2$ have enthalpies 10 times as large), and the calculation does not agree with experiment as well as many. Because there can be only one set of numbers for each compound, Drago developed statistical methods for averaging experimental data from many different combinations. In many cases, the agreement between calculated and experimental enthalpies is within 5%.

One phenomenon not well accounted for by other approaches is seen in Table 6-8.[22] It shows a series of four acids and five bases in which both $E$ and $C$ increase. In most descriptions of bonding, as electrostatic (ionic) bonding increases, covalent bonding decreases, but these data show both increasing at the same time. Drago argued that this means that the $E$ and $C$ approach explains acid-base adduct formation better than the HSAB theory described earlier.

## EXAMPLE

Calculate the enthalpy of adduct formation predicted by Drago's $E$, $C$ equation for the reactions of $I_2$ with diethyl ether and diethyl sulfide.

| | $E_A$ | $E_B$ | $C_A$ | $C_B$ | $\Delta H$ (kcal/mol) | Experimental $\Delta H$ |
|---|---|---|---|---|---|---|
| Diethyl ether | \-([1.00 | × 0.963] | + [1.00 | × 3.25]) | = −4.21 | −4.2 |
| Diethyl sulfide | \-([1.00 | × 0.339] | + [1.00 | × 7.40]) | = −7.74 | −7.8 |

Agreement is very good, with the product $C_A \times C_B$ by far the dominant factor. The softer sulfur reacts more strongly with the soft $I_2$.

## EXERCISE 6-6

Calculate the enthalpy of adduct formation predicted by Drago's $E$, $C$ equation for the following combinations and explain the trends in terms of the electrostatic and covalent contributions:

a. $BF_3$ reacting with ammonia, methylamine, dimethylamine, and trimethylamine

b. Pyridine reacting with trimethylboron, trimethylaluminum, and trimethylgallium

**TABLE 6-8**
**Acids and Bases with Parallel Changes in $E$ and $C$**

| Acids | $C_A$ | $E_A$ |
|---|---|---|
| $CHCl_3$ | 0.154 | 3.02 |
| $C_6H_5OH$ | 0.442 | 4.33 |
| $m\text{-}CF_3C_6H_4OH$ | 0.530 | 4.48 |
| $B(CH_3)_3$ | 1.70 | 6.14 |

| Bases | $C_B$ | $E_B$ |
|---|---|---|
| $C_6H_6$ | 0.681 | 0.525 |
| $CH_3CN$ | 1.34 | 0.886 |
| $(CH_3)_2CO$ | 2.33 | 0.987 |
| $(CH_3)_2SO$ | 2.85 | 1.34 |
| $NH_3$ | 3.46 | 1.36 |

[21]R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **1955**, *77*, 2164.
[22]R. S. Drago, *J. Chem. Educ.*, **1974**, *51*, 300.

Drago's system emphasized the two factors involved in acid-base strength (electrostatic and covalent) in the two terms of his equation for enthalpy of reaction. Pearson's system put more obvious emphasis on the covalent factor. Pearson[23] proposed the equation $\log K = S_A S_B + \sigma_A \sigma_B$, with the inherent strength $S$ modified by a softness factor $\sigma$. Larger values of strength and softness then lead to larger equilibrium constants or rate constants. Although Pearson attached no numbers to this equation, it does show the need to consider more than just hardness or softness in working with acid-base reactions. However, his more recent development of absolute hardness based on orbital energies returns to a single parameter and considers only gas phase reactions. Both Drago's $E$ and $C$ parameters and Pearson's HSAB are useful, but neither covers every case, and it is usually necessary to make judgments about reactions for which information is incomplete. With $E$ and $C$ numbers available, quantitative comparisons can be made. When they are not, the qualitative HSAB approach can provide a rough guide for predicting reactions. Examination of the tables also shows little overlap of the examples chosen by Drago and Pearson.

An additional factor that has been mentioned frequently in this chapter is solvation. Neither of the two quantitative theories takes this factor into account. Under most conditions, reactions will be influenced by solvent interactions, and they can promote or hinder reactions, depending on the details of these interactions.

## 6-4 ACID AND BASE STRENGTH

### 6-4-1 MEASUREMENT OF ACID-BASE INTERACTIONS

Interaction between acids and bases can be measured in many ways:
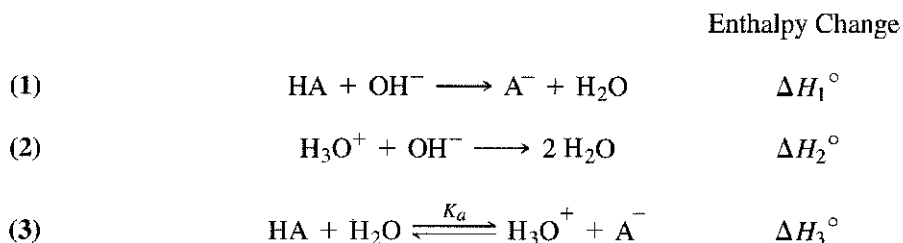
1. Changes in boiling or melting points can indicate the presence of adducts. Hydrogen-bonded solvents such as water and methanol and adducts such as $BF_3 \cdot O(C_2H_5)_2$ have higher boiling points or melting points than would otherwise be expected.

2. Direct calorimetric methods or temperature dependence of equilibrium constants can be used to measure enthalpies and entropies of acid-base reactions. The following section gives more details on use of data from these measurements.

3. Gas phase measurements of the formation of protonated species can provide similar thermodynamic data.

4. Infrared spectra can provide indirect measures of bonding in acid-base adducts by showing changes in bond force constants. For example, free CO has a C—O stretching band at 2143 cm$^{-1}$, and CO in $Ni(CO)_4$ has a C—O band at 2058 cm$^{-1}$.

5. Nuclear magnetic resonance coupling constants provide a similar indirect measure of changes in bonding on adduct formation.

6. Ultraviolet or visible spectra can show changes in energy levels in the molecules as they combine.

Different methods of measuring acid-base strength yield different results, which is not surprising when the physical properties being measured are considered. Some aspects of acid-base strength are explained in the following section, with brief explanations of the experimental methods used.

---

[23]R. G. Pearson, *J. Chem. Educ*, **1968**, *45*, 581.

## 6-4-2 THERMODYNAMIC MEASUREMENTS

The enthalpy change of some reactions can be measured directly, but for those that do not go to completion (as is common in acid-base reactions), thermodynamic data from reactions that do go to completion can be combined using Hess's law to obtain the needed data. For example, the enthalpy and entropy of ionization of a weak acid, HA, can be found by measuring (1) the enthalpy of reaction of HA with NaOH, (2) the enthalpy of reaction of a strong acid (such as HCl) with NaOH, and (3) the equilibrium constant for dissociation of the acid (usually determined from the titration curve).

Enthalpy Change

(1) $$HA + OH^- \longrightarrow A^- + H_2O \qquad \Delta H_1^{\,\circ}$$

(2) $$H_3O^+ + OH^- \longrightarrow 2\,H_2O \qquad \Delta H_2^{\,\circ}$$

(3) $$HA + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} H_3O^+ + A^- \qquad \Delta H_3^{\,\circ}$$

From the usual thermodynamic relationships,

(4) $$\Delta H_3^{\,\circ} = \Delta H_1^{\,\circ} - \Delta H_2^{\,\circ}$$

[because Reaction (3) = Reaction (1) − Reaction (2)]

(5) $$\Delta S_3^{\,\circ} = \Delta S_1^{\,\circ} - \Delta S_2^{\,\circ}$$

(6) $$\Delta G_3^{\,\circ} = -RT \ln K_a = \Delta H_3^{\,\circ} - T\Delta S_3^{\,\circ}$$

Rearranging (6):

(7) $$\ln K_a = -\Delta H_3^{\,\circ}/RT + \Delta S_3^{\,\circ}/R$$

Naturally, the final calculation can be more complex than this when HA is already partly dissociated in the first reaction, but the approach remains the same. It is also possible to measure the equilibrium constant at different temperatures and use Equation (6) to calculate $\Delta H^\circ$ and $\Delta S^\circ$. On a plot of $\ln K_a$ versus $1/T$, the slope is $-\Delta H_3^{\,\circ}/R$ and the intercept is $\Delta S_3^{\,\circ}/R$. This method works as long as $\Delta H^\circ$ and $\Delta S^\circ$ do not change appreciably over the temperature range used. This is sometimes a difficult condition. Data for $\Delta H^\circ$, $\Delta S^\circ$, and $K_a$ for acetic acid are given in Table 6-9.

**TABLE 6-9**
**Thermodynamics of Acetic Acid Dissociation**

| | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) |
|---|---|---|
| $H_3O^+ + OH^- \rightleftharpoons 2\,H_2O$ | −55.9 | −80.4 |
| $HOAc + OH^- \rightleftharpoons H_2O + OAc^-$ | −56.3 | −12.0 |

| HOAc $\rightleftharpoons$ H$^+$ + OAc$^-$ | | | | | |
|---|---|---|---|---|---|
| $T$ (K) | 303 | 308 | 313 | 318 | 323 |
| $K_a$ ($\times 10^{-5}$) | 1.750 | 1.728 | 1.703 | 1.670 | 1.633 |

NOTE: $\Delta H^\circ$ and $\Delta S^\circ$ for these reactions change rapidly with temperature. Calculations based on these data are valid only over the limited temperature range given above.

---

**EXERCISE 6-7**

Use the data in Table 6-9 to calculate the enthalpy and entropy of reaction for dissociation of acetic acid using (a) Equations (4) and (5) and (b) the temperature dependence of $K_a$ of Equation (7) by graphing ln $K_a$ versus $1/T$.

---

## 6-4-3 PROTON AFFINITY

One of the purest measures of acid-base strength, but one difficult to relate to solution reactions, is gas phase proton affinity:[24]

$$BH^+(g) \longrightarrow B(g) + H^+(g) \qquad \text{proton affinity} = \Delta H$$
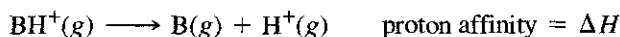
A large proton affinity means it is difficult to remove the hydrogen ion; this means that B is a strong base and $BH^+$ is a weak acid in the gas phase. In favorable cases, mass spectroscopy and ion cyclotron resonance spectroscopy[25] can be used to measure the reaction indirectly. The voltage of the ionizing electron beam in mixtures of B and $H_2$ is changed until $BH^+$ appears in the output from the spectrometer. The enthalpy of formation for $BH^+$ can then be calculated from the voltage of the electron beam, and combined with enthalpies of formation of B and $H^+$ to calculate the enthalpy change for the reaction.

In spite of the simple concept, the measured values of proton affinities have large uncertainties because the molecules involved frequently are in excited states (with excess energy above their normal ground states) and some species do not yield $BH^+$ as a fragment. In addition, under common experimental conditions, the proton affinity must be combined with solvent or other environmental effects to fit the actual reactions. However, gas phase proton affinities are useful in sorting out the different factors influencing acid-base behavior and their importance. For example, the alkali metal hydroxides, which are of equal basicity in aqueous solution, have gas phase basicities in the order LiOH < NaOH < KOH < CsOH. This order matches the increase in the electron-releasing ability of the cation in these hydroxides. Proton affinity studies have also shown that pyridine and aniline, shown in Figure 6-14, are stronger bases than ammonia in the gas phase, but they are weaker than ammonia in aqueous solution,[26] presumably because the interaction of the ammonium ion with water is more favorable than the interaction with the pyridinium or anilinium ions. Other comparisons of gas phase data with solution data allow at least partial separation of the different factors influencing reactions.
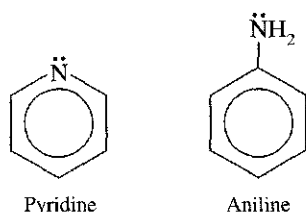
Pyridine        Aniline

**FIGURE 6-14** Pyridine and Aniline Structures.

## 6-4-4 ACIDITY AND BASICITY OF BINARY HYDROGEN COMPOUNDS

The binary hydrogen compounds (compounds containing only hydrogen and one other element) range from the strong acids HCl, HBr, and HI to the weak base $NH_3$. Others, such as $CH_4$, show almost no acid-base properties. Some of these molecules in order of increasing gas phase acidities from left to right are shown in Figure 6-15.

[24]H. L. Finston and A. C. Rychtman, *A New View of Current Acid-Base Theories*, John Wiley & Sons, New York, 1982, pp. 53–62.

[25]R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders, Philadelphia, 1977, pp. 552–565.

[26]H. L. Finston and A. C. Rychtman, *A New View of Current Acid-base Theories*, John Wiley & Sons, New York, 1982, pp. 59–60.

**FIGURE 6-15** Acidity of Binary Hydrogen Compounds. Enthalpy of dissociation in kJ/mole for the reaction $AH(g) \longrightarrow A^-(g) + H^+(g)$ (numerically the same as the proton affinity). (Data from J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **1979**, *101*, 6046; $AsH_3$ value from J. E. Bartmess and R. T. McIver, Jr., *Gas Phase Ion Chemistry*, M. T. Bowers, ed., Academic Press, New York, 1979, p. 87.)
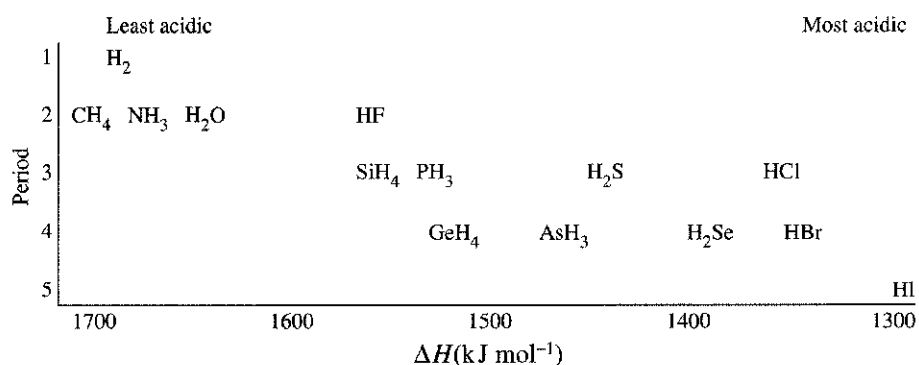


Two apparently contradictory trends are seen in these data. Acidity increases with increasing number of electrons in the central atom, either going across the table or down, but the electronegativity effects are opposite for the two directions, as shown in Figure 6-16.

Within each group (column of the periodic table), acidity increases on going down the series, as in $H_2Se > H_2S > H_2O$. The strongest acid is the largest, heaviest member, low in the periodic table, containing the nonmetal of lowest electronegativity of the group. An explanation of this is that the conjugate bases ($SeH^-$, $SH^-$, and $OH^-$) of the larger molecules have lower charge density and therefore a smaller attraction for hydrogen ions (the $H—O$ bond is stronger than the $H—S$ bond, which in turn is stronger than the $H—Se$ bond). As a result, the larger molecules are stronger acids and their conjugate bases are weaker.

On the other hand, within a period, acidity is greatest for the compounds of elements toward the right, with greater electronegativity. The electronegativity argument cannot be used, because in this series the more electronegative elements form the stronger acids. Although it may have no fundamental significance, one explanation that assists in remembering the trends divides the $-1$ charge of each conjugate base evenly among the lone pairs. Thus, $NH_2^-$ has a charge of $-1$ spread over two lone pairs, or $-\frac{1}{2}$ on each, $OH^-$ has a charge of $-1$ spread over three lone pairs, or $-\frac{1}{3}$ on each, and $F^-$ has a charge of $-1$ spread over four lone pairs, or $-\frac{1}{4}$ on each lone pair. The amide ion, $NH_2^-$, has the strongest attraction for protons, and is therefore the strongest of these three conjugate bases and ammonia is the weakest acid of the three. The order of acid strength follows this trend, $NH_3 < H_2O < HF$.

The same general trends persist when the acidity of these compounds is measured in aqueous solution. The reactions are more complex, forming aquated ions, but the overall effects are similar. The three heaviest hydrohalic acids (HCl, HBr, HI) are equally
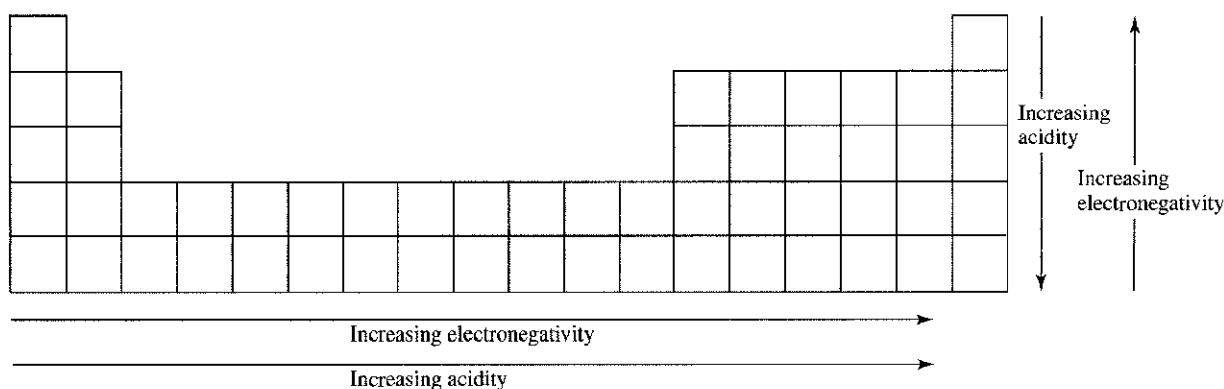


**FIGURE 6-16** Trends in Acidity and Electronegativity of Binary Hydrides.

strong in water, because of the leveling effect of the water. (Details of the leveling effect and other solvent effects are considered in greater detail in Sections 6-4-9 and 6-4-10.) All the other binary hydrogen compounds are weaker acids, with their acid strength decreasing toward the left in the periodic table. Methane and ammonia exhibit no acidic behavior in aqueous solution, nor do silane ($SiH_4$) and phosphine ($PH_3$).

## 6-4-5 INDUCTIVE EFFECTS

Substitution of electronegative atoms or groups, such as fluorine or chlorine, in place of hydrogen on ammonia or phosphine results in weaker bases. The electronegative atom draws electrons toward itself, and as a result the nitrogen or phosphorus atom has less negative charge and its lone pair is less readily donated to an acid. For example, $PF_3$ is a much weaker base than $PH_3$.
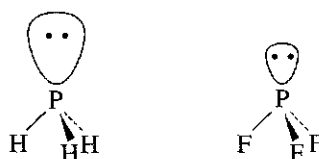
A similar effect in the reverse direction results from substitution of alkyl groups for hydrogen. For example, in amines the alkyl groups contribute electrons to the nitrogen, increasing its negative character and making it a stronger base. Additional substitutions increase the effect, with the following resulting order of base strength in the gas phase:

$$NMe_3 > NHMe_2 > NH_2Me > NH_3$$
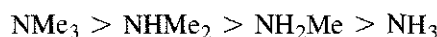
These **inductive effects** are similar to the effects seen in organic molecules containing electron-contributing or electron-withdrawing groups. Once again, caution is required in applying this idea to other compounds. The boron halides do not follow this argument because $BF_3$ and $BCl_3$ have significant $\pi$ bonding that increases the electron density on the boron atom. Inductive effects would make $BF_3$ the strongest acid because the large electronegativity of the fluorine atoms draws electrons away from the boron atom. In fact, the acid strength is in the order $BF_3 < BCl_3 \leq BBr_3$.

## 6-4-6 STRENGTH OF OXYACIDS

In the series of oxyacids of chlorine, the acid strength in aqueous solution is in the order

$$HClO_4 > HClO_3 > HClO_2 > HOCl$$
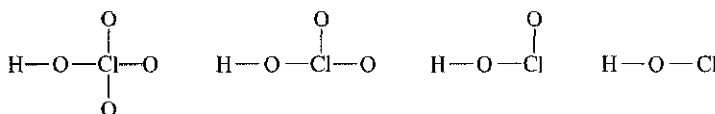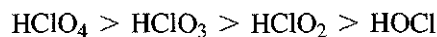
Pauling suggested a rule that predicts the strength of such acids semiquantitatively, based on $n$, the number of *nonhydrogenated oxygen atoms* per molecule. Pauling's equation describing the acidity at 25° C is $pK_a \approx 9 - 7n$. Several other equations have been proposed; $pK_a \approx 8 - 5n$ fits some acids better. (Remember: the stronger the acid, the smaller the $pK_a$.) The $pK_a$ values of the acids above are then

| Acid | Strongest $HClO_4$ | $HClO_3$ | $HClO_2$ | Weakest $HOCl$ |
|---|---|---|---|---|
| $n$ | 3 | 2 | 1 | 0 |
| $pK_a$ (calculated by $9 - 7n$) | $-12$ | $-5$ | 2 | 9 |
| $pK_a$ (calculated by $8 - 5n$) | $-7$ | $-2$ | 3 | 8 |
| $pK_a$ (experimental) | $(-10)$ | $-1$ | 2 | 7.2 |

where the experimental value of $HClO_4$ is somewhat uncertain. Neither equation is very accurate, but either provides approximate values.

For oxyacids with more than one ionizable hydrogen, the $pK_a$ values increase by about 5 units with each successive proton removal:

| | $H_3PO_4$ | $H_2PO_4^-$ | $HPO_4^{2-}$ | $H_2SO_4$ | $HSO_4^-$ |
|---|---|---|---|---|---|
| $pK_a$ (by $9 - 7n$) | 2 | 7 | 12 | $-5$ | 0 |
| $pK_a$ (by $8 - 5n$) | 3 | 8 | 13 | $-2$ | 3 |
| $pK_a$ (experimental) | 2.15 | 7.20 | 12.37 | $<0$ | 2 |

The molecular explanation for these approximations hinges on electronegativity. Because each nonhydrogenated oxygen is highly electronegative, it draws electrons away from the central atom, increasing the positive charge on the central atom. This positive charge in turn draws the electrons of the hydrogenated oxygen toward itself. The net result is a weaker O—H bond (lower electron density in these bonds), which makes it easier for the molecule to act as an acid by losing the $H^+$. As the number of highly electronegative oxygens increases, the acid strength of the molecule also increases.
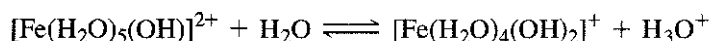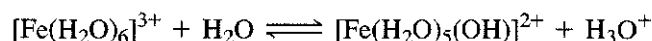
The same argument can be seen from the point of view of the conjugate base. The negative charge of the conjugate base is spread over all the nonhydrogenated oxygens. The larger the number of these oxygens to share the negative charge, the more stable and weaker the conjugate base and the stronger the hydrogenated acid. This explanation gives the same result as the first: the larger the number of nonhydrogenated oxygens, the stronger the acid.
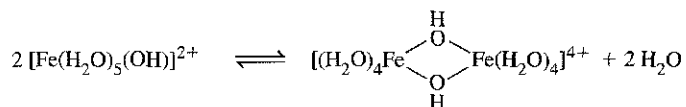
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**EXERCISE 6-8**

a. Calculate approximate $pK_a$ values for $H_2SO_3$, using both the equations above.

b. $H_3PO_3$ has one hydrogen bonded directly to the phosphorus. Calculate approximate $pK_a$ values for $H_3PO_3$, using both the equations above.

---

## 6-4-7 ACIDITY OF CATIONS IN AQUEOUS SOLUTION

Many positive ions exhibit acidic behavior in solution. For example, $Fe^{3+}$ in water forms an acidic solution, with yellow or brown iron species formed by reactions such as

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

$$[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H_3O^+$$

In less acidic (or more basic) solutions, hydroxide or oxide bridges between metal atoms form, the high positive charge promotes more hydrogen ion dissociation, and a large aggregate of hydrated metal hydroxide precipitates. A possible first step in this process is

$$2 \, [Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [(H_2O)_4Fe \underset{\underset{H}{O}}{\overset{\overset{H}{O}}{\diagup\diagdown}} Fe(H_2O)_4]^{4+} + 2 \, H_2O$$

In general, metal ions with larger charges and smaller radii are stronger acids. The alkali metals show essentially no acidity, the alkaline earth metals show it only slightly, 2+ transition metal ions are weakly acidic, 3+ transition metal ions are moderately acidic, and ions that would have charges of 4+ or higher as monatomic ions are such strong acids in aqueous solutions that they exist only as oxygenated ions. Some examples of acid dissociation constants are given in Table 6-10.

**TABLE 6-10**
**Hydrated Metal Ion Acidities**

| Metal Ion | $K_a$ | Metal Ion | $K_a$ |
|---|---|---|---|
| $Fe^{3+}$ | $6.7 \times 10^{-3}$ | $Fe^{2+}$ | $5 \times 10^{-9}$ |
| $Cr^{3+}$ | $1.6 \times 10^{-4}$ | $Cu^{2+}$ | $5 \times 10^{-9}$ |
| $Al^{3+}$ | $1.1 \times 10^{-5}$ | $Ni^{2+}$ | $5 \times 10^{-10}$ |
| $Sc^{3+}$ | $1.1 \times 10^{-5}$ | $Zn^{2+}$ | $2.5 \times 10^{-10}$ |

NOTE: These are equilibrium constants for $[M(H_2O)_m]^{n+} + H_2O \rightleftharpoons [M(H_2O)_{m-1}(OH)]^{(n-1)+} + H_3O^+$.

Solubility of the metal hydroxide is also a measure of cation acidity. The stronger the cation acid, the less soluble the hydroxide. Generally, transition metal 3+ ions are acidic enough to form hydroxides that precipitate even in the slightly acidic solutions formed when their salts are dissolved in water. The yellow color of iron(III) solutions mentioned earlier is an example. A slight precipitate is also formed in concentrated solutions unless acid is added. When acid is added, the precipitate dissolves and the color disappears (Fe(III) is very faintly violet in concentrated solutions, colorless in dilute solutions). The 2+ $d$-block ions and $Mg^{2+}$ precipitate as hydroxides in neutral or slightly basic solutions, and the alkali and remaining alkaline earth ions are so weakly acidic that no pH effects are measured. Some solubility products are given in Table 6-11.
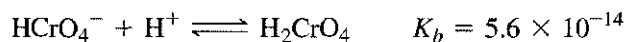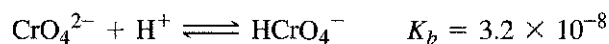
**TABLE 6-11**
**Solubility Product Constants**

| Metal Hydroxide | $K_{sp}$ | Metal Hydroxide | $K_{sp}$ |
|---|---|---|---|
| $Fe(OH)_3$ | $6 \times 10^{-38}$ | $Fe(OH)_2$ | $8 \times 10^{-16}$ |
| $Cr(OH)_3$ | $7 \times 10^{-31}$ | $Cu(OH)_2$ | $2.2 \times 10^{-20}$ |
| $Al(OH)_3$ | $1.4 \times 10^{-34}$ | $Ni(OH)_2$ | $2 \times 10^{-15}$ |
| | | $Zn(OH)_2$ | $7 \times 10^{-18}$ |
| | | $Mg(OH)_2$ | $1.1 \times 10^{-11}$ |

NOTE: These are equilibrium constants for the reaction $M(OH)_n(s) \rightleftharpoons M^{n+}(aq) + n \, OH^-$.

At the highly charged extreme, the free metal cation is no longer a detectable species. Instead, ions such as permanganate ($MnO_4^-$), chromate ($CrO_4^{2-}$), uranyl ($UO_2^+$), dioxovanadium ($VO_2^+$), and vanadyl ($VO^{2+}$) are formed, with oxidation

numbers of 7, 6, 5, 5, and 4 for the metals, respectively. Permanganate and chromate are strong oxidizing agents, particularly in acidic solutions. These ions are also very weak bases. For example,

$$CrO_4{}^{2-} + H^+ \rightleftharpoons HCrO_4{}^- \qquad K_b = 3.2 \times 10^{-8}$$

$$HCrO_4{}^- + H^+ \rightleftharpoons H_2CrO_4 \qquad K_b = 5.6 \times 10^{-14}$$

In concentrated acid, the dichromate ion is formed by loss of water:

$$2\,HCrO_4{}^- \rightleftharpoons Cr_2O_7{}^{2-} + H_2O$$
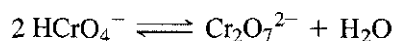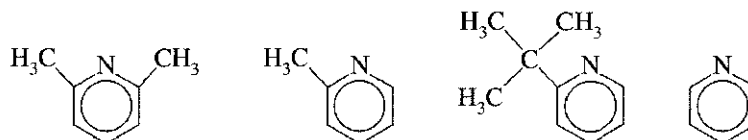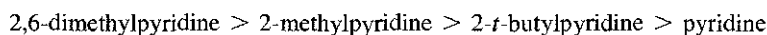
## 6-4-8 STERIC EFFECTS

There are also steric effects that influence acid-base behavior. When bulky groups are forced together by adduct formation, their mutual repulsion makes the reaction less favorable. Brown has contributed a great deal to these studies.[27] He described molecules as having F (front) strain or B (back) strain, depending on whether the bulky groups interfere directly with the approach of an acid and a base to each other or whether the bulky groups interfere with each other when VSEPR effects force them to bend away from the other molecule forming the adduct. He also called effects from electronic differences within similar molecules I (internal) strain. Many reactions involving substituted amines and pyridines were used to sort out these effects.

### EXAMPLE

Reactions of a series of substituted pyridines with hydrogen ions show the order of base strengths to be

2,6-dimethylpyridine > 2-methylpyridine > 2-*t*-butylpyridine > pyridine



which matches the expected order for electron donation (induction) by alkyl groups (the *t*-butyl group has counterbalancing inductive and steric effects). However, reaction with larger acids such as $BF_3$ or $BMe_3$ shows the following order of basicity:

pyridine > 2-methylpyridine > 2,6-dimethylpyridine > 2-*t*-butylpyridine
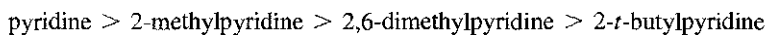
Explain the difference between these two series.

The larger fluorine atoms or methyl groups attached to the boron and the groups on the *ortho* position of the substituted pyridines interfere with each other when the molecules approach each other, so reaction with the substituted pyridines is less favorable. Interference is greater with the 2,6-substituted pyridine and greater still for the *t*-butyl substituted pyridine. This is an example of F strain.

### EXERCISE 6-9

Based on inductive arguments, would you expect boron trifluoride or trimethylboron to be the stronger acid in reaction with $NH_3$? Is this the same order expected for reaction with the bulky bases in the preceding example?

[27]H.C. Brown, *J. Chem. Soc.*, **1956**, 1248.

**TABLE 6-12**
**Methyl Amine Reactions**

| Amine | $\Delta H$ of Hydrogen Ion Addition (kJ/mol) | $pK_b$ (Aqueous) | $\Delta H$ of Adduct Formation | | |
| --- | --- | --- | --- | --- | --- |
| | | | $BF_3$ (Order) | $BMe_3$ (kJ/mol) | $B(t\text{-}Bu)_3$ (Order) |
| $NH_3$ | −846 | 4.75 | 4 | −57.53 | 2 |
| $CH_3NH_2$ | −884 | 3.38 | 2 | −73.81 | 1 |
| $(CH_3)_2NH$ | −912 | 3.23 | 1 | −80.58 | 3 |
| $(CH_3)_3N$ | −929 | 4.20 | 3 | −73.72 | 4 |
| $(C_2H_5)_3N$ | −958 | | | ~−42 | |
| Quinuclidine | −967 | | | −84 | |
| Pyridine | −912 | | | −74.9 | |

Gas phase measurements of proton affinity show the sequence of basic strength $Me_3N > Me_2NH > MeNH_2 > NH_3$, as predicted on the basis of electron donation (induction) by the methyl groups and resulting increased electron density and basicity of the nitrogen.[28] When larger acids are used, the order changes, as shown in Table 6-12. With both $BF_3$ and $BMe_3$, $Me_3N$ is a much weaker base, very nearly the same as $MeNH_2$. With the even more bulky acid tri(*t*-butyl)boron, the order is nearly reversed from the proton affinity order, although ammonia is still weaker than methylamine. Brown has argued that these effects are from crowding of the methyl groups at the back of the nitrogen as the adduct is formed (B strain). It may also be argued that some direct interference is also present as well.

When triethylamine is used as the base, it does not form an adduct with trimethylboron, although the enthalpy change for such a reaction is slightly favorable. Initially, this seems to be another example of B strain, but examination of molecular models shows that one ethyl group is normally twisted out to the front of the molecule, where it interferes with adduct formation. When the alkyl chains are linked into rings, as in quinuclidine (1-azabicyclo[2.2.2]octane), adduct formation is more favorable because the potentially interfering chains are pinned back and do not change on adduct formation. The proton affinities of quinuclidine and triethylamine are nearly identical, 967 and 958 kJ/mol. When mixed with trimethylboron, whose methyl groups are large enough to interfere with the ethyl groups of triethylamine, the quinuclidine reaction is twice as favorable as that of triethylamine (−84 versus −42 kJ/mol for adduct formation). Whether the triethylamine effect is due to interference at the front or the back of the amine is a subtle question, because the interference at the front is indirectly caused by other steric interference at the back between the ethyl groups.

## 6-4-9 SOLVATION AND ACID-BASE STRENGTH

A further complication appears in the amine series. In aqueous solution, the methyl-substituted amines have basicities in the order $Me_2NH > MeNH_2 > Me_3N > NH_3$, as given in Table 6-12 (a smaller $pK_b$ indicates a stronger base); ethyl-substituted

[28]M. S. B. Munson, *J. Am. Chem. Soc.*, **1965**, *87*, 2332; J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **1968**, *90*, 6561; J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Am. Chem. Soc.*, **1971**, *93*, 3914.
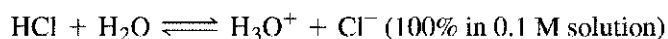
amines are in the order $Et_2NH > EtNH_2 = Et_3N > NH_3$. In both series, the trisubstituted amines are weaker bases than expected, because of the reduced solvation of their protonated cations. Solvation energies (absolute values) for the reaction
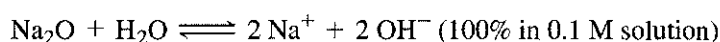
$$R_nH_{4-n}N^+(g) + H_2O \longrightarrow R_nH_{4-n}N^+(aq)$$
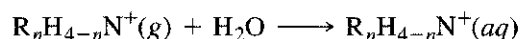
are in the order $RNH_3^+ > R_2NH_2^+ > R_3NH^+$.[29] Solvation is dependent on the number of hydrogen atoms available for hydrogen bonding to water to form $H—O\cdots H—N$ hydrogen bonds. With fewer hydrogens available for such hydrogen bonding, the more highly substituted molecules are less basic. Competition between the two effects (induction and solvation) gives the scrambled order of solution basicity.

## 6-4-10 NONAQUEOUS SOLVENTS AND ACID-BASE STRENGTH

Reactions of acids or bases with water are only one aspect of solvent effects. Any acid will react with a basic solvent and any base will react with an acidic solvent, with the extent of the reaction varying with their relative strengths. For example, acetic acid (a weak acid) will react with water to a very slight extent, but hydrochloric acid (a strong acid) reacts completely, both forming $H_3O^+$, together with the acetate ion and chloride ion, respectively.

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^- \text{ (about 1.3\% in 0.1 M solution)}$$

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \text{ (100\% in 0.1 M solution)}$$

Similarly, water will react slightly with the weak base ammonia and completely with the strong base sodium oxide, forming hydroxide ion in both cases, together with the ammonium ion and the sodium ion:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \text{ (about 1.3\% in 0.1 M solution)}$$

$$Na_2O + H_2O \rightleftharpoons 2\,Na^+ + 2\,OH^- \text{ (100\% in 0.1 M solution)}$$

These reactions show that water is **amphoteric**, with both acidic and basic properties.

The strongest acid possible in water is the hydronium (oxonium) ion, and the strongest base is the hydroxide ion, so they are formed in reactions with the stronger acid HCl and the stronger base $Na_2O$, respectively. Weaker acids and bases react similarly, but only to a small extent. In glacial acetic acid solvent (100% acetic acid), only the strongest acids can force another hydrogen ion onto the acetic acid molecule, but acetic acid will react readily with any base, forming the conjugate acid of the base and the acetate ion:

$$H_2SO_4 + HOAc \rightleftharpoons H_2OAc^+ + HSO_4^-$$

$$NH_3 + HOAc \rightleftharpoons NH_4^+ + OAc^-$$
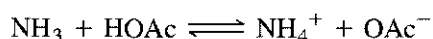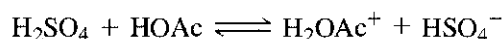
The strongest base possible in pure acetic acid is the acetate ion; any stronger base reacts with acetic acid solvent to form acetate ion, as in

$$OH^- + HOAc \longrightarrow H_2O + OAc^-$$
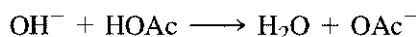
This is called the **leveling effect**, in which acids or bases are brought down to the limiting conjugate acid or base of the solvent. Because of this, nitric, sulfuric, perchloric,

[29]E. M. Arnett, *J. Chem. Educ.*, **1985**, *62*, 385 reviews the effects of solvation, with many references.

pH Range possible in different solvents

| -20 | -10 | 0 | 10 | 20 | 30 |
|---|---|---|---|---|---|

$H_2SO_4$

HOAc

EtOH

$H_2O$

$NH_3$

$Et_2O$

$C_6H_{14}$

Approximate $pK$ values of acids in water

| -20 | -10 | 0 | 10 | 20 | 30 |
|---|---|---|---|---|---|

$HClO_4$  HCl  $HNO_3$  HF

$H_3PO_4$  $H_2PO_4^-$  $HPO_4^{2-}$

$H_2SO_4$  $HSO_4^-$

$C_6H_5COOH$

$NH_4^+$

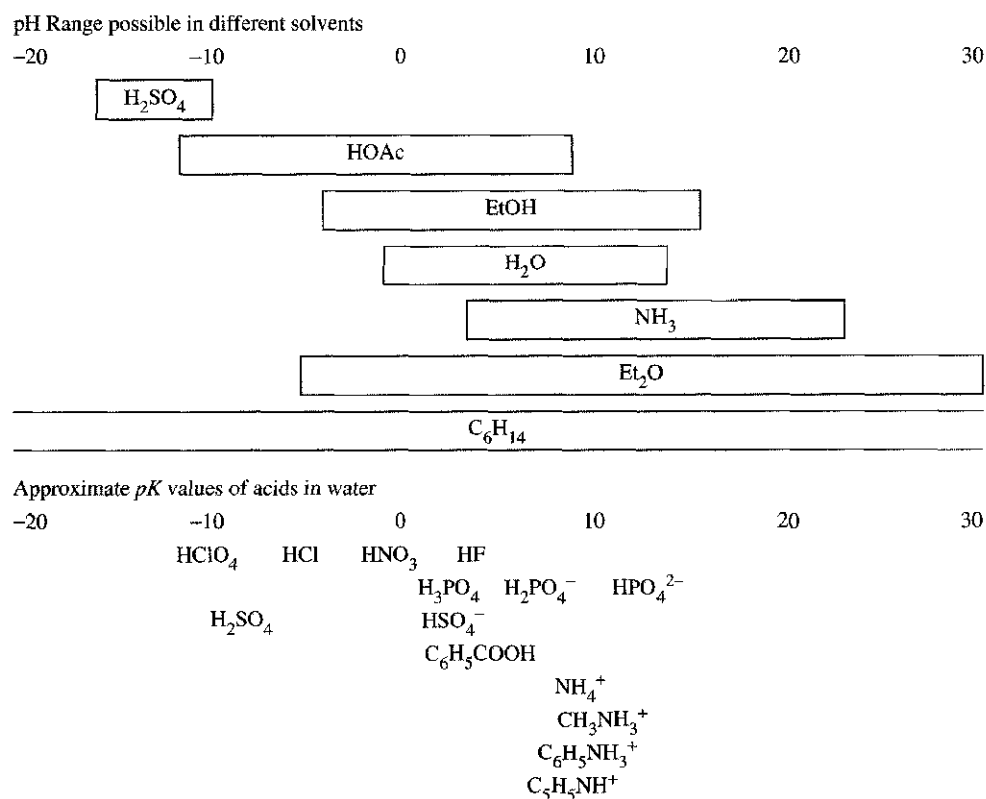$CH_3NH_3^+$

$C_6H_5NH_3^+$

$C_5H_5NH^+$

**FIGURE 6-17** The Leveling Effect and Solvent Properties. (Adapted from R. P. Bell, *The Proton in Chemistry*, 2nd edition, 1973, p. 50. Second edition, copyright © 1973 by R. P. Bell. Used by permission of Cornell University Press.)

and hydrochloric acids are all equally strong acids in dilute aqueous solutions, reacting to form $H_3O^+$, the strongest acid possible in water. In acetic acid, their acid strength is in the order $HClO_4 > HCl > H_2SO_4 > HNO_3$, based on their ability to force a second hydrogen ion onto the carboxylic acid to form $H_2OAc^+$. Therefore, acidic solvents allow separation of strong acids in order of strength; basic solvents allow a similar separation of bases in order of strength. On the other hand, even weak bases appear strong in acidic solvents and weak acids appear strong in basic solvents.

This concept provides information that is frequently useful in choosing solvents for specific reactions, and in describing the range of pH that is possible for different solvents, as shown in Figure 6-17.

Inert solvents, with neither acidic nor basic properties, allow a wider range of acid-base behavior. For example, hydrocarbon solvents do not limit acid or base strength because they do not form solvent acid or base species. In such solvents, the acid or base strengths of the solutes determine the reactivity and there is no leveling effect. Balancing the possible acid-base effects of a solvent with requirements for solubility, safety, and availability is one of the challenges for experimental chemists.

**EXAMPLE**

What are the reactions that take place and the major species in solution at the beginning, midpoint, and end of the titration of a solution of ammonia in water by hydrochloric acid in water?

**Beginning**  $NH_3$ and a very small amount of $NH_4^+$ and $OH^-$ are present. As a weak base, ammonia dissociates very little.

**Midpoint**  The reaction taking place during the titration is $H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O$, because HCl is a strong acid and completely dissociated. At the midpoint,

equal amounts of $NH_3$ and $NH_4^+$ are present, along with about $5.4 \times 10^{-10}$ M $H_3O^+$ and $1.8 \times 10^{-5}$ M $OH^-$ (because pH $= pK_a$ at the midpoint, pH $= 9.3$). $Cl^-$ is the major anion present.

**End point** All $NH_3$ has been converted to $NH_4^+$, so $NH_4^+$ and $Cl^-$ are the major species in solution, along with about $2 \times 10^{-6}$ M $H_3O^+$ (pH about 5.7).

**After the end point** Excess HCl has been added, so the $H_3O^+$ concentration is now larger, and the pH is lower. $NH_4^+$ and $Cl^-$ are still the major species.

### EXERCISE 6-10

What are the reactions that take place and the major species in solution at the beginning, midpoint, and end of the following titrations? Include estimates of the extent of reaction (i.e., the acid dissociates completely, to a large extent, or very little).

a. Titration of a solution of acetic acid in water by sodium hydroxide in water.

b. Titration of a solution of acetic acid in pyridine by tetramethylammonium hydroxide in pyridine.

## 6-4-11 SUPERACIDS

Acid solutions more acidic than sulfuric acid are called **superacids**,[30] for which George Olah won the Nobel Prize in Chemistry in 1994. The acidity of such solutions is frequently measured by the Hammett acidity function:[31]

$$H_0 = pK_{BH^+} - \log\frac{[BH^+]}{[B]}$$

where B and $BH^+$ are a nitroaniline indicator and its conjugate acid. The stronger the acid, the more negative its $H_0$ value. On this scale, pure sulfuric acid has an $H_0$ of $-11.9$. Fuming sulfuric acid (oleum) is made by dissolving $SO_3$ in sulfuric acid. This solution contains $H_2S_2O_7$ and higher polysulfuric acids, all of them stronger acids than $H_2SO_4$. Other superacid solutions and their acidities are given in Table 6-13.
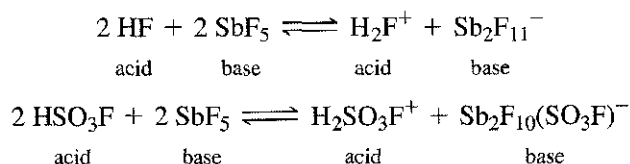
**TABLE 6-13**
**Superacids**

| Acid | | $H_0$ |
|---|---|---|
| Sulfuric acid | $H_2SO_4$ | $-11.9$ |
| Hydrofluoric acid | HF | $-11.0$ |
| Perchloric acid | $HClO_4$ | $-13.0$ |
| Fluorosulfonic acid | $HSO_3F$ | $-15.6$ |
| Trifluoromethanesulfonic acid (triflic acid) | $HSO_3CF_3$ | $-14.6$ |
| Magic Acid* | $HSO_3F$-$SbF_5$ | $-21.0$ to $-25$ (depending on concentration) |
| Fluoroantimonic acid | HF-$SbF_5$ | $-21$ to $-28$ (depending on concentration) |

NOTE: * Magic Acid is a registered trademark of Cationics, Inc., Columbia, SC.

[30]G. Olah and G. K. S. Prakash, *Superacids*, John Wiley & Sons, New York, 1985; G. Olah, G. K. S. Prakash, and J. Sommer, *Science*, **1979**, *206*, 13; R. J. Gillespie, *Acc. Chem. Res.*, **1968**, *1*, 202.

[31]L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **1932**, *54*, 2721.

The Lewis superacids formed by the fluorides are a result of transfer of anions to form complex fluoro anions:

$$2\,HF \,+\, 2\,SbF_5 \;\rightleftharpoons\; H_2F^+ \,+\, Sb_2F_{11}^-$$

$$\text{acid} \qquad \text{base} \qquad\qquad \text{acid} \qquad \text{base}$$

$$2\,HSO_3F \,+\, 2\,SbF_5 \;\rightleftharpoons\; H_2SO_3F^+ \,+\, Sb_2F_{10}(SO_3F)^-$$

$$\text{acid} \qquad\quad \text{base} \qquad\qquad \text{acid} \qquad\quad \text{base}$$

These acids are very strong Friedel-Crafts catalysts. For this purpose, the term superacid applies to any acid stronger than $AlCl_3$, the most common Friedel-Crafts catalyst. Other fluorides, such as those of arsenic, tantalum, niobium, and bismuth, also form superacids. Many other compounds exhibit similar behavior; additions to the list of superacids include $HSO_3F$-$Nb(SO_3F)_5$ and $HSO_3F$-$Ta(SO_3F)_5$, synthesized by oxidation of niobium and tantalum in $HSO_3F$ by $S_2O_6F_2$.[32] Their acidity is explained by reactions similar to those for $SbF_5$ in fluorosulfonic acid. Crystal structures of a number of the oxonium salts of $Sb_2F_{11}^-$ and cesium salts of several fluorosulfato ions have more recently been determined,[33] and $AsF_5$ and $SbF_5$ in HF have been used to protonate $H_2Se$, $H_3As$, $H_3Sb$, $H_2Se$, $H_4P_2$, $H_2O_2$, and, $H_2S_2$.[34]

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**GENERAL REFERENCES**   W. B. Jensen, *The Lewis Acid-Base Concepts: An Overview*, Wiley-Interscience, New York, 1980, and H. L Finston and Allen C. Rychtman, *A New View of Current Acid-Base Theories*, John Wiley & Sons, New York, 1982, provide good overviews of the history of acid-base theories and critical discussions of the different theories. R. G. Pearson's *Hard and Soft Acids and Bases*, Dowden, Hutchinson, & Ross, Stroudsburg, PA, 1973, is a review by one of the leading exponents of HSAB. For other viewpoints, the references provided in this chapter should be consulted.

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**PROBLEMS**   Additional acid-base problems may be found at the end of Chapter 8.

6-1   For each of the following reactions identify the acid and the base. Also indicate which acid-base definition (Lewis, solvent system, Brønsted) applies. In some cases, more than one definition may apply.

a. $BF_3 \,+\, 2\,ClF \longrightarrow [Cl_2F]^+ \,+\, [BF_4]^-$

b. $HClO_4 \,+\, CH_3CN \longrightarrow CH_3CNH^+ \,+\, ClO_4^-$

c. $PCl_5 \,+\, ICl \longrightarrow [PCl_4]^+ \,+\, [ICl_2]^-$

d. $NOF \,+\, ClF_3 \longrightarrow [NO]^+ \,+\, [ClF_4]^-$

e. $2\,ClO_3^- \,+\, SO_2 \longrightarrow 2\,ClO_2 \,+\, SO_4^{2-}$

f. $Pt \,+\, XeF_4 \longrightarrow PtF_4 \,+\, Xe$

g. $XeO_3 \,+\, OH^- \longrightarrow [HXeO_4]^-$

h. $2\,HF \,+\, SbF_5 \longrightarrow [H_2F]^+ \,+\, [SbF_6]^-$

i. $2\,NOCl \,+\, Sn \longrightarrow SnCl_2 \,+\, 2\,NO$ (in $N_2O_4$ solvent)

j. $PtF_5 \,+\, ClF_3 \longrightarrow [ClF_2]^+ \,+\, [PtF_6]^-$

k. $(benzyl)_3N \,+\, CH_3COOH \longrightarrow (benzyl)_3NH^+ \,+\, CH_3COO^-$

l. $BH_4^- \,+\, 8\,OH^- \longrightarrow B(OH)_4^- \,+\, 4\,H_2O$

6-2   Baking powder is a mixture of aluminum sulfate and sodium hydrogen carbonate, which generates a gas and makes bubbles in biscuit dough. Explain what the reactions are.

[32]W. V. Cicha and F. Aubke, *J. Am. Chem. Soc.*, **1989**, *111*, 4328.

[33]D. Zhang, S. J. Rettig, J. Trotter, and F. Aubke, *Inorg. Chem.*, **1996**, *35*, 6113.

[34]R. Minkwitz, A. Kormath, W. Sawodny, and J. Hahn, *Inorg. Chem.*, **1996**, *35*, 3622, and references therein.