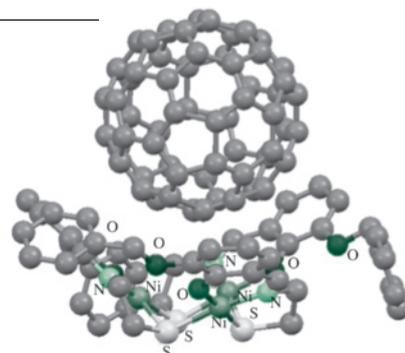


Acid–Base and Donor–Acceptor Chemistry



6.1 Acid–Base Models as Organizing Concepts

A long-standing chemical objective is to organize reactions by using models to account for trends and gain insight into what properties of reactants are prerequisites for chemical change. Analyzing trends among similar reactions permits discovery of structure–function relationships (for example, how do molecular geometry and electronic structure influence reactivity?) and guides the design of molecules for practical use.

Classifying substances as acids and bases has been important since ancient times; alchemists used neutralization—the ubiquitous reaction of an acid and base to form salt and water—to compile observations about different substances that engaged in similar reactions. Without modern structural analysis tools, such as X-ray crystallography and NMR spectroscopy, alchemists used their senses: they observed the tastes of acids (sour) and bases (bitter) and color changes of indicators. Many acid–base definitions have been devised, but only a few have been widely adopted.

This chapter discusses the major acid–base models and their application in inorganic chemistry. After a historical introduction ([Section 6.1.1](#)), the models are presented in the rough order of their development. Among these are the ones attributed to Arrhenius ([Section 6.2](#)), Brønsted–Lowry ([Section 6.3](#)), and Lewis ([Section 6.4](#)). These sections emphasize the challenges associated with quantifying acidity and basicity, and relationships between acid/base strength and molecular structure. The 1960s application of molecular orbitals (i.e., HOMO/LUMO interactions) to frame Lewis acid–base reactions ([Section 6.4.1](#)) permeates inorganic chemistry and dramatically expands the perspective on what constitutes an acid–base reaction. Extension of HOMO/LUMO interactions to intermolecular forces is covered in [Section 6.5](#). For example, acid–base molecular orbital concepts permit rationalization of host–guest interactions ([Section 6.5.2](#)) involving C_{60} (figure above*). Finally, the concept of “hard” and “soft” acids and bases is discussed in [Section 6.6](#).

6.1.1 History of Acid–Base Models

The history of chemistry is marked with many acid–base models. A limitation of most early models is that they are applicable to only specific classes of compounds or a narrow set of conditions. One such limiting idea in the eighteenth century was that all acids contained oxygen; oxides of nitrogen, phosphorus, sulfur, and the halogens all form aqueous acids. However, by the early nineteenth century, this definition was regarded as too narrow; many compounds had been discovered that did not contain oxygen but showed behavior associated

*Molecular structure drawing created with CIF data from E. C. Constable, G. Zhang, D. Häussinger, C. E. Housecroft, J. A. Zampese, *J. Am. Chem. Soc.*, **2011**, *133*, 10776, with hydrogen atoms omitted for clarity.

with acids. By 1838, Liebig broadened the definition of acids to “compounds containing hydrogen, in which the hydrogen can be replaced by a metal.”¹ The early twentieth century featured the introduction of some models rarely evoked today. The Lux–Flood definition² is based on oxide (O^{2-}) as the unit transferred between acids and bases. The Usanovich definition³ proposes that classification of an acid–base reaction only requires salt formation. The all-inclusive aspect of the Usanovich definition, which included oxidation–reduction reactions, was criticized as too broad. The electrophile–nucleophile approach of Ingold⁴ and Robinson,⁵ part of the organic chemistry vernacular, is essentially the Lewis theory with terminology related to reactivity: electrophilic reagents are acids and nucleophilic reagents are bases. **Table 6.1** summarizes the history of acid–base definitions.

6.2 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 the late nineteenth century (Arrhenius received the 1903 Nobel Prize in Chemistry). **Arrhenius acids** yield hydrogen ions* in aqueous solution; **Arrhenius bases** yield hydroxide ions in aqueous solution. The neutralization of hydrogen and hydroxide ions to form water, the net ionic equation of



is a classic Arrhenius acid–base reaction, with a salt (in this case NaCl) and water as products. The Arrhenius concept is useful in aqueous solutions, but does not apply to the many reactions that occur in other inorganic solvents, organic solvents, the gas phase, or the solid state.

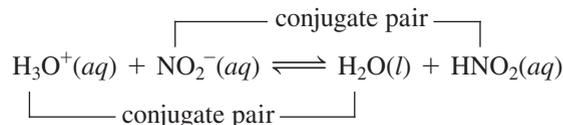
TABLE 6.1 Acid–Base Definition History

Description	Date	Definitions		Examples	
		Acid	Base	Acid	Base
Liebig	~1776	Oxide of N, P, S	Reacts with acid	SO_3	NaOH
	1838	H replaceable by metal	Reacts with acid	HNO_3	NaOH
Arrhenius	1894	Forms hydronium ion	Forms hydroxide ion	HCl	NaOH
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

*The original Arrhenius concept did not include solvation. In modern practice, H_3O^+ , the *hydronium* ion, is commonly used as an abbreviation of $\text{H}^+(aq)$, and this is the practice in this book. The International Union of Pure and Applied Chemistry (IUPAC) recommends *oxonium* for H_3O^+ . Frequently the shorthand H^+ notation is used, for which the IUPAC recommends the term *hydrogen ion*, rather than *proton*.

6.3 Brønsted–Lowry Concept

Brønsted⁶ and Lowry⁷ 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. For example, the Brønsted–Lowry reaction of a strong acid with the weak base nitrite in aqueous solution would be:



The strong acid hydronium loses (donates) H^+ to the base NO_2^- to form H_2O (the conjugate base of H_3O^+) and HNO_2 (the conjugate acid of NO_2^-).

In principle, the Brønsted–Lowry acidity of a general acid HB could be measured in the gas phase by determining the equilibrium constant of



However, typically large and positive ΔG° values associated with gaseous ionization render this acidity measurement problematic. Examination of the explicit HB ionization above is impossible in solution; independent H^+ ions do not exist in solution because of their strong interaction with solvent molecules.

The Brønsted–Lowry model explicitly dictates that acids generate different conjugate acids depending on the solvent used. For example, H_2SO_4 yields H_3O^+ on ionization in water but H_3SO_4^+ on ionization in sulfuric acid. Acid strength in solution is inherently tied to the solvent. The acidity or basicity ranking of a series of solutes determined in one solvent may therefore be different in another solvent. The Brønsted–Lowry strategy is to compare *conjugate acids and bases*, species differing only in the presence or absence of a proton, and describe reactions as occurring between a stronger acid and a stronger base to form a weaker acid and a weaker base, as in the example of H_3O^+ reacting with NO_2^- . A stronger acid has a greater tendency to transfer a hydrogen ion than a weaker acid, and a stronger base has a greater tendency to accept a proton than a weaker base. The equilibrium always favors the formation of *weaker* acids and bases. In the example above, H_3O^+ is a stronger acid than HNO_2 , and NO_2^- is a stronger base than H_2O ; the equilibrium lies to the right.

Brønsted–Lowry examples can be shown in **amphoteric** solvents that can function as an acid or a base and whose conjugates play vital roles. Examples of amphoteric solvents are in **Table 6.2**.

TABLE 6.2 Properties of Amphoteric Solvents

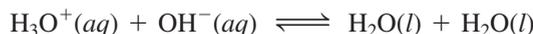
Solvent	Acid Cation	Base Anion	$pK_{\text{ion}}(25^\circ\text{C})$	Boiling Point ($^\circ\text{C}$)
Sulfuric acid, H_2SO_4	H_3SO_4^+	HSO_4^-	3.4 (10°)	330
Hydrogen fluoride, HF	H_2F^+	HF_2^-	~ 12 (0°)	19.5
Water, H_2O	H_3O^+	OH^-	14.0	100
Acetic acid, CH_3COOH	$\text{CH}_3\text{COOH}_2^+$	CH_3COO^-	14.45	118.2
Methanol, CH_3OH	CH_3OH_2^+	CH_3O^-	16.6	64.7
Ammonia, NH_3	NH_4^+	NH_2^-	27	-33.4
Acetonitrile, CH_3CN	CH_3CNH^+	CH_2CN^-	34.4	81

Data from W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice Hall, Englewood Cliffs, NJ, 1970, pp. 99–101 and M. Rosés, *Anal. Chim. Acta*, **1993**, 276, 223 (pK_{ion} for acetonitrile).

EXERCISE 6.1

Calculate the concentration of CH_3CNH^+ in CH_3CN at 25°C .

Consider the net ionic equation for the reaction of a strong acid (HCl) and strong base (NaOH) in aqueous solution. In water, the acid H_3O^+ from the ionization of HCl and base OH^- from the dissociation of NaOH engage in Brønsted–Lowry proton transfer to form H_2O . The net ionic equation features the conjugate acid and base of water as reactants:

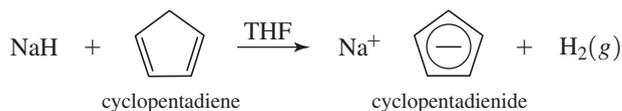


This class of Brønsted–Lowry reaction can be carried out in any amphoteric solvent. For example, liquid ammonia, NH_3 (the conjugate acid of NH_2^- and conjugate base of NH_4^+), is a useful solvent for reactions impossible to carry out in the stronger oxidant water. While NH_2^- reacts vigorously with H_2O to yield its conjugate acid NH_3 , and OH^- (the conjugate base of H_2O), NH_4Cl and NaNH_2 react in liquid ammonia via the net ionic Brønsted–Lowry equation



Because NH_4^+ is a stronger acid than its conjugate (NH_3), and NH_2^- is a stronger base than its conjugate (also NH_3), the products are favored.

The Brønsted–Lowry concept can be applied in any solvent, regardless whether the solvent possesses hydrogen atoms that can participate. For example, cyclopentadienide, $[\text{C}_5\text{H}_5]^-$, a common anion in organometallic chemistry, can be prepared in tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$) via reaction of sodium hydride and cyclopentadiene (C_5H_6). The Brønsted–Lowry acidity of C_5H_6 is enhanced because the resulting negative charge is delocalized within aromatic $[\text{C}_5\text{H}_5]^-$; hydride is an extremely strong base that reacts vigorously with water, and this reaction must be carried out under anhydrous conditions.



The classification of H_2 as a conjugate acid (of the strong base hydride) is noteworthy. It highlights that any molecule containing hydrogen can in principle function as a Brønsted–Lowry acid, even if some (for example, aliphatic hydrocarbons, H_2) only function as acids under extraordinary conditions.*

EXERCISE 6.2

Organolithium reagents are sources of strong Brønsted–Lowry bases in nonaqueous media. The equilibria between hydrocarbons and organolithium reagents can be predicted via the Brønsted–Lowry concept. Which side of the following Li/H exchange equilibrium should be favored if C_6H_6 is a stronger acid than *n*-butane?***

**6.3.1 Nonaqueous Solvents and Acid–Base Strength**

The $\text{H}_3\text{O}^+/\text{H}_2\text{O}/\text{OH}^-$ reference for quantifying relative acid and base strengths is only useful when the examined acid is inherently weaker than H_3O^+ or the examined base is weaker than OH^- . Hydronium ion and hydroxide ion are the strongest acid and base,

*The solvent tetrahydrofuran is another molecule with exceedingly low Brønsted–Lowry acidity that resists deprotonation by sodium hydride.

**The Brønsted–Lowry preference is achieved very slowly in this case, but rapid Li/H exchange occurs upon addition of tetramethylethylenediamine (TMEDA) that enhances *n*- $\text{C}_4\text{H}_9\text{Li}$ reactivity.

respectively, than can exist in water. Acids inherently stronger than H_3O^+ cannot be differentiated by their aqueous ionization; this is called the **leveling effect**. Due to leveling, nitric, sulfuric, perchloric, and hydrochloric acids are all equally strong acids in dilute aqueous solutions, essentially ionizing quantitatively to H_3O^+ and the corresponding conjugate base. In these cases, more strongly acidic solvents are necessary to differentiate acidity. For example, acetic acid, like water, is amphoteric, and can accept protons from acids classified as strong in water, resulting in *partial* ionization. The $\text{CH}_3\text{COOH}_2^+$ ion is the strongest acid that can exist in glacial acetic acid (100% acetic acid). The solvent sets a limit on the effective strength of the dissolved acid.



In glacial acetic acid, the relative acid strength of $\text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$ can be determined. In the same way, basic solvents permit the differentiation of bases that could not be accomplished in a less basic solvent.

A key perspective on leveling is that the classification of a substance as “weak” or “strong” is stringently tied to the solvent. A weak aqueous base may be strong in a more acidic solvent. Weak aqueous acids appear strong in basic solvents. For example, the equilibrium position of

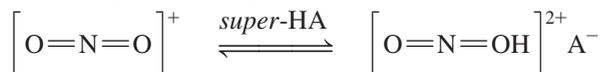


lies much further to the right in glacial acetic acid than the ammonia ionization equilibrium in water.

Nonamphoteric solvents, with neither Brønsted–Lowry acidic nor basic properties, do not limit solute acidity or basicity because the solute does not react with the solvent. In these solvents, the inherent solute acid or base strength determines the reactivity, without a leveling effect. For example, hydride sources (e.g., LiAlH_4 , NaH) are commonly employed as Brønsted–Lowry bases or reducing agents in organic solvents (for example, Et_2O , hydrocarbons) where no acid–base reaction with the solvent is possible. In these cases, reaction conditions are often heterogeneous; the hydride source remains insoluble due to its lack of significant interaction with the solvent. The acid–base effects of the solvent, and the compatibility of reactants with intended solvents must be always considered when planning reactions.

6.3.2 Brønsted–Lowry Superacids

From a Brønsted–Lowry perspective, designing molecules with exceedingly weak conjugate bases results in acids that could potentially transfer protons to species that could not be appreciably protonated by leveled acids in either water (H_3O^+) or sulfuric acid (H_2SO_4^+). George Olah won the Nobel Prize in Chemistry in 1994 for the discovery and application of **superacids**, acid solutions more acidic than sulfuric acid. Olah proposed using superacids to protonate monocationic species (for example, nitronium ion, below) to produce useful concentrations of dicationic (charge = 2+) ions with increased reactivity. He coined the term *superelectrophilic activation* to describe the result of generating small organic ions bearing a large amount of positive charge.⁸



A variety of dicationic superelectrophiles have been synthesized,⁹ and tricationic species formed via protonation of triaryl methanols were reported recently.¹⁰ These species exhibit new reactions resulting from the effects of closely oriented positive charges.

Superacid acidity is measured by the Hammett acidity function:¹¹

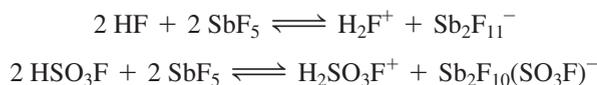
$$H_0 = pK_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

where B and BH⁺ are a nitroaniline indicator and its conjugate acid, respectively. The stronger the acid, the more negative its H_0 value. On this scale, the H_0 of 100% sulfuric acid is -11.9 (Table 6.3).

The term *Magic Acid* was coined upon observation that a mixture of antimony pentafluoride and fluorosulfonic acid dissolved a candle, demonstrating the ability of the acid to protonate hydrocarbons. The ability of superacids to activate hydrocarbons, and particularly methane, via protonation, is an area of intense interest, since methane is the primary component of natural gas. The abundance of methane makes it attractive as a feedstock for synthesis of more complex molecules. Computational studies have proposed structures with 2-center 3-electron bonds for CH₅⁺, CH₆²⁺, and even CH₇³⁺, but these species have not been isolated.*

Methanesulfonyl chloride, CH₃SO₂Cl, can be prepared from CH₄ and SO₂Cl₂ in sulfuric acid or triflic acid in the presence of a radical initiator.¹² Sulfonation of CH₄ to methanesulfonic acid (CH₃SO₃H) has been achieved with SO₃ in H₂SO₄ in the presence of a radical initiator.¹³ Dissolving SO₃ in sulfuric acid results in “fuming sulfuric acid.” This superacidic solution contains H₂S₂O₇ and higher polysulfuric acids, all of them stronger than H₂SO₄.

Complex fluorinated anions are formed in solutions of Magic Acid and HF-AF₅ (A = As, Sb) that serve as counterions to superelectrophilic cations.



Superacid media from AsF₅ and SbF₅ in HF can protonate H₂S, H₂Se, AsH₃, SbH₃, and H₂O₂.¹⁴ An example of the utility of one such reaction has been protonation of H₂S in superacid media to yield [H₃S][SbF₆], useful as a reagent in the synthesis of [(CH₃S)₃S][SbF₆], the first trithiosulfonium salt with three RS substituents.¹⁵

Water is a strong base in superacid media; the presence of H₂O in HF-AsF₅ or HF-SbF₅ results quantitatively in the hydronium salts [H₃O][AsF₆] and [H₃O][SbF₆].¹⁶ This ability of superacids to generate an anhydrous environment (but not aprotic!) by converting trace amounts of water to hydronium has been exploited to prepare solutions of low oxidation state metal cations from metal(II) oxides. These oxides immediately react to form water, which is protonated to form hydronium. Divalent metal ions have been isolated as [H₃O][M][AsF₆]₃ (M = Mn, Co, Ni) by conversion of the corresponding metal oxides in HF-AsF₅ media.¹⁷ Related reactions have been achieved with Ln₂O₃ (Ln = lanthanide element)¹⁸ and CdO;¹⁹ some of the resulting salts incorporate fluoride, [SbF₆][−], and [Sb₂F₁₁][−].

TABLE 6.3 Common Superacids and Their Acidities

Acid		H_0
Hydrofluoric acid ^a	HF	-11.0
Sulfuric acid	H ₂ SO ₄	-11.9
Perchloric acid	HClO ₄	-13.0
Trifluoromethanesulfonic acid (triflic acid)	HSO ₃ CF ₃	-14.6
Fluorosulfonic acid	HSO ₃ F	-15.6
<i>Magic Acid</i> ^b	HSO ₃ F—SbF ₅	-21 to -25^c
Fluoroantimonic acid	HF—SbF ₅	-21 to -28^c

^a HF is not a superacid but is included for comparison. It is noteworthy that while HF is a weak acid in dilute aqueous solution, concentrated HF is significantly stronger.

^b *Magic Acid* is a registered trademark of Cationics, Inc., Columbia, SC.

^c Depending on concentration (how much SbF₅ has been added)

*G. Rasul, G. A. Olah, G. K. Surya Prakash, *J. Phys. Chem. A.*, **2012**, *116*, 756. Protonated methane, CH₅⁺, has been reported in superacid solutions.

6.3.3 Thermodynamic Measurements in Solution

Various thermodynamic approaches have been used to probe acidity and basicity in solutions. The impact of solvation effects must always be considered when designing these experiments.

Comparing Acidity

A defining property for any acid is its strength. One way to assess the strengths of aqueous acids is to quantify the enthalpy change of



Direct measurement of this enthalpy change is complicated since weak acids do not ionize completely (that is, the above reaction is generally an equilibrium with a relatively large concentration of unionized HA). A traditional strategy is to apply Hess's law using thermodynamic data from reactions that essentially go to completion. For example, the enthalpy of ionization of weak acid HA can be determined by measuring (1) the enthalpy change for the reaction of HA with NaOH, and (2) the enthalpy change for the reaction of H_3O^+ and NaOH:



This strategy is not straightforward since HA is partly ionized before OH^- is added, complicating ΔH_1 determination, but this approach is an acceptable starting point. It is also possible to measure K_a (via titration curves) at different temperatures and use the van't Hoff equation

$$\ln K_a = \frac{-\Delta H_3}{RT} + \frac{\Delta S_3}{R}$$

to simultaneously determine ΔH_3 and ΔS_3 . The slope of a plot of $\ln K_a$ versus $\frac{1}{T}$ is $\frac{-\Delta H_3}{R}$ and the intercept is $\frac{\Delta S_3}{R}$. The accuracy of this method requires that the acid ionization ΔH_3 and ΔS_3 do not change appreciably over the temperature range used. Data for the ΔH° , ΔS° , and K_a for acetic acid are given in **Table 6.4**.

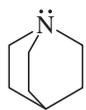
EXERCISE 6.3

Use the data in Table 6.4 to calculate the enthalpy and entropy changes associated with aqueous acetic acid ionization (the third equation in the table), and examine the temperature dependence of K_a by graphing $\ln K_a$ versus $\frac{1}{T}$. How do the ΔH° values obtained via these two approaches compare?

TABLE 6.4 Thermodynamics of Acetic Acid Ionization

	$\Delta H^\circ(\text{kJ/mol})$		$\Delta S^\circ(\text{J/mol} \cdot \text{K})$		
$\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \longrightarrow 2 \text{H}_2\text{O}(l)$	-55.9		80.4		
$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$	-56.3		-12.0		
$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$					
T (K)	303	308	313	318	323
$K_a(\times 10^{-5})$	1.750	1.728	1.703	1.670	1.633

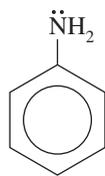
NOTE: ΔH° and ΔS° for these reactions change rapidly with temperature. Calculations based on these data are valid only over the limited temperature range given above.



Quinuclidine



Pyridine



Aniline

Comparing Basicity

Basicity has also been probed by measuring the enthalpies of proton transfer reactions between weak bases and strong acids. A Brønsted basicity scale has been established by measuring the enthalpy changes associated with the protonation of weak bases in fluorosulfonic acid (HSO_3F , a superacid [Section 6.3.2]). Enthalpies of protonation for a series of nitrogen bases (Table 6.5; increasingly negative ΔH values correspond to stronger basicity towards HSO_3F) rank in a way that compares favorably with the ranking of the corresponding conjugate acid pK_{BH^+} values (for aqueous solution).²⁰ The more positive the pK_{BH^+} , the weaker the conjugate acid and the stronger the conjugate nitrogen base.* These data imply that various molecular properties, for example inductive and steric effects (Section 6.3.6), are significant in influencing acid/base behavior.

6.3.4 Brønsted–Lowry Gas-Phase Acidity and Basicity

The purest measures of acid–base strength are gas-phase acidity and basicity parameters, where solvent effects are not applicable:

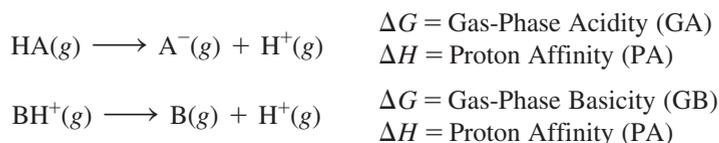


TABLE 6.5 Basicity of Selected Nitrogen Bases with Water and Fluorosulfonic Acid

Base	$pK_{\text{BH}^+}(\text{H}_2\text{O})$	$-\Delta H(\text{HSO}_3\text{F}, \text{kJ/mol})$
Di- <i>n</i> -butylamine	11.25	194.1
Quinuclidine	11.15	191.6
Diethylamine	11.02	199.5
Dimethylamine	10.78	197.4
Triethylamine	10.72	205.7
Ethylamine	10.68	195.9
Methylamine	10.65	193.9
Tri- <i>n</i> -butylamine	9.93	189.2
Trimethylamine	9.80	196.8
2,4,6-Trimethylpyridine	7.43	178.5
2,6-Dimethylpyridine	6.72	170.3
4-Methylpyridine	6.03	163.4
Pyridine	5.20	161.3
Aniline	4.60	142.3
3-Bromopyridine	2.85	144.9
2-Bromopyridine	0.90	126.2
2-Chloropyridine	0.72	132.5
3,5-Dichloropyridine	0.67	128.4

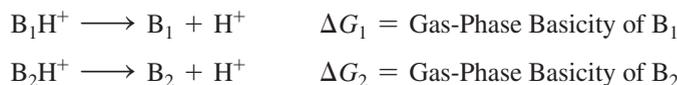
Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5. The pK_{BH^+} of ammonia is 9.25.

*Note that these bases are ranked on their basicity towards water; the ranking on the basis of measurements in HSO_3F is different. This is one example of the challenges associated with basicity determinations; basicity rankings of the same bases typically vary with the solvent used.

Proton affinities and gas-phase basicities have been determined for thousands of neutral organic bases; the literature on these parameters is significantly more extensive than on gas-phase acidities. For the majority of bases, the thermodynamic parameters PA and GB are large and positive; the reaction is essentially bond breaking without the benefit of any solvation of the products. Increasing proton affinity and gas-phase basicity magnitudes indicate increasing difficulty to remove the hydrogen; the more positive these values, the stronger B as a base, and the weaker the acid BH^+ in the gas phase.²¹ Laurence and Gal have criticized the terminology associated with proton affinity and gas-phase basicity since an affinity is formally a chemical potential while proton affinity is defined as an enthalpy.*

While direct measurement of PA and GB via the reactions shown above is practically impossible, these values have been estimated, with the accuracy improving with advances in chemical instrumentation. In the early twentieth century, Born–Haber thermodynamic cycles were employed to estimate proton affinities. As with all approaches based on thermodynamic cycles (Section 5.3.2), uncertainties in the data used to construct a cycle propagate to the calculated values (in this case the proton affinity).

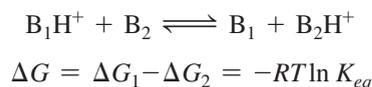
Modern mass spectrometry, photoionization techniques, and ion cyclotron resonance spectroscopy²² revolutionized gas-phase basicity determination. These techniques have permitted extremely accurate absolute gas-phase basicities to be obtained for a few molecules via thermodynamic cycles using electron affinity and ionization energy data.^{23, **} Absolute gas-phase basicities for even a few molecules provide valuable references for determination of GB values for bases for which direct GB determination is problematic. The mathematical approach is conceptually straightforward. Consider the general GB equations for B_1 and B_2 :



Subtraction of the second reaction from the first leads to



The ΔG for this reaction can be calculated from the equilibrium constant



Ion-trapping and flow reactor mass spectrometry permit gas-phase ions and neutral molecules to be confined and attain equilibrium after a sufficient number of collisions. The equilibrium constant can then be deduced by measurement of gas partial pressures (for B_1 and B_2) and mass spectrometric ion intensities (for gaseous B_1H^+ and B_2H^+). The resulting ΔG provides the *difference* in gas-phase basicity between B_1 and B_2 . If the absolute gas-phase basicity of either base is known, then the GB value of the other can be determined. Proton affinities are subsequently determined via $\Delta G = \Delta H - T\Delta S$, with the “entropy of basicity” approximated via quantum chemical approaches. Table 6.6 lists proton affinity and gas-phase basicities for nitrogen bases, with the bases ranked in order of descending gas-phase basicity. The majority of organic bases exhibit GB values between 700 and 1000 kJ/mol. Compilations of PA and GB values are available.²⁴

*Chemical potential is defined as $\left(\frac{\partial G}{\partial n}\right)_{P,T}$.

**The details of these measurements are beyond the scope of this text. Because they require an ionizing electron beam, measured proton affinities and gas-phase basicities for many species have large uncertainties, because the molecules involved frequently are in excited states (with excess energy above their ground states), and some species do not yield the necessary acid as a gaseous fragment. Relatively few molecules are ideally suited for this analysis.

TABLE 6.6 Gas-Phase Basicity and Proton Affinities for Nitrogen Bases

Base	GB (kJ/mol)	PA (kJ/mol)
Tri- <i>n</i> -butylamine	967.6	998.5
Quinuclidine	952.5	983.3
Triethylamine	951.0	981.8
Di- <i>n</i> -butylamine	935.3	968.5
2,6-Dimethylpyridine	931.1	963.0
Diethylamine	919.4	952.4
Trimethylamine	918.1	948.9
4-Methylpyridine	915.3	947.2
Pyridine	898.1	930.0
Dimethylamine	896.5	929.5
3-Bromopyridine	878.2	910.0
Ethylamine	878.0	912.0
2-Bromopyridine	873.0	904.8
2-Chloropyridine	869.0	900.9
Methylamine	864.5	899.0
Aniline	850.6	882.5
Ammonia	819.0	853.6

Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5.

6.3.5 Brønsted–Lowry Superbases

Thermodynamic data for quinuclidine (PA = 983.3 kJ/mol) and its conjugate acid ($pK_a = 11.15$ in water) underscore its relatively high basicity. What is the upper limit on Brønsted–Lowry basicity that is still compatible with high selectivity for deprotonation? While leveling limits the operative strength of all Brønsted–Lowry bases inherently stronger than hydroxide in water, extremely basic carbanions (for example, Grignard and organolithium reagents) are ubiquitous in organic synthesis. The high nucleophilicity of these carbanions lowers their tolerance towards many functional groups, and motivates the synthesis of strong Brønsted–Lowry bases that exhibit broader tolerance and extremely high selectivity for deprotonation reactions.²⁵ The aforementioned carbanions are *both* strongly Brønsted–Lowry basic and nucleophilic; one virtue of uncharged organic bases is their lowered nucleophilicity. There is also motivation to conduct deprotonations in syntheses without inorganic hydroxides.²⁶

Superbases have been classified as those with gas-phase proton affinities > 1000 kJ/mol,²⁷ greater than the bases listed in Table 6.6. Examples of organic superbases are shown in **Figure 6.1**. These are weak bases in water but exhibit superbasic characteristics in organic solvents.

The organic superbase, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), is a workhorse for organic synthesis (PA = 1048 kJ/mol). 1,8-Bis(dimethylamino)naphthalene (PA = 1028 kJ/mol) is sometimes called a “proton sponge.” Its strong Brønsted–Lowry basicity is believed to arise from two effects: (1) the relief of steric hindrance of two dimethylamino substituents in close proximity (if the nonbonding pairs adopt opposite positions to reduce *lp*–*lp* repulsion, the methyl groups are brought into close proximity), and (2) the formation of a strong intramolecular hydrogen bond upon protonation.²³ It is instructive that the considerably more flexible 1,3-bis(dimethylamino)propane is also a superbase (PA = 1035 kJ/mol) even though this molecule is not susceptible to the sterically enforced *lp*–*lp* repulsion present

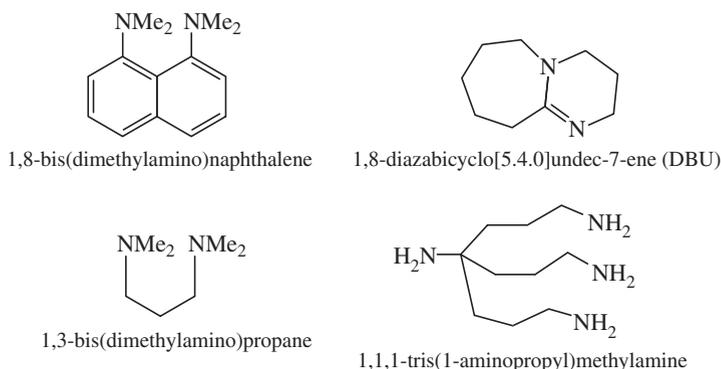


FIGURE 6.1 Organic Superbases.

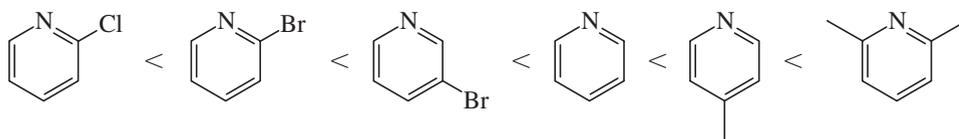
in 1,8-bis(dimethylamino)naphthalene. The inductive effect of alkyl vs. aryl substitution appears more important than the relief of *lp*–*lp* repulsion in affording superbasic characteristics when these two molecules are compared. The addition of propylamine substituents to methylamine affords $\text{NH}_2\text{C}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$ (PA = 1072 kJ/mol).²⁸ Upon protonation, the propylamine arms are postulated to wrap around, bringing more nitrogen atoms into contact with the proton, stabilizing the conjugate acid.

The possibility of using 2,6-disubstituted pyridines and 2,6,7-trisubstituted quinuclidines, where the substituents feature remote atoms with lone pairs to stabilize the hydrogen upon protonation, are proposed superbases that have been explored by computational approaches.²⁹ There is interest in synthesizing macrocyclic proton chelators as catalytically active organic superbases,³⁰ and a new structural motif for superbases featuring caged secondary amines has been reported.³¹ The alkali metal hydroxides, of equal basicity in aqueous solution, have proton affinities* in the order LiOH (1000 kJ/mol) < NaOH < KOH < CsOH (1118 kJ/mol). This order matches the increasing ionic character of the alkali metal-hydroxide bonds.

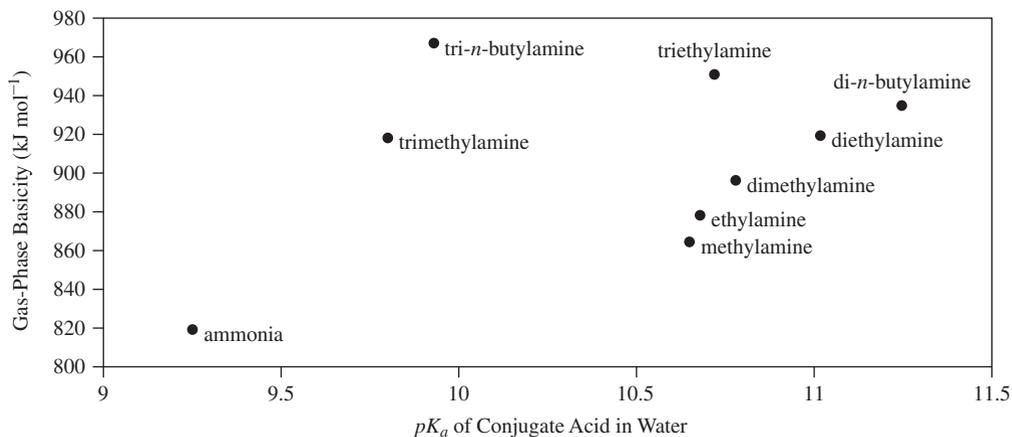
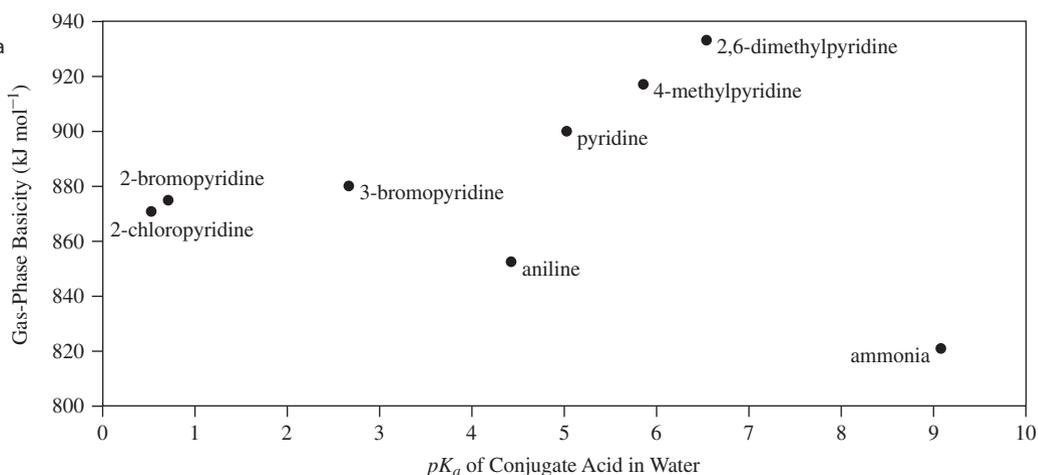
6.3.6 Trends in Brønsted–Lowry Basicity

Correlations between gas-phase and aqueous basicity data provide a starting point to consider the importance of electronic, steric, and solvation effects on proton transfer reactions. Figures 6.2 and 6.3 provide such correlations, by plotting gas-phase basicity versus aqueous basicity (on the basis of conjugate acid pK_a) for nitrogen bases listed in Tables 6.5 and 6.6. Higher placement on the *y*-axis indicates higher basicity in the gas phase, while increasing conjugate acid pK_a indicates higher basicity in water. Initial inspection of these graphs reveals that higher gas-phase basicity does not necessarily translate to higher aqueous basicity (for example, tri-*n*-butylamine relative to di-*n*-butylamine), just as higher aqueous basicity does not always correlate well with higher gas-phase basicity (for example, ammonia relative to 2,6-dimethylpyridine). Exploring these data uncovers trends in Brønsted–Lowry basicity and highlights the essential role of the solvent in influencing basicity.

Inductive effects are useful to rationalize trends in Figures 6.2 and 6.3. For example, both gas-phase and aqueous basicity increase as:



*Proton affinities of inorganic hydroxides cannot be obtained from direct proton transfer measurements, but rather from Born–Haber cycles using other thermodynamic data.

FIGURE 6.2 Gas-Phase Basicity vs. pK_a for Ammonia and Alkyl-substituted Amines.**FIGURE 6.3** Gas-Phase Basicity vs. pK_a for Ammonia and Aromatic Amines.

The substitution of alkyl groups for hydrogen within the series of ammonia to primary amines to secondary amines results in progressively more electron-rich nitrogen centers and stronger Brønsted–Lowry bases. Within this series, a longer alkyl chain enhances the effect. Similarly, methylpyridines are stronger Brønsted–Lowry bases than pyridine. The substitution of highly electronegative atoms or groups (for example, fluorine, chlorine, CF_3 or CF_3SO_2) results in weaker bases by drawing electron density away from the Brønsted basic atom. The halopyridines are dramatically weaker bases than pyridine. The gas-phase acidities in **Table 6.7** illustrate the impact of increasing CF_3SO_2 substitution.

TABLE 6.7 Impact of CF_3SO_2 Substitution on Gas-Phase Acidity

Acid	GA (kJ/mol)
$\text{CF}_3\text{SO}_2\text{CH}_3$	1422
$\text{CF}_3\text{SO}_2\text{NH}_2$	1344
$(\text{CF}_3\text{SO}_2)_2\text{NH}$	1221
$(\text{CF}_3\text{SO}_2)_2\text{CH}_2$	1209

Data from J.-F. Gal, P.-C. Maria, E. D. Raczynska, *J. Mass Spectrom.*, **2001**, 36, 699.

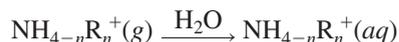
Inductive effects provide a reasonable way to rationalize this gas-phase basicity ranking:



Since tri-*n*-butylamine is more basic than triethylamine in the gas phase, we postulate that trimethylamine is less basic than the secondary amines since two longer alkyl groups and hydrogen enrich the electron density at nitrogen more than three methyl groups. Perhaps more interesting is the aqueous basicity ranking of the amines below, which appears to contradict the inductive rationalization of their gas-phase values; the tertiary amines are weaker than expected.

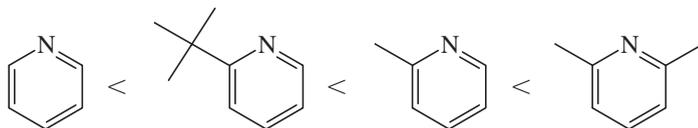


In addition, in aqueous solution, the methyl-substituted amines have basicities in the order $\text{NHMe}_2 > \text{NH}_2\text{Me} > \text{NMe}_3 > \text{NH}_3$ as given in Table 6.5, and shown in Figure 6.2. The ethyl-substituted amines are in the order $\text{NHEt}_2 > \text{NEt}_3 > \text{NH}_2\text{Et} > \text{NH}_3$. In these series, the tertiary amines are weaker than expected because of the reduced solvation of their protonated cations. Solvation enthalpy magnitudes for the general reaction



are in the order $\text{NH}_3\text{R}^+ > \text{NH}_2\text{R}_2^+ > \text{NHR}_3^+$.^{*} Solvation is dependent on the number of hydrogen atoms available to form $\text{O} \cdots \text{H} - \text{N}$ hydrogen bonds with water. With fewer hydrogen atoms available for hydrogen bonding, the more highly substituted molecules are rendered less basic. Competition between these induction and solvation effects gives the scrambled order of solution basicity. The maximal opportunity for hydrogen bonding with aqueous NH_4^+ plays an important role in the solution basicity of NH_3 being stronger than all the bases in Figure 6.3 even though NH_3 exhibits the lowest gas-phase basicity among these bases. Figure 6.3 also shows that pyridine and aniline have higher gas-phase basicities than ammonia, but are weaker bases than NH_3 in aqueous solution. The higher basicity of NH_3 in water is also attributed to enhanced hydrogen bonding with NH_4^+ relative to the pyridinium or anilinium ions.³²

Steric effects are less obvious from these correlations. For example, 2,6-dimethylpyridine, despite the steric bulk adjacent the nitrogen atom, is more basic than 4-methylpyridine in both solution and the gas phase. However, consider the following basicity ranking in aqueous solution:



One might expect 2-*t*-butylpyridine to be more basic than 2-methylpyridine on the basis of inductive effects, but the tertiary butyl steric bulk attenuates the basicity on steric grounds by making the nitrogen less accessible and more difficult to solvate upon protonation. Another steric effect deals with a geometry change that accompanies protonation; the potential of steric hindrance in the conjugate acid may attenuate basicity. While steric hindrance often plays major roles in understanding Lewis acidity/basicity (Section 6.4.7), the small proton size renders these steric effects less important in gauging the Brønsted–Lowry basicity of amines. For example, the gas-phase basicities of quinuclidine (1-azabicyclo[2.2.2]octane, 952.5 kJ/mol) and triethylamine (951.0 kJ/mol) are nearly identical, even though the geometric parameters associated with the cyclic quinuclidine system remains essentially unchanged upon protonation, while a greater structural change accompanies conversion of triethylamine to triethylammonium ion.

^{*}E. M. Arnett, *J. Chem. Ed.*, **1985**, 62, 385 reviews the effects of solvation, with many references.

6.3.7 Brønsted–Lowry Acid Strength of Binary Hydrogen Compounds

The binary hydrogen compounds (those containing only hydrogen and one other element) range from the strong acids HCl, HBr, and HI to the weak base NH₃. Others, such as CH₄, 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 6.4**.

Two seemingly contradictory trends are seen in these data. Acidity increases with increasing numbers of electrons in the central atom, either going across the table or down; but the electronegativity effects are opposite for the two directions (**Figure 6.5**). Within each column of the periodic table, acidity increases going down the series, as in H₂Se > H₂S > H₂O. 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[−]) with the larger main group atoms 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 used above is not applicable here, because in this series, the more electronegative elements form the stronger acids. The order of acid strength follows this trend: NH₃ < H₂O < HF.

The same general acidity trends are observed in aqueous solution. The three heaviest hydrohalic acids—HCl, HBr, and HI—are equally strong in water because of the leveling effect. All the other binary hydrogen compounds are weaker acids, their strength decreasing toward the left in the periodic table. Methane and ammonia exhibit no acidic behavior in aqueous solution, nor do silane (SiH₄) and phosphine (PH₃).

FIGURE 6.4 Acidity of Binary Hydrogen Compounds. Enthalpy of ionization in kJ/mol for the reaction $\text{HA}(g) \rightarrow \text{A}^-(g) + \text{H}^+(g)$, (the same as the proton affinity, Section 6.3.4).

(Data from J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **1979**, *101*, 6046; AsH₃ 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.)

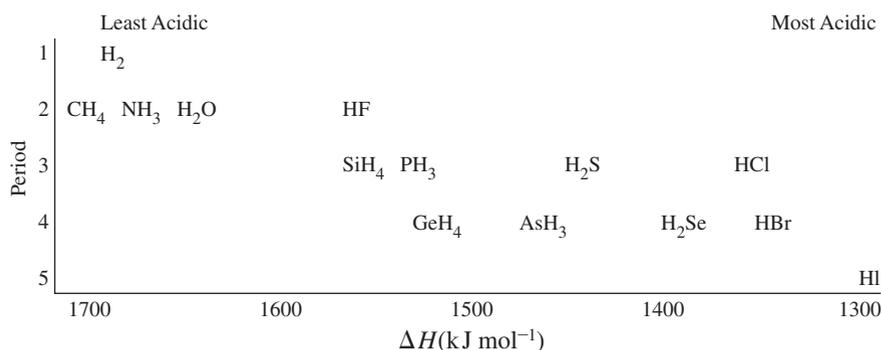
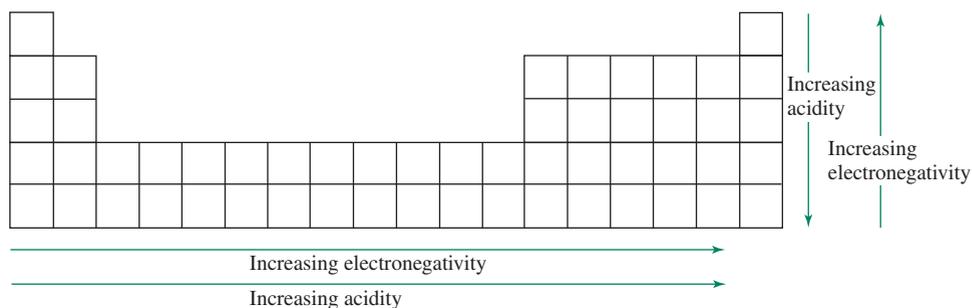
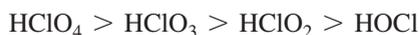


FIGURE 6.5 Trends in Acidity and Electronegativity of Binary Hydrides.

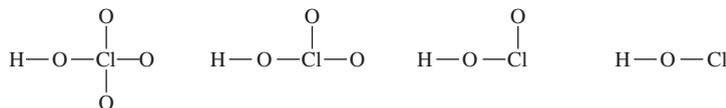


6.3.8 Brønsted–Lowry Strength of Oxyacids

The acid strength of the oxyacids of chlorine in aqueous solution rank as



The pK_a values of these acids are below.



Acid	Strongest HClO_4	HClO_3	HClO_2	Weakest HOCl
pK_a (298 K)	(-10)	-1	2	7.2

For oxyacids with multiple ionizable hydrogens, the pK_a values increase by about five units with each successive proton removal:

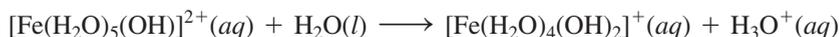
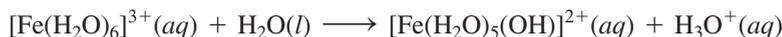
	H_3PO_4	H_2PO_4^-	HPO_4^{2-}	H_2SO_4	HSO_4^-
pK_a (298 K)	2.15	7.20	12.37	<0	2

The trends in these pK_a values are rationalized on the basis of electronegativity and resonance arguments. Oxygen atoms have a high electronegativity, and influence the distribution of electron density in molecules. In the case of oxyacids, the electronegativity of a terminal oxygen atom is greater than the group electronegativity of OH (Section 3.2.3). The net result is that the electron density supporting the O—H bond decreases (along with the bond strength) as the number of oxygen atoms increases. This renders the O—H bond more susceptible to the heterolytic cleavage associated with Brønsted–Lowry proton transfer. As the number of oxygen atoms increases, oxyacid acid strength increases.

The negative charge of oxyacid conjugate bases is stabilized by delocalization, represented by resonance forms where each terminal oxygen atom is progressively assigned a negative charge. The conjugate base is stabilized to a greater extent as the number of oxygen atoms increases for this negative charge delocalization. The more effectively the negative charge is delocalized, the weaker the conjugate base, and the stronger the acid.

6.3.9 Brønsted–Lowry Acidity of Aqueous Cations

Transition metal cations exhibit acidic behavior in solution; the impact of a positively charged metal ion on its bound water molecules is related to the inductive effect in oxyacids. The O—H bonds of water bound to transition metal ions are weakened since bonding electron density is drawn towards the metal. For example, aqueous Fe^{3+} is acidic, with yellow or brown iron species formed by reactions where proton transfer occurs from solvated water molecules resulting in bound hydroxide



In more basic solutions, hydroxide or oxide bridges form between metal atoms, resulting in cations with rather high positive charge. The higher positive charge further enhances the acidity of bound water molecules, and eventually metal hydroxide precipitates. A possible first step in this process is

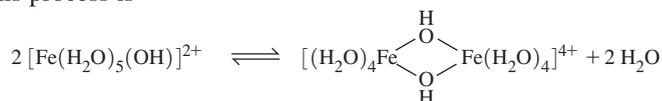


TABLE 6.8 Hydrated Metal Ion Brønsted–Lowry Acidities (298 K)

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

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

Metal ions with larger charges and smaller radii are stronger acids. The alkali metal cations show essentially no acidity, the alkaline earth metal cations 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. At this highly charged extreme, the free metal cation is no longer a detectable species. Instead, ions such as permanganate (MnO₄[−]), chromate (CrO₄^{2−}), uranyl (UO₂⁺), dioxovanadium (VO₂⁺), and vanadyl (VO²⁺) are formed, with oxidation numbers of 7, 6, 5, 5, and 4 for the metals, respectively. Acid-dissociation constants for transition metal ions are given in **Table 6.8**.

6.4 Lewis Acid–Base Concept and Frontier Orbitals

Lewis³³ defined a base as an **electron-pair donor** and an acid as an **electron-pair acceptor**.^{*} Modern inorganic chemistry extensively uses the Lewis definition, which encompasses the Brønsted–Lowry definition, since H⁺ accepts an electron pair from a Brønsted base during protonation. The Lewis definition dramatically expands the acid list to include metal ions and main group compounds, and provides a framework for nonaqueous reactions. The Lewis definition includes reactions such as



with the silver ion as an acid and ammonia as a base. In this class of reaction, the Lewis acid and base combine to provide an **adduct**. The bond that links the Lewis acid and base is called a *coordinate covalent* or *dative bond*; this bond features a shared pair of electrons that originated from the Lewis base.^{**} The boron trifluoride–ammonia adduct, BF₃ · NH₃, is a classical Lewis acid–base complex. The BF₃ molecule described in Sections 3.1.4 and 5.4.6 is trigonal planar. The B—F bonds are highly polarized by virtue of the large difference in electronegativity between fluorine and boron; the boron is frequently described as electron deficient. The electrons housed in the HOMO of the ammonia molecule interact with the empty LUMO of the BF₃—which has a large contribution from the boron 2p_z orbital (Figure 5.32)—to form the adduct. The molecular orbitals involved are depicted in **Figure 6.6**, and their energy levels are shown in **Figure 6.7**. The driving force for adduct formation is stabilization of the electrons in the donor HOMO.

The B—F bonds in BF₃ · NH₃ are bent away from the ammonia into a nearly tetrahedral geometry. The related boron trifluoride–diethyl ether adduct, BF₃ · O(C₂H₅)₂, is used in synthesis. The HOMO of diethyl ether features significant electron density at the oxygen, as reflected in the Lewis structure via two nonbonding pairs at the oxygen. These electrons are relatively high in energy and can be stabilized via interaction with a suitable LUMO. In this case, the HOMO electrons attack the boron-centered LUMO, changing the

^{*}A Lewis base is also called a **nucleophile**, and a Lewis acid is also called an **electrophile**.

^{**}In a standard covalent bond, like that in H₂, each atom formally provides one electron to each bonding pair.

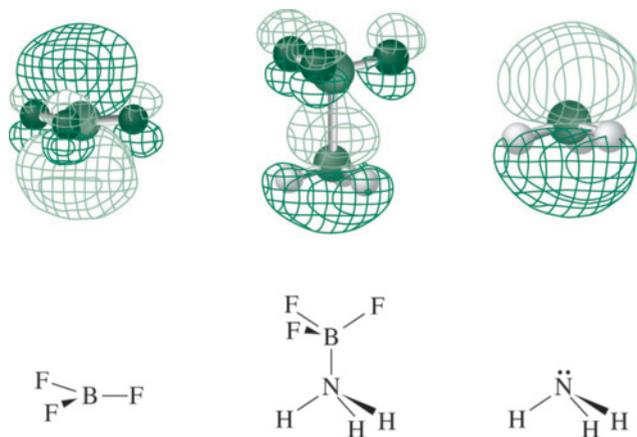


FIGURE 6.6 Donor–Acceptor Bonding in $\text{BF}_3 \cdot \text{NH}_3$.

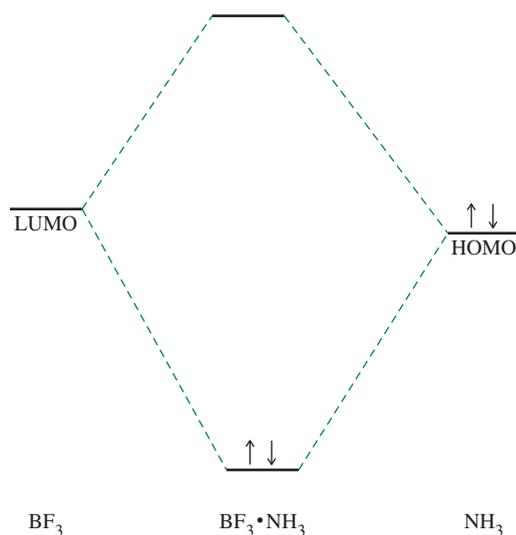


FIGURE 6.7 Simplified Energy Level Diagram for the Donor–Acceptor Bonding in $\text{BF}_3 \cdot \text{NH}_3$.

geometry around B from planar to nearly tetrahedral, as shown in **Figure 6.8**. 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 roughly 125° . At this temperature the dative bond dissociates to give BF_3 and $\text{O}(\text{CH}_2\text{CH}_3)_2$. The chemical and physical properties of adducts are often dramatically different than those of the component Lewis acid and base.

Lewis acid–base adducts involving metal ions are called **coordination compounds**; their chemistry will be discussed in Chapters 9 through 14.

6.4.1 Frontier Orbitals and Acid–Base Reactions³⁴

The molecular orbital description of acid–base reactions in Section 6.4 uses **frontier molecular orbitals**, those at the occupied–unoccupied frontier, which can be further illustrated by $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$. In this reaction, the a_1 orbital containing the lone-pair electrons of the ammonia molecule (Figure 5.30) combines with the empty $1s$ orbital of the

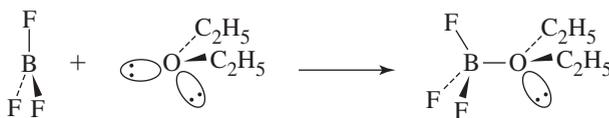


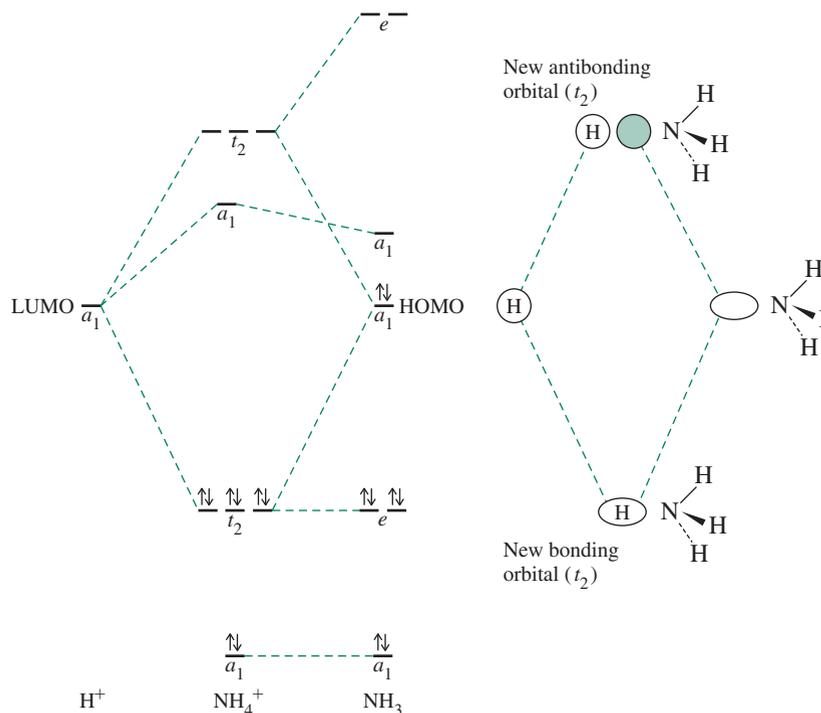
FIGURE 6.8 Boron Trifluoride–Ether Adduct Formation from a Lewis Perspective.

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 6.9**. 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, accompanied by the change in symmetry from C_{3v} to T_d , gives the eight orbitals of 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 $\text{NH}_3 + \text{H}^+$. The HOMO of the base NH_3 interacts with the LUMO of the acid H^+ resulting in a change in symmetry to make a new set of orbitals, one bonding and one antibonding.

In most Lewis acid–base reactions, a *HOMO–LUMO combination forms new HOMO and LUMO orbitals of the product*. Frontier orbitals whose shapes and symmetries allow significant overlap, and whose energies are similar, form useful bonding and antibonding orbitals. If the orbital combinations have no useful overlap, no net bonding is possible, and they cannot form acid–base products.*

When the shapes of the HOMO of one species and the LUMO of another species match, whether or not a stable adduct forms depends on the orbital energies. Formation of a robust dative bond requires a reasonably close energy match between these orbitals. As the energies of these orbitals get more disparate, electron transfer from the HOMO to the LUMO becomes more likely, resulting in a possible oxidation–reduction reaction (without adduct formation). A fascinating aspect of the Lewis model is that a single species can act as an oxidizing agent, a Lewis acid, a Lewis base, or a reducing agent, depending on the other reactant. Indeed, since every molecule by definition possesses a HOMO and a LUMO, every molecule in principle can function as a Lewis acid or base. Although predictions using this approach are difficult when the orbital energies are not known, this perspective is useful to rationalize many reactions, as illustrated in the following examples.

FIGURE 6.9 $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$
Molecular Energy Levels.



*In less common 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.

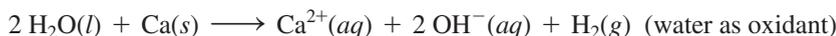
EXAMPLE 6.1

Water plays different roles that can be rationalized from the perspective of frontier orbital interactions.

Water as oxidizing agent

An example would be the reaction of water with calcium. In this situation, the water frontier orbitals are significantly lower in energy than the frontier orbitals of calcium (the alkali metals react similarly but have only one electron in their highest *s* orbital).* The energies are sufficiently different that no adduct can form, but electron transfer occurs from the Lewis base to the Lewis acid. One would never classify Ca as a Lewis base in introductory chemistry but it is one within this model!

From simple electron transfer from calcium to water, we might expect formation of H_2O^- , but electron transfer into the antibonding H_2O LUMO results in O—H bond weakening, leading to formation of hydrogen gas; H_2O is reduced to H_2 and OH^- , and Ca is oxidized to Ca^{2+} :



While the relatively wide energy gap between the participating Ca and H_2O orbitals plays an important role in the driving force of this reaction, the thermodynamics associated with ion solvation and gas evolution are vital as well.

Solvation of an anion

If orbitals with matching shapes have similar energies, the resulting adduct bonding orbitals will have lower energy than the Lewis base HOMO, and a net decrease in energy (stabilization of electrons in the new HOMO) drives the formation of an adduct. Adduct stability depends 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 frontier orbitals) is its interaction with the chloride ion:



The product is solvated chloride. In this case, water is the acceptor, using as LUMO an antibonding orbital centered primarily on the hydrogen atoms (Figure 5.28). The chloride HOMO is a $3p$ orbital occupied by an electron pair. This frontier orbital approach can be applied to many ion–dipole interactions.

Solvation of cation

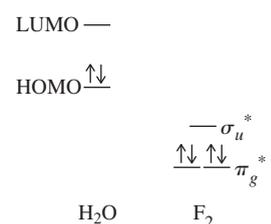
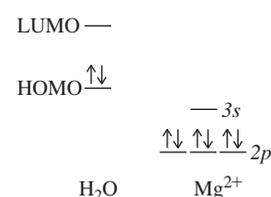
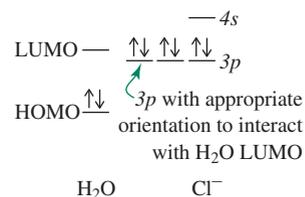
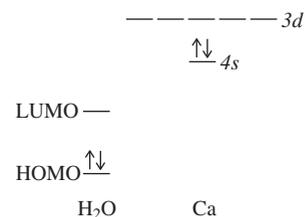
A reactant with frontier orbitals lower in energy than those of water (for example, Mg^{2+}) allows water to act as a donor. In this example, the resulting adduct is a solvated metal cation:



Water plays its traditional role as a Lewis base, contributing a lone pair primarily from the HOMO, which is the oxygen atom $2p_y$ orbital (Figure 5.28). The magnesium ion LUMO (Mg^{2+} is the Lewis acid) is the vacant $3s$ orbital. This model provides an introductory perspective of the driving force for the formation of hydrated metal cations. More details are provided in Chapter 10.

Water as reducing agent

Finally, if the reactant has frontier orbitals much lower than the water orbitals (F_2 , for example), water acts as a reductant and transfers electrons to the other reactant.



*Frontier orbitals can be *atomic* as well as molecular orbitals.

The fate of the H_2O is not the instantaneous result of electron transfer (H_2O^+) but the formation of molecular oxygen and hydrogen ions:



We can now express 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.

An excellent energy match between the base's HOMO and the acid's LUMO leads to adduct formation with a coordinate covalent bond. More disparate energy gaps between the frontier orbitals can result in oxidation–reduction reactions initiated by electron transfer from the base to the acid. While this model must be considered in concert with other considerations (most notably thermodynamics) to predict the fate of potential reactants, the frontier orbital perspective provides a conceptual framework for analyzing reactions.

6.4.2 Spectroscopic Support for Frontier Orbital Interactions

Reactions of I_2 as a Lewis acid with Lewis basic solvents dramatically show the effect of adduct formation. The spectral changes caused by the changes in energy of the participating electronic energy levels (Figures 6.10 and 6.11) are striking. The upper I_2 energy levels are shown on the left in Figure 6.10, with a bond order of 1 due to the filled $9\sigma_g$ and $4\pi_u$ bonding orbitals and $4\pi_g^*$ antibonding orbitals. Gaseous I_2 is violet, absorbing light near 500 nm to affect electronic excitation from the $4\pi_g^*$ level to the $9\sigma_u^*$ level. This absorption, broadened due to excitation from gaseous I_2 in ground and excited vibrational and rotational states, removes photons from the yellow, green, and blue parts of the visible spectrum, transmitting red and violet that combine to afford the observed violet color.

In solvents such as hexane, with frontier orbitals neither amenable to robust adduct formation nor electron transfer with I_2 , the electronic structure of iodine is essentially unchanged, and the color remains essentially the same violet; the absorption spectra of gaseous I_2 and solutions of I_2 in hexane are nearly identical in the visible range (Figure 6.11). However, in benzene and other π -electron solvents, the color becomes more reddish; and in good donors—such as ethers, alcohols, and amines—the color becomes distinctly brown. The solubility of I_2 also increases as the ability of the solvent to interact as a donor towards I_2 is enhanced. Interaction of a solvent donor orbital with the $9\sigma_u^*$ I_2 LUMO results in a lower occupied bonding orbital and a higher unoccupied antibonding orbital. As a result, the $\pi_g^* \rightarrow \sigma_u^*$ transition for the $\text{I}_2 + \text{donor}$ adduct is shifted higher in energy, and the absorbance peak is blue-shifted. The transmitted color shifts toward brown (combined red, yellow, and green), as more of the yellow and green light passes through. Water is a poor donor towards the I_2 LUMO; I_2 is very slightly soluble in water. In contrast, I^- , an excellent donor towards the I_2 LUMO; I^- reacts with I_2 to form I_3^- , which is very soluble in water giving a brown solution. When the interaction between the donor and I_2 is strong, the adduct LUMO is shifted to higher energy, resulting in the donor–acceptor transition ($\pi_g^* \rightarrow \sigma_u^*$) increasing in energy. The coordinate covalent bonds formed in these adducts are called **halogen bonds** (Section 6.4.5).

In addition to the donor–acceptor absorption, a new ultraviolet band (230 to 400 nm, marked CT in Figure 6.11) appears upon adduct formation. This absorption is associated with the transition $\sigma \rightarrow \sigma^*$ between the two orbitals formed by the interaction between the frontier orbitals. Because the donor orbital (in this case, from the solvent or I^-) contributes the most to lower σ adduct orbital, and the I_2 LUMO contributes the most to the σ^* adduct orbital, the CT 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 (CT)** for this transition. The energy of this transition is less predictable, because it depends on the energy of the donor orbital. These transitions result in electron density being shifted

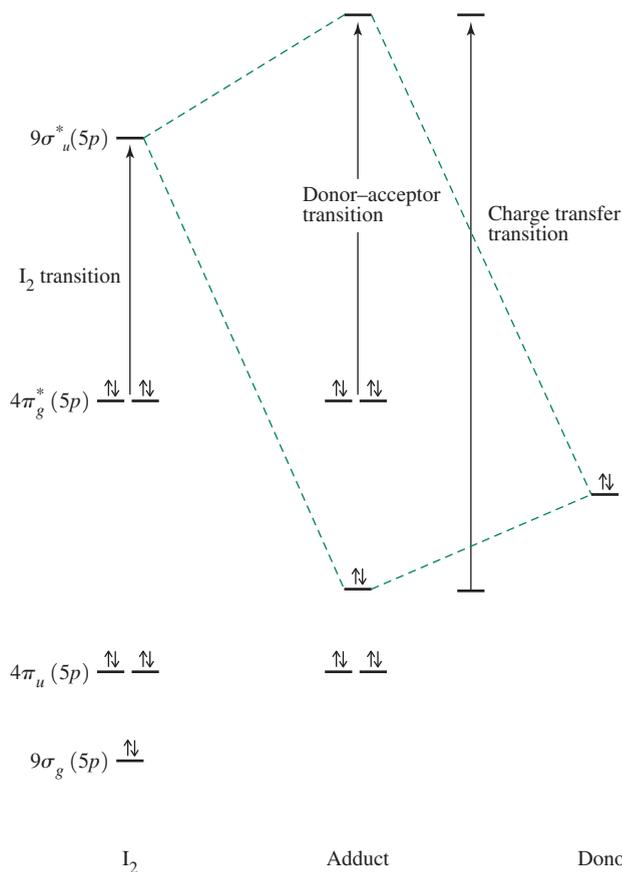


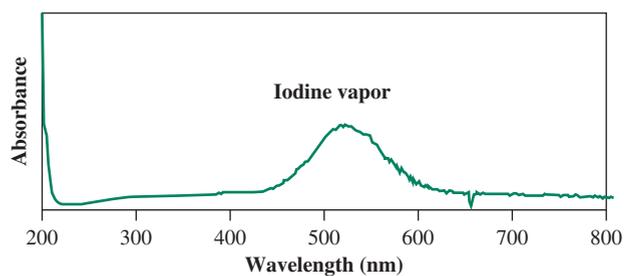
FIGURE 6.10 Electronic Transitions in I₂ Adducts.

from one adduct region to another upon excitation. Charge-transfer phenomena are evident in many adducts, and provide further experimental evidence for the utility of the frontier orbital reactivity model. Charge-transfer in transition-metal complexes is discussed in Chapter 11.

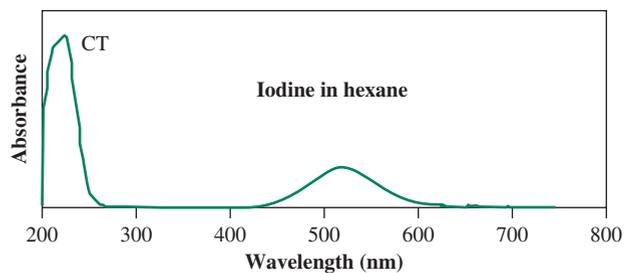
6.4.3 Quantification of Lewis Basicity

Significant effort has been devoted to quantifying Lewis basicity. From this standpoint, **Lewis basicity** is defined as *the thermodynamic tendency of a substance to act as a Lewis base*. Comparative measures of this property are provided by the equilibrium constants for adduct formation of Lewis bases with a common reference acid.³⁵ A major challenge is identifying a reference acid that is suitable to assess a variety of bases. Because Lewis basicity is a complicated phenomenon that is modified subtly by electronic and steric effects, the basicity ranking for a set of Lewis bases can vary depending on the reference acid used. As previously discussed for proton affinity (Section 6.3.4), gas-phase measurements are ideal to measure Lewis basicities without the complication of solvation effects. However, in practice, most thermodynamic data for Lewis bases have been obtained in solution, with important attention paid to solvent selection. An ideal solvent for these studies would dissolve a variety of bases yet not itself react significantly towards these solutes as a Lewis acid.* In addition, a Lewis base may be rendered less basic towards a given Lewis acid in one solvent relative to another solvent. Selecting a single solvent that meets these criteria for many Lewis bases is a tall order.

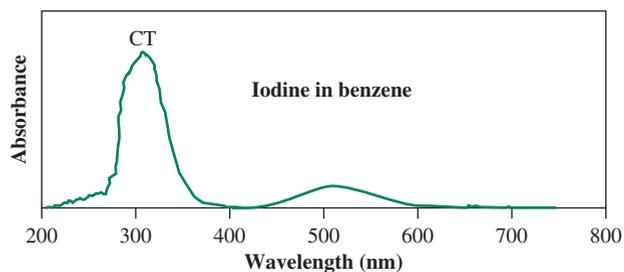
*In essence, a solvent is desired that will primarily interact with solutes via dispersion forces. Solvents in this category (for example, hydrocarbons) typically are limited to relatively nonpolar solutes. Sometimes more polar solvents must be employed, rendering the quantification of Lewis basicity more complicated as the enthalpy associated with solvation plays an increasing role.

FIGURE 6.11 Spectra of I_2 with Different Bases.

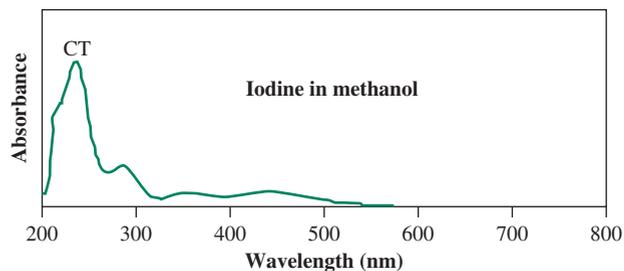
I_2 vapor is purple or violet, absorbing near 520 nm, with no charge-transfer bands.



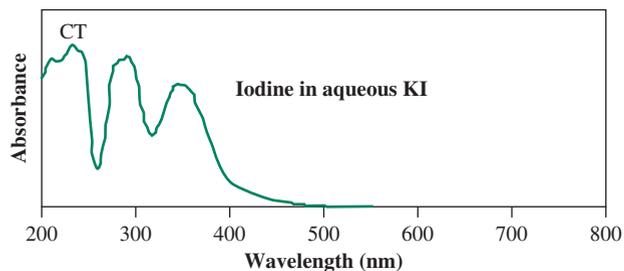
I_2 in hexane is purple or violet, absorbing near 520 nm, with a charge-transfer band at about 225 nm.



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

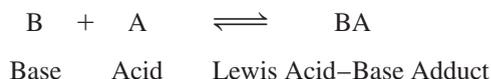


I_2 in methanol is yellow brown, absorbing near 450 nm, with a charge-transfer band near 240 nm and a shoulder at 290 nm.



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

With this experimental design challenge in mind, quantifying Lewis basicity is simple in theory. The equilibrium constants for adduct formation (K_{BA} , more commonly expressed as $\log K_{BA}$) can be ranked via increasing K_{BA} or $\log K_{BA}$ to communicate increasing Lewis basicity of the base employed for adduct formation.



$$K_{BA} = \frac{[BA]}{[B][A]}$$

The solubilities of I_2 in different solvents provide a qualitative way to assess the Lewis basicity of these solvents towards I_2 . **Table 6.9** provides $\log K_{BA}$ values for the formation of adducts of the Lewis acid I_2 with Lewis bases in the solvents CCl_4 and CHCl_3 . It is interesting that these five bases exhibit the same Lewis basicity *ranking* towards I_2 in these solvents. However, the absolute basicities are quite different; for example, *N,N*-dimethylformamide is roughly five times more basic towards I_2 in CCl_4 than in CHCl_3 . And on the basis of these data, $(\text{C}_6\text{H}_5)_3\text{P}=\text{Se}$ is slightly more basic towards I_2 in CHCl_3 than in CCl_4 , while all the other bases are more basic towards this acid in CCl_4 .

The spectroscopic evidence for I_2 adduct formation (**Section 6.4.2**) suggests that spectroscopic measurement of Lewis basicity is possible. The requirement is that the reference Lewis acid must exhibit a spectroscopic change upon adduct formation (for example, an NMR chemical shift, change in UV-Vis or IR spectrum) that can be attributed primarily to the strength of the coordinate covalent bond within the adduct. While these spectral measurements are generally routine (Figure 6.11), their reliability in accurately assessing Lewis basicity must be confirmed via correlating these data (for example, how much did the chemical shift or visible absorption change?) to K_{BA} or ΔH° values for the complexation reactions.

6.4.4 The BF_3 Affinity Scale for Lewis Basicity

The Lewis acid BF_3 is the most commonly employed reference to probe Lewis basicity. The affinity of BF_3 towards many bases has been measured in dichloromethane solution where the affinity is defined as the magnitude of the enthalpy change of adduct formation:



These enthalpies must be corrected for the ΔH° for BF_3 dissolving in the solvent. Upon this adjustment, increasing BF_3 affinities indicate stronger coordinate covalent bonding, consequently increasing Lewis basicity of the base towards BF_3 . Some BF_3 affinities are listed in **Table 6.10**. Steric and electronic effects suggested by these data will be discussed in **Sections 6.4.6** and **6.4.7**.

TABLE 6.9 $\log K_{BA}$ for I_2 • Lewis Base Adducts in Different Solvents (298 K)

Lewis Base	$\log K_{BA}$ in CCl_4	$\log K_{BA}$ in CHCl_3
Tetrahydrofuran	0.12	−0.44
<i>N,N</i> -dimethylformamide	0.46	−0.22
$(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$	1.38	0.89
$(\text{C}_6\text{H}_5)_3\text{P}=\text{S}$	2.26	2.13
$(\text{C}_6\text{H}_5)_3\text{P}=\text{Se}$	3.48	3.65

Data from *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, p. 33, 91–101, 295–302.

TABLE 6.10 BF_3 Affinities for Lewis Bases in CH_2Cl_2 (298 K)

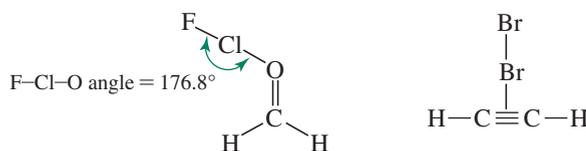
Lewis Base	BF_3 Affinity (kJ/mol)
4-dimethylaminopyridine	151.55
trimethylamine	139.53
3-methylpyridine	130.93
4-phenylpyridine	129.50
pyridine	128.08
2-methylpyridine	123.44
2-phenylpyridine	103.34
trimethylphosphine	97.43
tetrahydrofuran	90.40
2-trifluoromethylpyridine	82.46
2- <i>tert</i> -butylpyridine	80.10
tetrahydrothiophene	51.62

Data from *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, p. 33, 91–101, 295–302.

Of the Lewis bases in Table 6.10, 4-dimethylaminopyridine has the highest BF_3 affinity and is the strongest Lewis base. What are the extremes in BF_3 affinities? This question is interesting; it communicates the wide range of molecules that can function as Lewis bases to BF_3 . The super (Brønsted) base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Figure 6.1) also has a very large BF_3 affinity (159.36 kJ/mol). Very low BF_3 affinities have been reported for ethene (5.4 kJ/mol) and propene (6.9 kJ/mol) in liquid nitrogen. These data cannot be directly compared to the values determined in dichloromethane (Table 6.10), however. In these adducts, the unsaturated hydrocarbons presumably use their π bonding HOMOs as the donor orbitals.³⁶ The role of olefin–borane complexes as intermediates in chemical synthesis has been proposed.³⁷

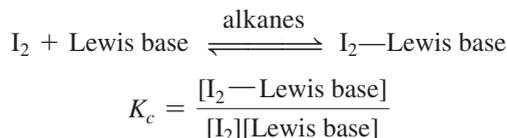
6.4.5 Halogen Bonds

The reactions of I_2 as a Lewis acid with donor solvents and Lewis bases have been discussed in Sections 6.4.2 and 6.4.3. The coordinate covalent bonds formed by the halogens (X_2) and interhalogens (XY, for example, ICl, discussed in Section 8.9.1) to Lewis bases are called **halogen bonds**.³⁸ These long known donor–acceptor interactions, featuring many similarities to hydrogen bonding (Section 6.5.1), have been “rediscovered” and show potential in drug design and material science.³⁹ Halogen bonds typically exhibit approximate 180° angles between the donor atom and the halogen acceptor, consistent with acceptance by the halogen σ^* LUMO, which lies along the halogen bond axis. As an example, the gas-phase structure of the ClF adduct with formaldehyde was determined by rotational spectroscopy, and an $\text{O} \cdots \text{Cl}—\text{F}$ angle of 176.8° was found, with the coordinate covalent bond in the expected location based on the formaldehyde HOMO and ClF LUMO.⁴⁰ In the gas phase acetylene— Br_2 adduct, the halogen LUMO interacts with the acetylene π bonding HOMO.⁴⁰



As described in Section 6.4.3, the Lewis acid I_2 is used to catalog Lewis basicity via determination of the equilibrium constants (K_c) associated with adduct formation.

The experimental challenge is determining the I_2 and I_2 —Lewis base adduct concentrations; these are often obtained via UV-Visible spectroscopy by examining charge transfer and donor–acceptor transitions (Section 6.4.2).



An extensive compilation of K_c values is available for a variety of main group Lewis bases, with most determined in heptane.⁴¹ There is interest in developing an I_2 affinity scale defined similarly as the BF_3 affinity scale (based on ΔH° of adduct formation). Many ΔH° values have been determined for reactions of I_2 with Lewis bases, but reconciliation of data obtained via different experimental conditions for reliable I_2 affinity comparisons remains a challenge.

How do we expect the bond within a halogen to change upon complexation with a Lewis base? Since adduct formation results in donation into the halogen σ^* LUMO, this bond should weaken and lengthen. The subsequent reduction in the halogen–halogen bond's force constant is shown by a decrease in the bond's stretching frequency, suggesting the possibility of assessing Lewis basicity by determining how much the stretching frequency decreases from that in free halogen. This initially seems a very attractive strategy; a change in spectroscopic property of only one bond could be correlated to Lewis basicity. Unfortunately, vibrational modes that feature considerable halogen or interhalogen stretching generally also include motion of the Lewis basic atom as well. Nevertheless, stretching frequency changes induced in I_2 , ICN, and ICl upon complexation have been tabulated for many complexes and correlated to Lewis basicity with reasonable effectiveness.* The infrared stretching frequency of the I—C bond in ICN (485 cm^{-1} uncomplexed) experiences red shifts (to lower energy) upon complexation ranging from 5 cm^{-1} (in benzene—ICN) to 107 cm^{-1} (in quinuclidine—ICN). The range in red shifts observed in I_2 complexes is not as dramatic; a maximum red shift of only 39.5 cm^{-1} was observed in piperidine— I_2 .** These red shifts correlate fairly well with $\log K_c$ values, especially when similar Lewis bases are compared.

Section 6.4.2 discussed that the donor–acceptor transition in I_2 —Lewis base complexes is modified depending on the extent of the donor interaction with the I_2 LUMO. The blue shift (to higher energy) in the $4\pi_g^* \rightarrow 9\sigma_u^*$ transition upon I_2 complexation has also been correlated to Lewis base strength. As shown in Figure 6.10, this transition increases in energy as the base strength increases. Table 6.11 lists blue shifts induced by selected bases, used to assess Lewis basicity.

6.4.6 Inductive Effects on Lewis Acidity and Basicity

Rationalization of the Lewis basicity ranking in Table 6.10 requires that inductive effects be considered. 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 Lewis base than PH_3 . A similar effect in the reverse direction results from substituting 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.



*The I_2 stretching mode is IR inactive, but vibrational modes with significant I—I contribution become active upon complexation. The free I_2 stretching band is 210 cm^{-1} on the basis of Raman spectroscopy.

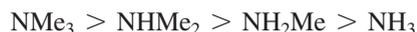
**For tabulated infrared shifts of ICN, I_2 , and ICl as well as $4\pi_g^* \rightarrow 9\sigma_u^*$ blue shifts: C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scale Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, pp. 286–306.

TABLE 6.11 Blue Shifts in the $4\pi_g^* \rightarrow 9\sigma_u^*$ Transition in I_2 Complexes in Heptane at 15° C

Lewis Base	Blue Shift (cm^{-1})
Pyridine	4560
Dimethylsulfide	3570
THF	2280
Diethyl ether	1950
Acetonitrile	1610
Toluene	580
Benzene	450

Data from *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, p. 33, 91–101, 295–302.

Additional substitution increases the effect, with the following resulting order of Lewis base strength in the gas phase:



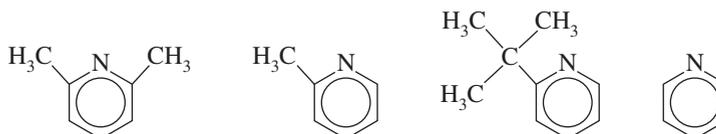
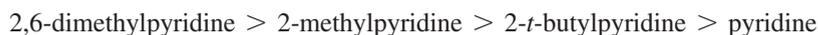
These **inductive effects** are similar to the effects seen in organic molecules containing electron-contributing or electron-withdrawing groups. Caution is required in applying this idea to other compounds. The boron halides do not follow this argument, because BF_3 and BCl_3 have significant π bonding that increases the electron density on the boron atom. Exclusive consideration of halogen electronegativity would lead to a prediction that BF_3 would be the strongest Lewis acid of the boron halides; the high electronegativity of fluorine atoms would be expected to draw electron density away from the boron most strongly. However, the varying boron–halogen bond lengths also play an important role. The relatively short B–F bonds in BF_3 permit the previously mentioned π bonding to partially quench some Lewis acidity at boron. Developing strategies to gauge the Lewis acidities of boron halides remains a contemporary pursuit.^{42,43} Calculations applying coupled cluster theory⁴¹ and the determination of boron’s valence deficiency⁴² are consistent with the Lewis acidity increasing as $\text{BF}_3 \ll \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$. As the halogen atom size increases, the B–X bond lengthens, and the π interaction that attenuates boron Lewis acidity decreases in importance.

6.4.7 Steric Effects on Lewis Acidity and Basicity

Steric effects also influence acid–base behavior. When bulky groups are forced together by adduct formation, their mutual repulsion makes the reaction less favorable. Brown, a major contributor to these studies,⁴⁴ described molecules as having front (F) strain or back (B) 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 internal (I) strain. Reactions involving substituted amines and pyridines were used to sort out these effects.

EXAMPLE 6.2

As discussed in [Section 6.3.6](#), reactions of a series of substituted pyridines with hydrogen ions show this order of Brønsted–Lowry base strengths:



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



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 6.4 Based on inductive arguments, would you expect boron trifluoride or trimethylboron to be the stronger acid in reaction with NH_3 ? Which of these acids would you expect to be stronger towards 2,6-dimethylpyridine or 2-*t*-butylpyridine?

Proton affinities (Table 6.6) show the gas-phase Brønsted–Lowry base strength ranking $\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2 > \text{NH}_3$, as predicted on the basis of electron donation by the methyl groups, resulting in increased electron density at nitrogen.⁴⁵ When larger Lewis acids than H^+ 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, with very nearly the same ΔH° for adduct formation as with MeNH_2 . With the 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 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 can be argued that some F strain is also present. When triethylamine is used as the base, it does not form a trimethylboron adduct, although the enthalpy change for such a reaction is weakly exothermic.* 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, 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, 983.3 and 981.8 kJ/mol (Table 6.6). When mixed with trimethylboron, whose methyl groups are large enough to interfere with the ethyl groups of triethylamine, the quinuclidine reaction is twice as exothermic as that of triethylamine (−84 vs. −42 kJ/mol). Whether the

TABLE 6.12 Rankings of the Enthalpies of Formation for Adduct Formation for Amines and Lewis Acids

Amine	Proton Affinity (Order)	BF_3 (Order)	ΔH° for amine— BMe_3 adduct formation (kJ/mol)	BMe_3 (Order)	$\text{B}(t\text{-Bu})_3$ (Order)
NH_3	4	4	−57.53	4	2
CH_3NH_2	3	2	−73.81	2	1
$(\text{CH}_3)_2\text{NH}$	2	1	−80.58	1	3
$(\text{CH}_3)_3\text{N}$	1	3	−73.72	3	4
$(\text{C}_2\text{H}_5)_3\text{N}$			~−42		
Quinuclidine			−84		
Pyridine			−74.9		

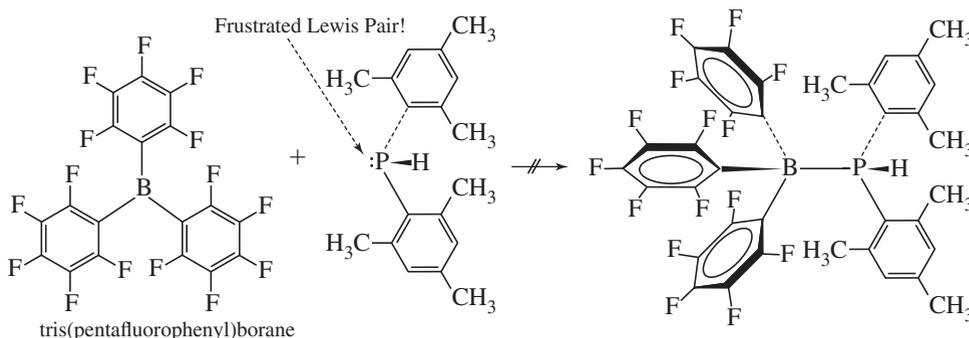
ΔH° Data from H. C. Brown, *J. Chem. Soc.*, **1956**, 1248.

*Keep in mind that all of these adduct formation reactions will have $\Delta S^\circ < 0$, so ΔH° must be sufficiently negative to render $\Delta G^\circ < 0$ for adduct formation.

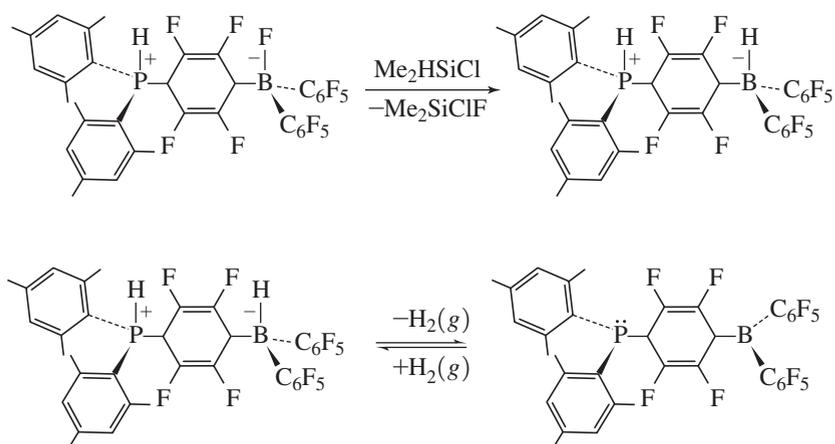
triethylamine effect is due to interference at the front or the back of the amine is a subtle question, because the interference at the front is indirectly caused by other steric interference at the back between the ethyl groups.

6.4.8 Frustrated Lewis Pairs

Does the presence of excessive steric bulk when a Lewis acid and a Lewis base attempt to form an adduct automatically render these species inert towards each other? The unique behavior of sterically **frustrated Lewis pairs (FLPs)**, pioneered by Stephan, is a vigorous research area with applications for small molecule activation* and catalysis.⁴⁶ The highly Lewis acidic and sterically bulky tris(pentafluorophenyl)borane⁴⁷ plays a role in many FLP reactions. The great promise of FLP chemistry was revealed by reactions between tris(pentafluorophenyl)borane and tertiary and secondary phosphines, where sterics preclude formation of classic adducts. A seminal example of a frustrated Lewis pair is that of the secondary phosphine di(2,4,6-trimethylphenyl)phosphine that is precluded from forming a classic adduct with tris(pentafluorophenyl)borane. The phosphine Lewis pair is “frustrated” since it cannot interact with boron to form the adduct.



Remarkably, the frustrated Lewis pair engages in nucleophilic attack at the *para* carbon of the borane, affording a **zwitterionic species**** after fluoride migration. This fluoride can be substituted for a hydrogen atom to give a zwitterion that *releases hydrogen gas upon heating*.⁴⁸ The product phosphino-borane reacts with hydrogen gas at ambient temperature to reform the zwitterion and is the first non-transition-metal molecule that can reversibly activate the H—H bond and release H₂.



*“Activation” in this sense refers to making an otherwise inert small molecule chemically reactive.

**A zwitterion is a species that contains at least one formal positive and negative charge.

Spectacular small molecule activation has been achieved with FLPs, including with H_2 ,⁴⁹ CO_2 ,⁵⁰ and N_2O .⁵¹ The chemistry enabled by frustrated Lewis pairs is being exploited to develop non-transition-metal catalysts that promise to substitute for catalysts that contain toxic and expensive heavy metals.⁵²

6.5 Intermolecular Forces

The frontier molecular orbital model for donor–acceptor complexes provides a convenient framework for a discussion of hydrogen bonding and receptor–guest interactions.

6.5.1 Hydrogen Bonding

Hydrogen bonding (introduced in Section 3.4) is relevant to most scientific disciplines. The definition of a hydrogen bond in terms of its covalent and ionic contributions continues to be debated. Its traditional definition, a force that arises between molecules that have an H atom bonded to a small, highly electronegative atom with lone pairs, usually N, O, or F, has been considerably broadened. The IUPAC Physical and Biophysical Chemistry Division has recommended a new definition⁵³ that includes the following themes.

A hydrogen bond $\text{X—H} \cdots \text{B}$ is formed from an attraction between an X—H unit (where the electronegativity of X is greater than of H), and a donor atom (B). The X—H and B components may be incorporated into larger molecular fragments. The interaction between these components can be either intermolecular or intramolecular. Hydrogen bonds can be described on the basis of varying relative contributions from three components:

- The polarity of X—H leads to an electrostatic contribution.
- The donor-acceptor nature of the interaction results in partial covalent character and charge transfer from B to X—H .
- Dispersion forces also contribute to hydrogen bonds.

The $\text{H} \cdots \text{B}$ strength increases as the electronegativity of X within the polar covalent X—H bond increases. For example, in the series N—H , O—H , and F—H , the $\text{H} \cdots \text{B}$ strength is greatest for interaction with F—H .

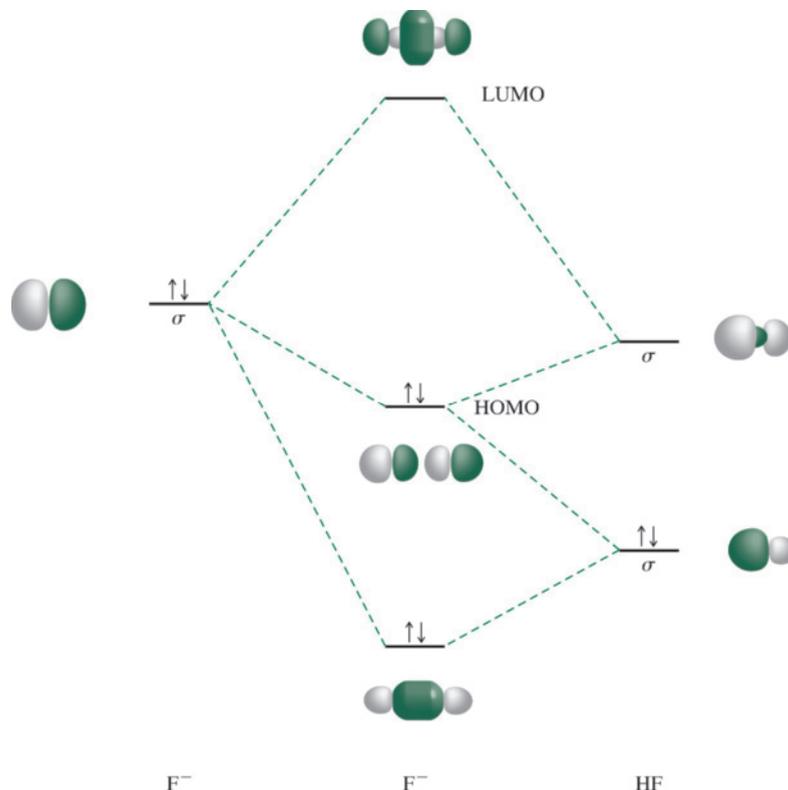
The IUPAC recommendations emphasize that experimental evidence is necessary to support the existence of a hydrogen bond.⁵⁴ Such evidence may be provided in a variety of ways:

- An $\text{X—H} \cdots \text{B}$ angle of 180° is indicative of a relatively strong hydrogen bond, with a short $\text{H} \cdots \text{B}$ distance. Increased deviation from $\text{X—H} \cdots \text{B}$ linearity indicates weaker hydrogen bonds, with longer $\text{H} \cdots \text{B}$ distances.
- The X—H infrared stretching frequency is red-shifted upon formation of $\text{X—H} \cdots \text{B}$, consistent with X—H weakening and lengthening. As the strength of the $\text{H} \cdots \text{B}$ bond increases, the X—H bond strength decreases. Hydrogen bond formation results in new vibrational modes with $\text{H} \cdots \text{B}$ contributions.
- The NMR chemical shift of the proton linking X and B is a sensitive function of the hydrogen bond strength. Typically these protons in $\text{X—H} \cdots \text{B}$ are deshielded relative to X—H . The extent of deshielding is correlated to the hydrogen bond strength.
- Experimental detection of hydrogen bonding requires that the magnitude of ΔG for $\text{X—H} \cdots \text{B}$ formation be larger than the thermal energy of the system.

The electrostatic component, the attraction of a bonded hydrogen atom to a region of relatively high electron density of the base (B), is considered the *dominant* contribution to most hydrogen bonds. Frontier molecular orbitals and the donor–acceptor model can be applied to understand the covalent contribution.

Very strong hydrogen bonding in the symmetric FHF^- ion was described via molecular orbital theory in [Section 5.4.1](#). The key interactions responsible for the covalent contribution to hydrogen bonding can be generated by combining HF molecular orbitals (see the energy-

FIGURE 6.12 Orbital Interactions Responsible for the Covalent Contribution to the Hydrogen Bonding in FHF^- . Figure 5.16 shows the full set of molecular orbitals. The orbitals shown here are labeled a_g , b_{1g} , and a_g in Figure 5.16.



level diagram preceding Exercise 5.3) with an atomic orbital of F^- , as shown in **Figure 6.12**. The nonbonding p_x and p_y 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 fluoride $2p_z$ with the σ and σ^* HF orbitals forms three product orbitals. In this case, these three orbitals are all symmetric about the central H nucleus. The lowest orbital is distinctly bonding, the middle (HOMO) orbital is essentially nonbonding, and the highest energy orbital (LUMO) is antibonding with respect to the hydrogen bond. From the donor–acceptor perspective, the fluoride $2p_z$ is the HOMO, and the HF σ^* orbital the LUMO. The “charge-transfer” aspect of hydrogen bonding formally refers to the creation of the HOMO in Figure 6.12, where electron density originally localized on the base (in this case fluoride) gains access to a delocalized orbital that includes both F atoms in FHF^- .

The linear arrangement of $\text{X—H} \cdots \text{B}$ hydrogen bonds supports this covalent contribution to the bonding since maximum overlap of the donor orbital with the σ^* LUMO of X—H requires approach along the X—H bond axis.

One IUPAC criterion for hydrogen bonding concerns application of infrared spectroscopy to measure the decrease in X—H stretching frequency (from weakening of the X—H bond) that accompanies hydrogen bond formation. Indeed, red shifts in the X—H stretching frequency upon $\text{X—H} \cdots \text{B}$ formation are used to assess hydrogen bond strengths. A scale based on the change in the $\nu(\text{OH})$ of methanol upon $\text{CH}_3\text{OH} \cdots \text{B}$ formation in CCl_4 has been employed. Approximately 800 $\Delta\nu(\text{OH})$ values, ranging from $\sim 3 \text{ cm}^{-1}$ with chloroform as the Lewis base to 488 cm^{-1} with tri(*n*-octyl)amine *N*-oxide as the Lewis base, have been reported.*

*For tabulated $\Delta\nu(\text{OH})$ values see C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, pp. 190–206.

EXAMPLE 6.3

The pK_a Slide Rule approach helps explain the *H-bond puzzle* posed earlier.

Consider the O—H···O hydrogen bond between hydronium ion and water in $[\text{OH}_3\cdots\text{OH}_2]^+$. In this case, the hydrogen bond donor (H_3O^+) is identical to the conjugate acid of the hydrogen bond acceptor (H_3O^+ is the conjugate acid of H_2O). The ΔpK_a between these species equals 0; the hydrogen bond is “strong.”

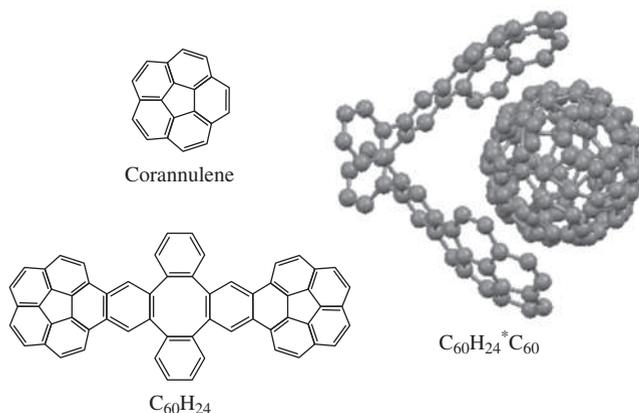
Now consider the O—H···O hydrogen bond between two water molecules in $\text{OH}_2\cdots\text{OH}_2$. The hydrogen bond donor is now H_2O ($pK_a = 15.7$) and the conjugate acid of the hydrogen bond acceptor is H_3O^+ ($pK_a = -1.7$). The ΔpK_a equals 17.4, and this hydrogen bond falls into the “medium” category.

6.5.2 Receptor–Guest Interactions*

Another important interaction can occur between molecules having extended pi systems, when their pi systems interact with each other to hold molecules or portions of molecules together. Such interactions are important on a large scale—for example, as a component of protein folding and other biochemical processes—and on a truly small scale, as in the function of molecular electronic devices. An interesting recent area of study in the realm of π – π interactions has been the design of concave receptors that can wrap around and attach to fullerenes such as C_{60} in what has been described as a “ball-and-socket” structure. Several such receptors, sometimes called *molecular tweezers* or *clips*, have been designed, involving porphyrin rings, corannulene and its derivatives, and other pi systems.⁵⁷ The first crystal structure of such a receptor–guest complex involving C_{60} , dubbed by the authors a “double-concave hydrocarbon buckycatcher,” is shown in **Figure 6.13**; it was synthesized simply by mixing approximately equimolar quantities of corannulene derivative $\text{C}_{60}\text{H}_{24}$ and C_{60} in toluene solution.⁵⁸

The product, called an **inclusion complex**, has two concave corannulene “hands” wrapped around the buckminsterfullerene; the distance between the carbons in the corannulene rings and the matching carbons on C_{60} is consistent with the distance expected for π – π interactions between the subunits of the structure (approximately 350 pm), with a shortest C···C distance of 312.8 pm. With no direct C—C covalent bonding, the binding between the fullerene and the corannulene units is attributed to pure π – π interactions. Subsequently, corannulene itself has been found to engage in host–guest complexing with C_{60} , although the shortest distance between the corannulene and fullerene is slightly longer than in the complex shown in Figure 6.13.⁵⁹ The electronic structure of the $\text{C}_{60}\text{H}_{24}$ complex

FIGURE 6.13 Receptor–Guest Complex $\text{C}_{60}\text{H}_{24}^*\text{C}_{60}$. Molecular structure drawing created using CIF data.



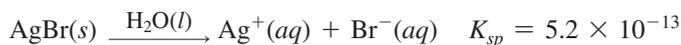
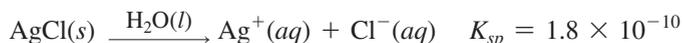
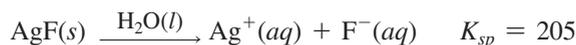
*Also called *receptor–substrate* or *host–guest interactions*.

has been studied in connection with the potential use of such complexes as building units in molecular electronics.⁶⁰ Similar receptor–guest complexes involving other molecular tweezers and C₆₀ have shown evidence of electron transfer from receptor to the fullerene on absorption of light (another example of charge-transfer transitions), and may be useful in the construction of photovoltaic devices.⁶¹

6.6 Hard and Soft Acids and Bases

Consider these experimental observations:

1. **Relative solubilities of halides.** The solubilities of silver halides in water decrease, going down the column of halogens in the periodic table:



Mercury(I) halides have a similar trend, with Hg₂F₂ the most soluble and Hg₂I₂ the least soluble. However, LiF is by far the *least* soluble of the lithium halides; its K_{sp} is 1.8×10^{-3} , but the other lithium halides are highly soluble in water. Similarly, MgF₂ and AlF₃ are less soluble than the corresponding chlorides, bromides, and iodides. How can one account for these divergent trends?

2. **Coordination of thiocyanate to metals.** As we will formally consider in Chapter 9, numerous ions and other groups can act as **ligands**, forming bonds to metal ions. Thiocyanate, SCN[−], has the capacity to bond through either its sulfur or nitrogen. When it bonds to a large, highly polarizable metal ion such as Hg²⁺, it attaches through sulfur ([Hg(SCN)₄]^{2−}); but when it bonds to smaller, less polarizable metals such as Zn²⁺, it attaches through nitrogen ([Zn(NCS)₄]^{2−}). How can this be explained?
3. **Equilibrium constants of exchange reactions.** When the ion [CH₃Hg(H₂O)]⁺—with CH₃ and H₂O attached as ligands to Hg²⁺—is reacted with other potential ligands, sometimes the reaction is favorable, sometimes not. For example, the reaction with HCl goes nearly to completion:



But the reaction with HF does not:



Is it possible to predict the relative magnitudes of such equilibrium constants?

To rationalize observations such as these, Pearson presented the concept of **hard and soft acids and bases (HSABs)**, designating polarizable acids and bases as **soft** and nonpolarizable acids and bases as **hard**.⁶² Much of the hard–soft distinction depends on polarizability, the degree to which a molecule or ion is 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. The HSAB concept is a useful guide to explain acid–base chemistry and other chemical phenomena.* Pearson stated, “Hard acids prefer to bind to hard bases, and

*For early discussions of the principles and theories of the HSAB concept, see R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581, and 643.

soft acids prefer to bind to soft bases.” Interactions between two hard or two soft species are stronger than those between one hard and one soft species. The three examples above can be interpreted in such terms, with reactions tending to favor hard–hard and soft–soft combinations.

Relative Solubilities

In these examples, the metal cation is the Lewis acid and the halide is the Lewis base. In the series of silver ion–halide reactions, the iodide ion is much softer (more polarizable) than the others and interacts more strongly with the silver ion, a soft cation. The result is a greater covalent contribution to the bonding in AgI relative to that with the other halides.

The lithium halides have solubilities roughly in the reverse order: $\text{LiBr} > \text{LiCl} > \text{LiI} > \text{LiF}$. The strong hard–hard interaction in LiF overcomes the tendency of LiF to be solvated by water. The weaker hard–soft interactions between Li^+ and 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 LiI is still much more soluble than LiF. Ahrland, Chatt, and Davies⁶³ organized these and other phenomena by dividing 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

Class (b) members are located primarily in a small region in the periodic table at the lower right-hand side of the transition metals. **Figure 6.14** identifies the elements that are always in class (b) and those commonly in class (b) when they have low oxidation states. The transition metals exhibit class (b) character in compounds in which their oxidation state is zero (primarily organometallic compounds). The class (b) ions form halides whose solubility is generally in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$; the solubility of class (a) halides in water is typically 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 opposite of the reactions of class (a) metal ions.

Ahrland, Chatt, and Davies explained the class (b) metals as having *d* electrons available for π bonding.* Elements farther left in the table have more class (b) character in low

FIGURE 6.14 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 from *Quarterly Reviews, Chemical Society*, issue 3, 12, 265–276 with permission from The Royal Society of Chemistry.)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1																	2
	3												B	C				10
	11																	18
	19		21				Mn	Fe	Co	Ni	Cu							36
	37		39			Mo	Tc	Ru	Rh	Pd	Ag	Cd				Te		54
	55			72		W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		86
	87			104														
																		71
																		103

*Metal–ligand bonding is discussed in Chapters 10 and 13.

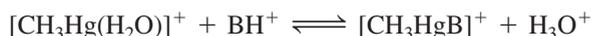
or zero oxidation states when more d electrons are present. Donor molecules or ions that have the most favorable enthalpies of reaction with class (b) metals are those that are readily polarizable and may have vacant d or π^* orbitals available for π bonding.

Coordination of Thiocyanate to Metals

We can now account for the two SCN^- bonding modes. The Hg^{2+} ion is much larger and more polarizable (softer) than the smaller, harder Zn^{2+} . The softer end of the thiocyanate ion is the sulfur. Consequently, the mercury ion $[\text{Hg}(\text{SCN})_4]^{2-}$ is a soft–soft combination, and the zinc ion $[\text{Zn}(\text{NCS})_4]^{2-}$ is a hard–hard combination, consistent with the HSAB prediction. Other soft cations such as Pd^{2+} and Pt^{2+} form thiocyanate complexes attached through the softer sulfur; harder cations such as Ni^{2+} and Cu^{2+} form N-bonded thiocyanates. Intermediate transition-metal ions can in some cases bond to either end of thiocyanate. For example, both $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ are known, forming an example of “linkage” isomers (Chapter 9).

Equilibrium Constants of Exchange Reactions

Consider the data in **Table 6.13** for reactions of aqueous methylmercury(II) cations



These may be considered *exchange reactions* in that they involve an exchange of water and base B on the mercury. They may also be considered examples of competition between H_2O and B for coordination at mercury—and also between H_2O and B for binding to H^+ . In reactions 1 through 4 the trend is clear: as the halide becomes larger and more polarizable ($\text{F}^- \rightarrow \text{I}^-$), the tendency for attachment to mercury(II) grows stronger—a soft–soft interaction between mercury(II) and the increasingly soft halide ion. Among the other examples, the relatively soft sulfur atoms in reactions 6 and 7 also can be viewed as leading to a soft–soft interaction with Hg^{2+} and a large equilibrium constant. In reactions 1 and 5, on the other hand, the harder F and O atoms from HF and H_2O are less able to compete for attachment to the soft mercury(II), and the equilibrium constants are small.

6.6.1 Theory of Hard and Soft Acids and Bases

Pearson⁶⁴ designated the class (a) metal ions of Ahrlund, Chatt, and Davies as *hard acids* and the class (b) ions as *soft acids*. Bases are also classified as hard or soft on the basis of polarizability: 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 reactants. Hard acids and bases are relatively small, compact, and nonpolarizable; soft acids and bases are larger and more polarizable. The hard acids include cations with a large positive charge (3+ or larger) or those whose

TABLE 6.13 Equilibrium Constants for Exchange Reactions of Mercury Complexes⁶⁵

Reaction	K (298 K)
1. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HF} \rightleftharpoons \text{CH}_3\text{HgF} + \text{H}_3\text{O}^+$	4.5×10^{-2}
2. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HCl} \rightleftharpoons \text{CH}_3\text{HgCl} + \text{H}_3\text{O}^+$	1.8×10^{12}
3. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HBr} \rightleftharpoons \text{CH}_3\text{HgBr} + \text{H}_3\text{O}^+$	4.2×10^{15}
4. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HI} \rightleftharpoons \text{CH}_3\text{HgI} + \text{H}_3\text{O}^+$	1×10^{18}
5. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}_3\text{O}^+$	5×10^{-7}
6. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{SH}^- \rightleftharpoons [\text{CH}_3\text{HgS}]^- + \text{H}_3\text{O}^+$	1×10^7
7. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HSCN} \rightleftharpoons \text{CH}_3\text{HgSCN} + \text{H}_3\text{O}^+$	5×10^6

d electrons are relatively unavailable for π bonding (e.g., alkaline earth ions, Al^{3+}). Hard acid cations that do not fit this description include Cr^{3+} , Mn^{2+} , Fe^{3+} , and Co^{3+} . Soft acids are those whose *d* electrons or orbitals are readily available for π bonding (neutral and 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 6.14** and **6.15** list bases and acids in terms of their hardness or softness.

The trends in bases are easier to see: fluoride is hard and iodide is soft. Again, more electrons and larger sizes lead to softer behavior. S^{2-} is softer than O^{2-} because it has more electrons spread over a 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 is larger. 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 6.6.2**.

TABLE 6.14 Hard and Soft Bases

Hard Bases	Borderline Bases	Soft Bases
		H^-
F^- , Cl^-	Br^-	I^-
H_2O , OH^- , O^{2-}		H_2S , SH^- , 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-}	$\text{S}_2\text{O}_3^{2-}$
NH_3 , RNH_2 , N_2H_4	$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_2	PR_3 , P(OR)_3 , AsR_3 , C_2H_4 , C_6H_6

Classifications from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

TABLE 6.15 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	$\text{B(CH}_3)_3$	BH_3 , Tl^+ , $\text{Tl(CH}_3)_3$
Al^{3+} , $\text{Al(CH}_3)_3$, AlCl_3 , AlH_3		
Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{3+}	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Rh^{3+} , Ir^{3+} , Ru^{3+} , Os^{2+}	Cu^+ , Ag^+ , Au^+ , Cd^{2+} , Hg_2^{2+} , Hg^{2+} , CH_3Hg^+ , $[\text{CO(CN)}_5]^{2-}$, Pd^{2+} , Pt^{2+} , Pt^{4+} , Br_2 , I_2
Ions with formal oxidation states of 4 or higher		Metals with zero oxidation state
HX (hydrogen-bonding molecules)		π acceptors: e.g., trinitrobenzene, quinines, tetracyanoethylene

Classifications from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

EXAMPLE 6.4

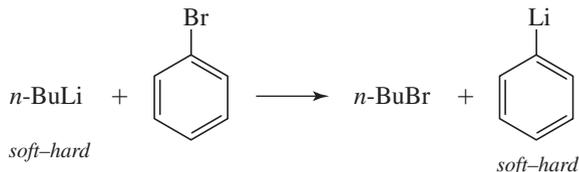
Is OH^- or S^{2-} more likely to form insoluble salts with 3+ transition-metal ions? Which is more likely to form insoluble salts with 2+ transition-metal ions?

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

- Will Cu^{2+} react more favorably with OH^- or NH_3 ? With O^{2-} or S^{2-} ?
- Will Fe^{3+} react more favorably with OH^- or NH_3 ? With O^{2-} or S^{2-} ?
- Will Ag^+ react more favorably with NH_3 or PH_3 ?
- Will Fe , Fe^{2+} , or Fe^{3+} react more favorably with CO ?

An acid or a base can be described as hard or soft and at the same time as strong or weak. Both characteristics must be considered to rationalize reactivity. For example, if the reactivity of two bases with similar softness is being compared, consideration of which base is stronger (from a Brønsted–Lowry perspective) can be helpful to assess which side of an equilibrium will be favored. For example, consider this classic organic reaction for the synthesis of phenyllithium.



Carbon-based nucleophiles are generally regarded as soft bases, and Li^+ is a hard acid. From this perspective alone, it would be difficult to rationalize that this reaction heavily favors the products, since the softness of the bases *n*-butyl and phenyl carbanions is similar. The significantly higher Brønsted–Lowry basicity of the *n*-butyl carbanion (pK_a of *n*-butane is ~50) relative to the phenyl carbanion (pK_a of benzene is ~43) plays a vital role in rationalizing the formation of phenyllithium.

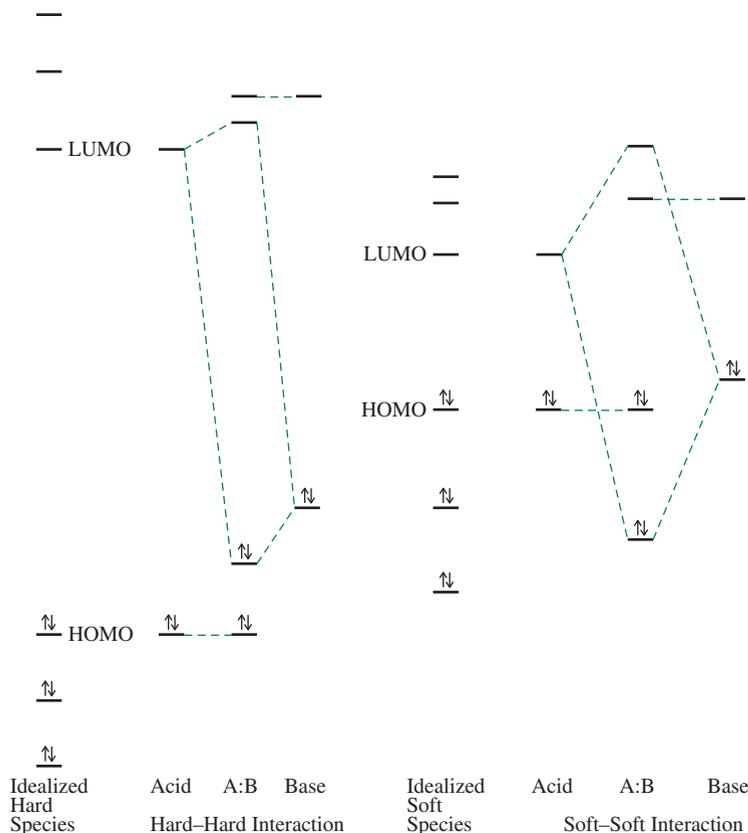
An oversimplified perspective considers the hard–hard interactions as primarily electrostatic (with a high ionic contribution), with the LUMO of the acid far above the HOMO of the base and relatively little change in orbital energies on adduct formation.⁶⁶ A soft–soft interaction involves HOMO and LUMO energies that are much closer and give a large change in orbital energies on adduct formation. Diagrams of such interactions, as shown in **Figure 6.15**, need to be used with caution. The small drop in energy in the hard–hard case only suggests a small covalent contribution to the bonding. Hard–hard interactions feature a relatively large ionic contribution that is not effectively represented in Figure 6.15. In this way, the small amount of stabilization suggested for hard–hard combinations often underestimates the bond strength. In many of the reactions described by the HSAB concept, the hard–hard interactions form stronger bonds relative to the soft–soft interactions.

6.6.2 HSAB Quantitative Measures

There are two major HSAB quantitative measures. One, developed by Pearson,⁶⁷ uses the hard–soft terminology and defines the **absolute hardness**, η , as half the difference between the ionization energy and the electron affinity (both in eV):

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

FIGURE 6.15 HOMO–LUMO Diagrams for Hard–Hard and Soft–Soft Interactions.



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 LUMO for a given molecule:

$$E_{HOMO} = -I \qquad E_{LUMO} = -A$$

Softness is defined as the inverse of hardness, $\sigma = \frac{1}{\eta}$. Because there are no electron affinities for anions, the values for the atoms and corresponding neutral molecules are used as approximate equivalents.

The halogens offer good examples of the use of these arguments. For the halogens, the trend in hardness (η) parallels the change in HOMO energies, because the LUMO energies are nearly the same, as shown in **Figure 6.16**. 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 the halogen molecules have very similar energies, and the HOMOs increase in energy from F_2 to I_2 . The absolute electronegativities decrease in the order $F_2 > Cl_2 > Br_2 > I_2$ as the HOMO energies increase. The hardness also decreases in the same order in which the difference between the HOMO and LUMO decreases. Data for a number of other species are given in **Table 6.16** and Appendix B-5.

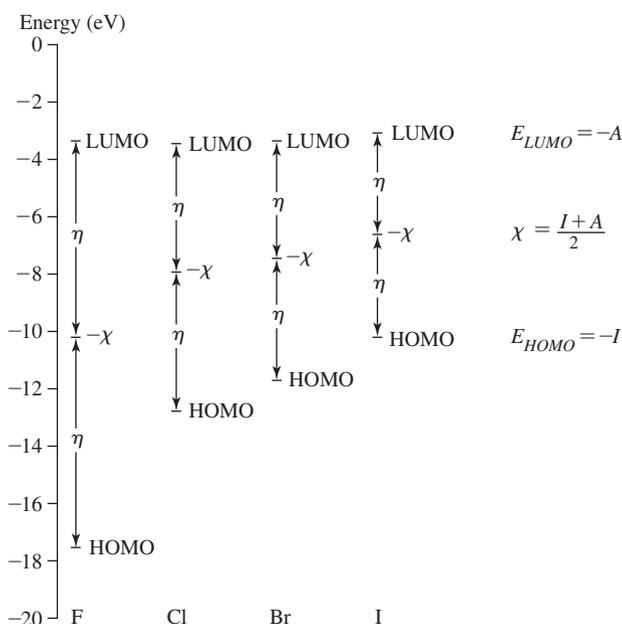


FIGURE 6.16 Energy Levels for Halogens. Relationships between absolute electronegativity (χ), absolute hardness (η), and HOMO and LUMO energies for the halogens.

EXERCISE 6.6

Confirm the absolute electronegativity and absolute hardness values for the following species, using data from Table 6.16 and Appendix B-5:

- Al^{3+} , Fe^{3+} , Co^{3+}
- OH^- , Cl^- , NO_2^-
- H_2O , NH_3 , PH_3

TABLE 6.16 Hardness Parameters (eV)

Ion	I	A	χ	η
Al^{3+}	119.99	28.45	74.22	45.77
Li^+	75.64	5.39	40.52	35.12
Na^+	47.29	5.14	26.21	21.08
K^+	31.63	4.34	17.99	13.64
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
PH_3	10.0	-1.9	4.1	6.0
F^-	17.42	3.40	10.41	7.01
Cl^-	13.01	3.62	8.31	4.70
Br^-	11.84	3.36	7.60	4.24
I^-	10.45	3.06	6.76	3.70

NOTE: The anion values are approximated as the same as the parameters for the corresponding neutral radicals or atoms. Data from R. G. Pearson, *Inorg. Chem.*, **1988**, 27, 734.

Drago and Wayland⁶⁸ proposed a quantitative system of acid–base parameters to account for reactivity by explicitly including electrostatic and covalent factors. This approach uses the equation $-\Delta H = E_A E_B + C_A C_B$ where ΔH is the enthalpy of the reaction $A + B \rightarrow AB$ 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 tendency to form covalent bonds. The subscripts refer to values assigned to the acid and base, with I_2 the reference acid and N,N -dimethylacetamide and diethyl sulfide as the reference bases. These values (in $kcal/mol$) 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 6.17** and Appendix B-6. Combining the values of these parameters for acid–base pairs gives the enthalpy of reaction ($kcal/mol$; multiplying by 4.184 J/cal converts to joules).

TABLE 6.17 C_A , E_A , C_B , and E_B Values ($kcal/mol$)

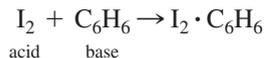
Acid	C_A	E_A
Trimethylboron, $B(CH_3)_3$	1.70	6.14
Boron trifluoride (gas), BF_3	1.62	9.88
Trimethylaluminum, $Al(CH_3)_3$	1.43	16.9
Iodine, I_2	1.00*	1.00*
Trimethylgallium, $Ga(CH_3)_3$	0.881	13.3
Iodine monochloride, ICl	0.830	5.10
Sulfur dioxide, SO_2	0.808	0.920
Phenol, C_6H_5OH	0.442	4.33
tert-butyl 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
Quinuclidine, $HC(C_2H_4)_3N$	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

*Reference values.

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

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 a low E_A . On the other hand, its high polarizability equips I_2 reasonably well for covalent interactions, 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.

The example of iodine and benzene shows how these parameters can be used:



$$-\Delta H = E_A E_B + C_A C_B \quad \text{or} \quad \Delta H = -(E_A E_B + C_A C_B)$$

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

The experimental ΔH is -1.3 kcal/mol, or -5.5 kJ/mol, 9% larger than the predicted value.⁶⁹ In many cases, the agreement between calculated and experimental enthalpies is within 5%. The agreement between the calculated and experimental values tends to improve with the strength of the adduct bond; the bonding in $I_2 \cdot C_6H_6$ is rather weak.

EXAMPLE 6.5

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

	E_A	E_B	C_A	C_B	$\Delta H(\text{kcal/mol})$	Experimental ΔH
Diethyl ether					$-([1.00 \times 0.963] + [1.00 \times 3.25]) = -4.21$	-4.2
Diethyl sulfide					$-([1.00 \times 0.339] + [1.00 \times 7.40]) = -7.74$	-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 6.7 Calculate the enthalpy of adduct formation predicted by Drago's E and C equation for the following combinations, and explain the trends in terms of the electrostatic and covalent contributions:

- BF_3 reacting with ammonia, methylamine, dimethylamine, and trimethylamine
- Pyridine reacting with trimethylboron, trimethylaluminum, and trimethylgallium

Drago's system emphasizes the two primary electronic factors involved in acid–base strength (the capability of a species to engage in electrostatic and covalent interactions) in his two-term enthalpy of reaction equation. Pearson put greater emphasis on the covalent factor. Pearson⁷⁰ proposed the equation $\log K = S_A S_B + \sigma_A \sigma_B$, with the inherent strength S modified by a softness factor σ . Larger values of strength and softness lead to larger equilibrium constants. Although Pearson attached no numbers to this equation, it does show the need to consider more than just hardness or softness in acid–base reactions. Absolute hardness is based on orbital energies, returns to a single parameter, and considers only gas-phase reactions. When E and C parameters are available for the reactions in question, quantitative comparisons regarding adduct bond strengths can be made. The qualitative HSAB approach, while sometimes challenging to apply due to the need to make judgments, provides a guide for predicting reactions. The terms *hard* and *soft* are entrenched in the chemical vernacular.

Solvation contributes to the driving force of many reactions, but neither the Drago nor the Pearson quantitative models take this factor into account. It is very difficult to develop broadly applicable models of reactivity. However, chemists continue to examine these important questions that probe the most fundamental contributions towards bond formation.

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C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley & Sons, New York, 2010, is an outstanding reference with respect to both tabulated data and discussion of methodology. G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond*, Oxford University Press, New York, 2009, provides an in-depth discussion of this topic. For an excellent review of superbases: *Superbases for Organic Synthesis: Guanidines, Amidines, and Phosphazenes and Related Organocatalysts*, Ishikawa, T., eds., Wiley, New York, 2009.

Problems

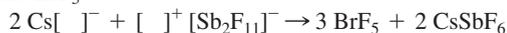
Additional acid–base problems are at the end of Chapter 8.

- 6.1 For each of the following reactions, identify the acid and the base. Also indicate which acid–base definition (Lewis, Brønsted–Lowry) applies. In some cases, more than one definition may apply.
- $\text{AlBr}_3 + \text{Br}^- \rightarrow \text{AlBr}_4^-$
 - $\text{HClO}_4 + \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{ClO}_4^-$
 - $\text{Ni}^{2+} + 6 \text{NH}_3 \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+}$
 - $\text{NH}_3 + \text{ClF} \rightarrow \text{H}_3\text{N} \cdots \text{ClF}$

- $2 \text{ClO}_3^- + \text{SO}_2 \rightarrow 2 \text{ClO}_2 + \text{SO}_4^{2-}$
 - $\text{C}_3\text{H}_7\text{COOH} + 2 \text{HF} \rightarrow [\text{C}_3\text{H}_7\text{C}(\text{OH})_2]^+ + \text{HF}_2^-$
- 6.2 For each of the following reactions, identify the acid and the base. Also indicate which acid–base definition (Lewis, Brønsted–Lowry) applies. In some cases, more than one definition may apply.
- $\text{XeO}_3 + \text{OH}^- \rightarrow [\text{HXeO}_4]^-$
 - $\text{Pt} + \text{XeF}_4 \rightarrow \text{PtF}_4 + \text{Xe}$
 - $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SeO}_4 \rightarrow \text{C}_2\text{H}_5\text{OH}_2^+ + \text{HSeO}_4^-$

- d. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{SH}^- \rightleftharpoons [\text{CH}_3\text{HgS}]^- + \text{H}_3\text{O}^+$
 e. $(\text{benzyl})_3\text{N} + \text{CH}_3\text{COOH} \rightarrow (\text{benzyl})_3\text{NH}^+ + \text{CH}_3\text{COO}^-$
 f. $\text{SO}_2 + \text{HCl} \rightarrow \text{OSO} \cdot \cdot \text{HCl}$

- 6.3 Baking powder is a mixture of aluminum sulfate and sodium hydrogencarbonate, which generates a gas and makes bubbles in biscuit dough. Explain what the reactions are.
 6.4 The conductivity of BrF_3 is increased by adding KF. Explain this increase, using appropriate chemical equations.
 6.5 The following reaction can be conducted as a titration in liquid BrF_3 :



- a. The ions in brackets contain both bromine and fluorine. Fill in the most likely formulas of these ions.
 b. What are the point groups of the cation and anion identified in part a?
 c. Is the cation in part a serving as an acid or base?
 6.6 Anhydrous H_2SO_4 and anhydrous H_3PO_4 both have high electrical conductivities. Explain.
 6.7 The gas-phase basicities for the nitrogen bases listed in Table 6.6 are uniformly less positive than the corresponding proton affinities. Explain.
 6.8 The proton affinities of acetone, diethylketone, and benzophenone are 812.0, 836.0, and 882.3 kJ/mol, respectively. Rationalize the ranking of these values. (Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5.)
 6.9 The gas-phase basicity of triphenylamine (876.4 kJ/mol) is less than that of triphenylphosphine (940.4 kJ/mol). Do you expect electronic or steric factors to contribute more to this difference? Explain. (Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5.)
 6.10 Correlation of gas-phase and aqueous-solution basicity data is instructive. Construct a graph of gas-phase basicity vs. pK_a of conjugate acids in water (like Figures 6.2 and 6.3) for the following Brønsted–Lowry bases using these data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5. Label each point clearly with the identity of the base.

	pK_a of Conjugate Acid	Gas-Phase Basicity (kJ/mol)
Methanol	−2.05	724.5
Ethanol	−1.94	746.0
Water	−1.74	660.0
Dimethylether	−2.48	764.5
Diethylether	−2.39	801.0

- a. Qualitatively, how well do these gas phase and solution data correlate? Explain.
 b. Rationalize the positions of the ethers on your graph relative to the alcohols and water.

- c. Qualitatively, how well do the gas phase and solution data correlate for the two ethers and the two alcohols? Are these trends the result of inductive or steric effects? Explain.

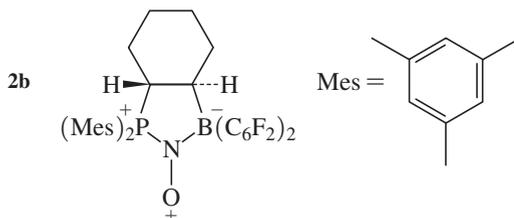
- d. Rationalize the seemingly paradoxical location of water in your graph relative to the other bases.
 6.11 Consider these BF_3 affinities for various sulfoxides from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 99. Rationalize this BF_3 affinity trend with inductive and resonance arguments.

Lewis base	Formula	BF_3 Affinity (kJ/mol)
Diphenylsulfoxide	Ph_2SO	90.34
Methyl phenyl sulfoxide	PhSOMe	97.37
Dimethyl sulfoxide	Me_2SO	105.34
Di- <i>n</i> -butyl sulfoxide	$(n\text{-Bu})_2\text{SO}$	107.60
Tetramethylene sulfoxide	$\text{cyclo}(\text{CH}_2)_4\text{SO}$	108.10

- 6.12 The development of new Lewis basicity scales is of ongoing interest. Maccarrone and Di Bella recently reported a scale of Lewis basicity that employs a zinc(II) complex as a reference Lewis acid (I. P. Oliveri, G. Maccarrone, S. Di Bella, *J. Org. Chem.*, **2011**, 76, 8879).
 a. What are the ideal characteristics of a reference acid discussed by these authors?
 b. Compare the relative Lewis basicities of quinuclidine and pyridine found by these authors to the BF_3 affinity for pyridine (Table 6.10) and the value for quinuclidine (150.01 kJ/mol). To what feature do these authors attribute the high basicities of these two nitrogen bases to their zinc(II) reference?
 c. What general trends do these authors report for alicyclic (that is, aliphatic and cyclic) and acyclic amines? How are these trends rationalized?
 6.13 If an equimolar mixture of $\text{P}(t\text{-C}_4\text{H}_9)_3$ and $\text{B}(\text{C}_6\text{F}_5)_3$ is mixed with 1 bar of the gas N_2O in bromobenzene solution, a white product is formed in good yield. A variety of NMR evidence has been gathered on the product: there is a single ^{31}P NMR resonance; ^{11}B and ^{19}F NMR are consistent with a 4-coordinate boron atom; and ^{15}N NMR indicates two nonequivalent nitrogen atoms. In addition, no gas is released in the reaction.
 a. Suggest the role of N_2O in this reaction.
 b. Propose a structure of the product. (See E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.*, **2009**, 131, 9918.)
 6.14 FLP chemistry continues to afford remarkable reactions that proceed without transition metals. Metal-free aromatic hydrogenation of *N*-bound phenyl rings can be achieved in the presence of H_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ to form *N*-cyclohexylammonium hydridoborate salts (T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.*, **2012**, 134, 4088).

- a. Sketch the reaction coordinate diagram in Figure 2 of this report, including the structures of intermediates and transition states.
- b. Discuss the hypothesized steps for initial addition of H^+ to the aromatic ring of *t*-BuNHPH.
- c. How does this diagram support the outcome of the reaction of *t*-BuNHPH, $B(C_6F_5)_3$, and H_2 in pentane (at 298 K) versus in refluxing toluene (383 K)?
- d. What happens if the utilized amine becomes *too* basic?

- 6.15** The ability of frustrated Lewis pairs to capture NO (nitric oxide) to afford aminoxyl radicals is a recent triumph of FLP chemistry (M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Peterson, G. Kehr, G. Erker, *J. Am. Chem. Soc.*, **2012**, *134*, 10156.) Use a molecular orbital argument to hypothesize why the N—O bond lengthens in complex **2b** relative to nitric oxide (HINT: Which orbital is likely the acceptor?).
- a. Use the arrow-pushing formalism to propose mechanisms for the reaction of **2b** with 1,4-cyclohexadiene, and of **2b** with toluene.
- b. Explain why C—O bond formation in the toluene reaction occurs exclusively at the primary carbon and not at a carbon atom within the aromatic ring.



- 6.16** Use the pK_a Slide Rule in P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.*, **2009**, *42*, 33 to answer these questions:
- a. Which forms a stronger hydrogen bond with water, HCN or HSCN?
- b. Identify two inorganic acids that are predicted to form strong hydrogen bonds with organic nitriles.
- c. Which organic acid in the Slide Rule is predicted to form the strongest hydrogen bond to organic sulfides?
- d. Water is a prototypical hydrogen bond donor. Classify the strengths of $A \cdots H_2O$ hydrogen bonds (for example, as strong, medium strong, medium, medium weak, or weak) with the following classes of acceptors: amines, triphosphines, sulfoxides, ketones, and nitro compounds.
- 6.17** The X-ray structure of $Br_3As \cdot C_6Et_6 \cdot AsBr_3$ (Et = ethyl) has been reported (H. Schmidbauer, W. Bublak, B. Huber, G. Müller, *Angew. Chem., Int. Ed.*, **1987**, *26*, 234).
- a. What is the point group of this structure?
- b. Propose an explanation of how the frontier orbitals of $AsBr_3$ and C_6Et_6 can interact to form chemical bonds that stabilize this structure.

- 6.18** When $AlCl_3$ and $OPCl_3$ are mixed, the product, $Cl_3Al—O—PCl_3$ has a nearly linear Al—O—P arrangement (bond angle 176°).

- a. Suggest an explanation for this unusually large angle.
- b. The O—P distance in $Cl_3Al—O—PCl_3$ is only slightly longer than the comparable distance in $OPCl_3$ even though the latter has a formal double bond. Suggest why there is so little difference in these bond distances. (See N. Burford, A. D. Phillips, R. W. Schurko, R. E. Wasylshen, J. F. Richardson, *Chem. Commun.*, **1997**, 2363.)

- 6.19** Of the donor–acceptor complexes $(CH_3)_3N—SO_3$ and $H_3N—SO_3$ in the gas phase,
- a. Which has the longer N—S bond?
- b. Which has the larger N—S—O angle?
- Explain your answers briefly. (See D. L. Fiacco, A. Toro, K. R. Leopold, *Inorg. Chem.*, **2000**, *39*, 37.)
- 6.20** Xenon difluoride, XeF_2 , can act as a Lewis base toward metal cations such as Ag^+ and Cd^{2+} .
- a. In these cases, do you expect the XeF_2 to exert its basicity through the lone pairs on Xe or those on F?
- b. $[Ag(XeF_2)_2]AsF_6$ and $[Cd(XeF_2)_2](BF_4)_2$ have both been synthesized. In which case, AsF_6^- or BF_4^- , do you expect the fluorines to act as stronger Lewis bases? Explain briefly. (See G. Tavcar, B. Zemva, *Inorg. Chem.*, **2005**, *44*, 1525.)

- 6.21** The ion NO^- can react with H^+ to form a chemical bond. Which structure is more likely, HON or HNO? Explain your reasoning.
- 6.22** The absorption spectra of solutions containing Br_2 are solvent dependent. When elemental bromine is dissolved in nonpolar solvents such as hexane, a single absorption band in the visible spectrum is observed near 500 nm. When Br_2 is dissolved in methanol, however, this absorption band shifts and a new band is formed.

- a. Account for the appearance of the new band.
- b. Is the 500 nm band likely to shift to a longer or shorter wavelength in methanol? Why?
- In your answers, you should show clearly how appropriate orbitals of Br_2 and methanol interact.

- 6.23** AlF_3 is insoluble in liquid HF but dissolves if NaF is present. When BF_3 is added to the solution, AlF_3 precipitates. Explain.
- 6.24** Why were most of the metals used in antiquity class (b) (*soft*, in HSAB terminology) metals?
- 6.25** The most common source of mercury is cinnabar (HgS), whereas Zn and Cd in the same group occur as sulfide, carbonate, silicate, and oxide. Why?
- 6.26** The difference between melting point and boiling point (in $^\circ C$) is given below for each of the Group IIB halides.

	F^-	Cl^-	Br^-	I^-
Zn^{2+}	630	405	355	285
Cd^{2+}	640	390	300	405
Hg^{2+}	5	25	80	100

What deductions can you draw?

- 6.27** a. Use Drago's *E* and *C* parameters to calculate ΔH for the reactions of pyridine and BF_3 and of pyridine and $B(CH_3)_3$. Compare your results with the reported experimental values

of -71.1 and -64 kJ/mol for pyridine— $B(CH_3)_3$ and -105 kJ/mol for pyridine— BF_3 .

- b. Explain the differences found in part a in terms of the structures of BF_3 and $B(CH_3)_3$.
- c. Explain the differences in terms of HSAB theory.
- 6.28** Repeat the calculations of the preceding problem using NH_3 as the base, and put the four reactions in order of the magnitudes of their ΔH values.
- 6.29** Compare the results of Problems 6.20 and 6.21 with the absolute hardness parameters of Appendix B-5 for BF_3 , NH_3 , and pyridine (C_5H_5N). What value of η would you predict for $B(CH_3)_3$? Compare NH_3 and $N(CH_3)_3$ as a guide.
- 6.30** CsI is much less soluble in water than CsF, and LiF is much less soluble than LiI. Why?
- 6.31** Rationalize the following data in HSAB terms:

	$\Delta H(\text{kcal})$
$CH_3CH_3 + H_2O \rightarrow CH_3OH + CH_4$	12
$CH_3COCH_3 + H_2O \rightarrow CH_3COOH + CH_4$	-13

- 6.32** Predict the order of solubility in water of each of the following series, and explain the factors involved.
- a. $MgSO_4$ $CaSO_4$ $SrSO_4$ $BaSO_4$
- b. $PbCl_2$ $PbBr_2$ PbI_2 PbS
- 6.33** In some cases CO can act as a bridging ligand between main-group and transition-metal atoms. When it forms a bridge between Al and W in the compound having the formula $(C_6H_5)_3Al$ —[bridging CO]— $W(CO)_2(C_5H_5)_2$, is the order of atoms in the bridge Al—CO—W or Al—OC—W? Briefly explain your choice.
- 6.34** Choose and explain:
- a. Strongest Brønsted acid: SnH_4 SbH_3 TeH_2
- b. Strongest Brønsted base: NH_3 PH_3 SbH_3
- c. Strongest base to H^+ (gas phase):
 NH_3 CH_3NH_2 $(CH_3)_2NH$ $(CH_3)_3N$
- d. Strongest base to BMe_3 : pyridine 2-methylpyridine 4-methylpyridine
- 6.35** B_2O_3 is acidic, Al_2O_3 is amphoteric, and Sc_2O_3 is basic. Why?
- 6.36** Predict the reactions of the following hydrogen compounds with water, and explain your reasoning.
- a. CaH_2
- b. HBr
- c. H_2S
- d. CH_4
- 6.37** List the following acids in order of their acid strength when reacting with NH_3 .
- BF_3 $B(CH_3)_3$ $B(C_2H_5)_3$ $B[C_6H_2(CH_3)_3]_3$
 $[C_6H_2(CH_3)_3] = 2,4,6\text{-trimethylphenyl}$
- 6.38** Choose the stronger acid or base in the following pairs, and explain your choice.
- a. CH_3NH_2 or NH_3 in reaction with H^+
- b. Pyridine or 2-methylpyridine in reaction with trimethylboron
- c. Triphenylboron or trimethylboron in reaction with ammonia

- 6.39** List the following acids in order of acid strength in aqueous solution:

a. $HMnO_4$ H_3AsO_4 H_2SO_3 H_2SO_4

b. $HClO$ $HClO_4$ $HClO_2$ $HClO_3$

- 6.40** Solvents can change the acid–base behavior of solutes. Compare the acid–base properties of dimethylamine in water, acetic acid, and 2-butanone.

- 6.41** HF has $H_0 = -11.0$. Addition of 4% SbF_5 lowers H_0 to -21.0 . Explain why SbF_5 should have such a strong effect and why the resulting solution is so strongly acidic that it can protonate alkenes.



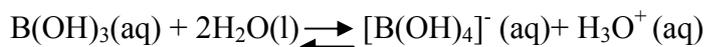
- 6.42** The reasons behind the relative Lewis acidities of the boron halides BF_3 , BCl_3 , and BBr_3 with respect to NH_3 have been controversial. Although BF_3 might be expected to be the strongest Lewis acid on the basis of electronegativity, the Lewis acidity order is $BBr_3 > BCl_3 > BF_3$. Consult the references listed below to address the following questions. (See also J. A. Plumley, J. D. Evanseck, *J. Phys. Chem. A*, **2009**, *113*, 5985.)

- a. How does the LCP approach account for a Lewis acidity order of $BBr_3 > BCl_3 > BF_3$? (See B. D. Rowsell, R. J. Gillespie, G. L. Heard, *Inorg. Chem.*, **1999**, *38*, 4659.)
- b. What explanation has been offered on the basis of the calculations presented in F. Bessac, G. Frenking, *Inorg. Chem.*, **2003**, *42*, 7990?

The following problems use molecular modeling software.

- 6.43** a. Calculate and display the molecular orbitals of NO^- . Show how the reaction of NO^- and H^+ can be described as a HOMO–LUMO interaction.
- b. Calculate and display the molecular orbitals of HNO and HON. On the basis of your calculations, and your answer to part a, which structure is favored?
- 6.44** Calculate and display the frontier orbitals of Br_2 , methanol, and the Br_2 –methanol adduct to show how the orbitals of the reactants interact.
- 6.45** a. Calculate and display the molecular orbitals of BF_3 , NH_3 , and the F_3B – NH_3 Lewis acid–base adduct.
- b. Examine the bonding and antibonding orbitals involved in the B–N bond in F_3B – NH_3 . Is the bonding orbital polarized toward the B or the N? The antibonding orbital? Explain briefly.
- 6.46** Section 6.4.5 includes a diagram of a halogen bond between Br_2 and acetylene.
- a. Use sketches to show how a π orbital of acetylene interacts with the LUMO of Br_2 to form the adduct.
- b. Calculate and display the molecular orbitals of the acetylene– Br_2 adduct. Describe the interactions that you observe between the π orbitals of acetylene and orbitals of Br_2 .

In aqueous solution, boric acid behaves as a weak acid (pKa 9.1) and the following equilibrium is established:



(a) Draw the structures of B(OH)_3 and $[\text{B(OH)}_4]^-$ (b) How would you classify the acidic behaviour of B(OH)_3 ? (c) The formula of boric acid may also be written as H_3BO_3 ; compare the acidic behaviour of this acid with that of H_3PO_3 .

2. When NaCN dissolves in water, the resulting solution is basic. Account for this observation given that pKa for HCN is 9.31.

3. Write equations to illustrate the amphoteric behaviour of $[\text{HCO}_3]^-$ in aqueous solution.

4. Which of the following oxides are likely to be acidic, basic or amphoteric in aqueous solution: (a) MgO; (b) SnO; (c) CO_2 ; (d) P_2O_5 ; (e) Sb_2O_3 ; (f) SO_2 ; (g) Al_2O_3 ; (h) BeO?

5. NaOH is a strong base but ClOH is a strong acid. Explain

6. SnCl_2 can act both as a Lewis acid and Lewis base. Explain

7. The dissolved iodine looks violet in non coordinating solvent like carbon tetrachloride while it looks brown in coordinating solvents like alcohols. Explain why?

8. The Lewis acid strength runs in the sequence:



9. SnCl_2 and SO_2 can act as both Lewis and Lewis bases. Explain?

10. Perchloric acid is a very strong acid while periodic acid is a weak acid.

11. B(OR)_3 is a weaker acid than B(R)_3