

Lewis Acid-Base Theory

William B. Jensen
University of Wisconsin
Madison, Wis. 53706

a reprint from Chemistry

Vol. 47, March 1974, pp. 11-14
April 1974, pp. 13-18
May 1974, pp. 14-18

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Part I Development

At the end of the 19th century the German chemist Wilhelm Ostwald spoke of a chemistry without substances. By this, he meant a chemistry whose general concepts did not depend on the properties of a particular element or substance. For example, originally oxidation and reduction were concepts that described the properties of a specific substance, oxygen. When something was oxidized it meant oxygen was added and when something was reduced, oxygen was removed.

Today most chemistry students use these terms to describe the loss and gain of electrons in a particular kind of chemical reaction. Most examples of adding or removing oxygen can be rationalized as special cases of this kind of electron transfer. Oxidation and reduction are general concepts and no longer depend on the properties or even the presence of oxygen. Similarly, the fulfillment of Ostwald's vision can be seen in the development of acid-base theory.

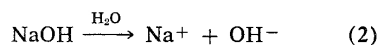
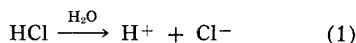
Early Theories

For a long time the exact meanings of the terms acid and base were vague. The terms were developed to classify substances having similar kinds of experimental behavior. Thus, all substances that were acids underwent similar chemical reactions, such as giving indicators the same color, and these reactions were very different from the typical basic reactions. More importantly, however, when an acid and a base reacted with one another, they destroyed or neutralized each other's characteristic acidic or basic properties. Acid-base theory was developed to clarify and explain this experimental behavior (1).

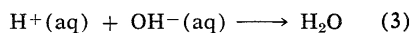
Probably the first attempt to explain the origin of acidity was made in the 18th century by the French chemist, Lavoisier, who claimed that all acids depend upon the presence of oxygen for their acidic properties. The English chemist, Davy, however, soon showed that, among other exceptions, hydrochloric acid, HCl, contained no oxygen and yet exhibited very definite acid behavior.

Arrhenius Definitions. Chemists who followed Davy began to think of hydrogen as the essential ingredient of acids. This idea persisted during the 19th century, and by

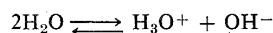
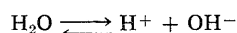
1887 the Swedish chemist, Arrhenius, developed his ionic theory that defined an acid as a substance which gave hydrogen ions on dissociation in water, and a base as a substance which gave hydroxide ions. Thus, HCl was an acid and NaOH was a base:



Neutralization of an acid by a base was the reaction of these two ions to form water:



Solvent System. At the beginning of the 20th century, chemists began to do a great deal of work in nonaqueous solvents, such as liquid ammonia and liquid sulfur dioxide. To classify the reactions occurring in these solvents, they used analogies based on reactions which take place in water, including those of Arrhenius acids and bases. Each solvent was considered to undergo a small amount of dissociation into a solvent cation and anion. In the case of water these products are H^+ and OH^- or, more accurately H_3O^+ and OH^- because, in reality, the hydrogen ion never exists unsolvated in solution. However, the hydronium ion, H_3O^+ , is often abbreviated as H^+ , as in Equations 1 and 3.



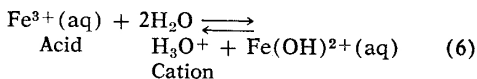
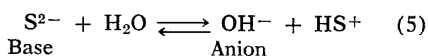
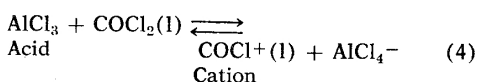
From this standpoint, an Arrhenius acid was merely a species which, on dissociation in water, caused an increase in concentration of the solvent cation, H_3O^+ , and an Arrhenius base was a species which, on dissocia-

Table I. Solvent System Definitions

Solvent	Cation	Anion	Typical acid	Typical base	Neutralization
H_2O	H^+	OH^-	HCl	NaOH	$\text{HCl} + \text{NaOH} \rightleftharpoons \text{NaCl} + \text{H}_2\text{O}$
$\text{NH}_3(\text{l})$	NH_4^+	NH_2^-	NH_4Cl	KNH_2	$\text{NH}_4\text{Cl} + \text{KNH}_2 \rightleftharpoons \text{KCl} + 2\text{NH}_3$
$\text{SO}_2(\text{l})$	SO^+	SO_3^-	SOCl_2	Na_2SO_3	$\text{SOCl}_2 + \text{Na}_2\text{SO}_3 \rightleftharpoons 2\text{NaCl} + 2\text{SO}_2$
$\text{COCl}_2(\text{l})$	COCl^+	Cl^-	AlCl_3	KCl	$(\text{COCl})^+(\text{AlCl}_2)^- + \text{KCl} \rightleftharpoons \text{KAlCl}_4 + \text{COCl}_2$
$\text{N}_2\text{O}_4(\text{l})$	NO^+	NO_2^-	NOCl	AgNO_3	$\text{NOCl} + \text{AgNO}_3 \rightleftharpoons \text{AgCl} + \text{N}_2\text{O}_4$

tion, caused an increase in the concentration of the solvent anion, OH^- . Neutralization (Equation 3) was the reaction between solvent cation and anion to produce the solvent itself. Any species which functioned similarly on dissociation in another solvent could be viewed as an acid or base in that solvent (Table I).

This concept of acids and bases was later extended to include those species which increased the solvent cation or anion concentration not only by dissociation, but by decomposing some of the solvent itself, that is, by causing solvolysis. Thus, aluminium trichloride, AlCl_3 , became an acid in liquid phosgene, COCl_2 , and species such as S^{2-} and Fe^{3+} became bases and acids when they underwent hydrolysis in water:

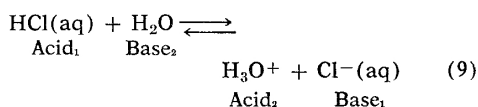
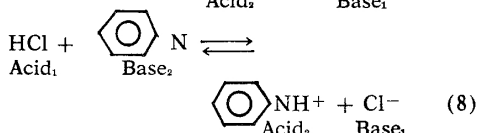
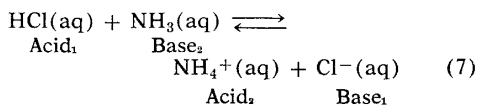


According to this concept, acid and base properties depend on the specific solvent involved and, thus, it became known as the solvent system definition of acids and bases.

Brönsted-Lowry Definitions. The solvent system definitions, however, failed to include many substances, particularly certain organic compounds that exhibit basic behavior. In addition, they made both the specific properties of the solvent and the phenomenon of ionic dissociation central to acid-base behavior and failed to recognize that acid-base reactions can occur in the gas phase and in nonionizable solvents such as benzene too. Hence, in 1923, J. N. Brönsted and T. M. Lowry each independently offered a new set of definitions. They defined an acid as any species that donates a proton to another species in a chemical reaction and a base as any species that accepts this proton. Because a proton is a hydrogen ion, the Arrhenius definitions are actually a special case of the Brönsted-Lowry definitions. An Arrhenius acid is a Brönsted acid that has dissociated in water by transferring its proton to the solvent: $\text{HB} + \text{H}_2\text{O} \rightleftharpoons \text{B}^- + \text{H}_3\text{O}^+$.

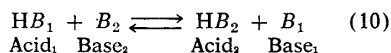
The definition of an acid as a proton donor allows such transfers to occur in inert solvents and in the gas phase, as well as in solvents having H^+ as their characteristic solvent cation. Because the Arrhenius base, OH^- , accepts a proton in neutralization

(Equation 3), it is also apparent that it is still a base according to the Brönsted definitions. The difference is that it is no longer the only base that can exist in water. Any species, molecular or ionic, that can accept a proton, whether in solution or in a gas phase reaction, is now considered a base. This includes ammonia, pyridine, and even water itself:



At equilibrium, Equation 7 can be visualized as a competition for the proton between Cl^- (base₁) and NH_3 (base₂). When Cl^- has the proton, it forms HCl , a potential proton donor, and, therefore, an acid. When NH_3 has the proton it forms the acid NH_4^+ . The potential acid formed by a base when it accepts a proton is called its conjugate acid, and the sets HCl (acid₁), Cl^- (base₁), and NH_4^+ (acid₂), NH_3 (base₂) are said to be conjugate acid-base pairs. The weaker base loses the proton more easily and is therefore the conjugate base of the stronger proton donor, or acid. Hence, the rules: Weak acids have strong conjugate bases; strong acids have weak conjugate bases.

One can see similar relationships for Equations 8 and 9, which can be expressed in general terms:

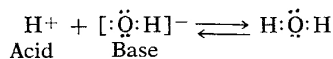


If the Brönsted definitions are applied to Equations 4, 5, and 6, we can see that the S^{2-} ion is still considered to be a base, but the reactions of AlCl_3 with liquid phosgene and of Fe^{3+} with water are no longer considered acid-base reactions.

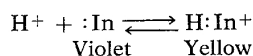
Lewis Definitions. Though Brönsted and Lowry generalized the idea of a base so that it no longer depended upon a specific substance, OH^- , or a specific solvent, their definition of an acid still depended upon the specific properties of the proton or hydrogen ion. In the same year, 1923, the American chemist G. N. Lewis took the next logical step—generalizing the definition of an acid. By this time, chemists realized that, to a first

concepts of acids and bases evolved. Lewis summarized this behavior for acids by saying (3) that they neutralize bases, have similar effects on indicators, displace one another in chemical reactions, and act often as catalysts.

Thus, for example, the Arrhenius base NaOH colors violet a water solution of the indicator crystal violet. The Arrhenius acid HCl neutralizes the base, and an excess of it causes the indicator to turn yellow. We can describe the reactions as follows:

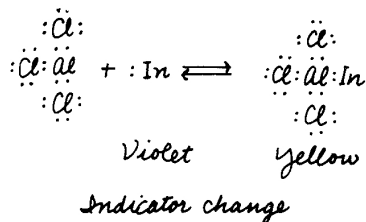
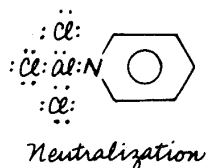
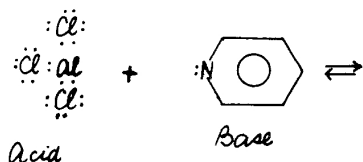


Neutralization



Indicator change, where :In
is a molecule of crystal violet

The Bronsted-Lowry base, pyridine, also colors violet a solution of crystal violet in chlorobenzene. When the Lewis acid, AlCl₃, is added, the basic properties of the pyridine solution gradually disappear, and an excess of AlCl₃ changes the indicator to yellow. This can be represented in a similar manner as:



WILLIAM B. JENSEN, whose drawings of famous chemists have illustrated several Chemistry articles, is interested in chemical curriculum and instruction and is currently working for a doctorate in inorganic chemistry at the University of Wisconsin.

AlCl₃ also can undergo displacement reactions and can function as a catalyst, as will be seen in Part 2.

Although the terms acid-base theory and acid-base definition have been used interchangeably throughout this discussion, the word theory actually is somewhat misleading. The Arrhenius, Bronsted-Lowry, and solvent system concepts are not theories as much as they are definitions. Unlike quantum mechanics or thermodynamics, they do not attempt to describe how chemical reactions take place in terms of the fundamental properties of matter. Rather, like chemical nomenclature, they help to organize and label the components of chemical systems. Hopefully, good acid-base definitions can function as something more than labels. On one hand, they should be specific enough to group substances accurately according to the experimental behavior characteristic of acids and bases, and on the other, they should be broad enough to suggest analogies and correlations among chemical phenomena which were not apparent before.

All of the definitions discussed so far are able to do this for certain specific chemical systems, and it might be argued that there can be no such thing as a right or wrong set of acid-base definitions. The set chosen depends only on what is to be described. This point of view is true in a sense, but if we wish to look at chemistry as a whole and to obtain a maximum overview of chemical phenomena, the Lewis definitions are superior by far. This should come as no surprise, for we have seen how the Lewis definitions were able to correlate the behavior of all of the chemical systems treated by the other acid-base definitions as well as systems not covered by them; for example, the AlCl₃-pyridine system and the SO₂-CaO system.

With the Lewis definitions, the terms acid and base have become general concepts— independent, as Ostwald would say, of the properties of any specific element or substance. More importantly, they are now stated in terms of one of the fundamental features of chemical change, electron rearrangement. It is to this single feature that they owe their ability to organize and unify the facts of chemistry—an ability we will examine in greater detail in Part 2.

Suggested Reading

- (1) Day, C. M., Selbin, J., "Theoretical Inorganic Chemistry," 2nd ed., chap. 9, 1969, Reinhold Books, New York, N.Y.
- (2) Lewis, G. N., "Valence and the Structure of Atoms and Molecules," p 141, 1966, Dover, New York, N.Y.
- (3) Lewis, G. N., *J. Franklin Inst.*, 1938, 226, 293.
- (4) Luder, W. F., Zuffanti, S., "The Electronic Theory of Acids and Bases," 2nd. ed., chap 1, 1961, Dover, New York, N.Y.

Lewis Acid-Base Theory

Part II. Applications

The Lewis acid-base definitions are often summarized as: A Lewis acid is any species (atom, molecule, or cation) which can accept a share in a pair of electrons from another species in a chemical reaction; a Lewis base is any species (atom, molecule, or anion) which can donate a share in a pair of electrons to another species in a chemical reaction. Before we see how effective these definitions can be in organizing the facts of chemistry, we should examine how best to interpret their meaning.

The first point to be considered is the impression, which many elementary textbooks give, that a Lewis acid accepts electrons to complete an octet of electrons in the outer shell of its central atom. Although many acids conform to this rule, quantum mechanics tells us that the number of electrons in the outer shell of an atom can equal up to $2n^2$, where n is the principal quantum number of the shell. The orbitals of these shells mix when atoms combine with one another and produce valence shells in the resulting molecules which have electron capacities that are often much greater than eight. Table I summarizes these facts for several periods of elements and lists for each period some examples of molecules and complex ions along with the number of valence electrons around the central atom in each.

It can be seen that the octet rule is actually an upper limit on the number of electrons which holds rigorously only for Period 2. Most elements beyond Period 2 fail to attain their quantum mechanically allowed maximum of valence electrons. The reasons for this vary. The increased repulsions among the electron pairs in the valence shell may outweigh any gains in bonding energy obtained by adding another pair to the shell, or it may simply be stereochemically impossible to squeeze any more ligands around the central atom. In any case, the important point is that, except for Period 2 elements, the octet rule is not a valid criterion for determining whether a species is electron deficient and, consequently, whether it is a good Lewis acid.

The second point to be considered is the meaning of the terms accept and donate a share in a pair of electrons. These terms are usually taken to mean that a Lewis acid and

base form a coordinate covalent bond with one another, or equivalently in molecular orbital theory, a molecular orbital. However, these labels can be applied to a range of bond types, from the homonuclear bond in H_2 , in which the electrons are shared equally, to the highly polar bond in HF , in which the more electronegative F atom accepts the greater amount of electron density from the pair. This variation in bond type can be represented by assuming the continuum in Figure 1, which shows the interaction between a series of simple acids, A , and bases, B .

At the far right of the continuum is the limiting case in which the electron pair is shared equally between A and B , as in H_2 . To the left, however, the pair becomes more and more centered on B , as in HF . Finally, at the extreme left, is the limiting case in which the pair has become essentially localized on B , as in NaF . Classically, the bonds on the far right of the continuum are designated as covalent, those in the center, polar covalent, and those on the far left, ionic. The key point is that, as the diagram implies, covalent, polar covalent, and ionic bonds do not differ in kind but only in degree, and there may be some justification for applying the Lewis definitions to all interactions where one species provides an electron pair for a bond, regardless of where that bond lies on the continuum.

This continuity is often disguised by the fact that as one approaches the far left of the continuum, it is usually possible to abandon the quantum mechanical model necessary for describing covalent bonding for a more simplistic model involving Coulomb's law and the electrostatic attraction of point charges. This switch to a simpler model creates the impression that a corresponding discontinuity in bond type has occurred and that there are two distinct and unrelated kinds of bonds—covalent and ionic.

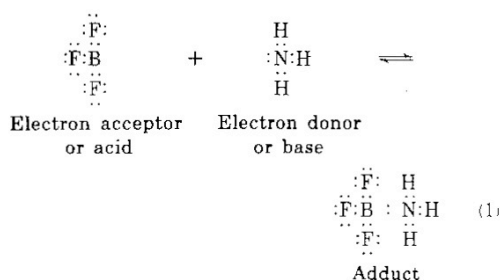
Table I

Period	n	$2n^2$	Example ions and molecules
1	1	2	$H:H$ ($2e$)
2	2	8	BF_3 ($6e$), CH_4, H_2O ($8e$)
3	3	18	PF_5 ($10e$), SF_6 ($12e$)
4	4	32	TiF_6^{-2} ($12e$), $Ni(NH_3)_6^{+2}$ ($20e$)
5	5	50	$SnCl_6^{-2}$ ($12e$), $Mo(CN)_8^{-4}$ ($18e$)
6	6	72	OsF_8 ($16e$)

Given that the different types of bonds represent only a difference in degree, it is still reasonable to ask whether this continuous variation in bond type can cause a corresponding variation in the behavior of Lewis acids and bases located at different extremes of the continuum. We will explicitly consider the answer to this question in Part III. There we will find that far from being a weakness in the Lewis definitions, this variation provides us with a means of making important predictions about acid-base reactions. For the time being, however, we will apply the Lewis definitions in a formal sense and will not consider whether the bonds formed lie to the left or to the right of the continuum of Figure 1.

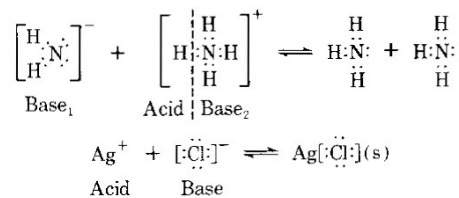
Inorganic Chemistry

Lewis acids are also called electron acceptors, and Lewis bases, electron donors. The reaction product of the two may be called an adduct, an addition compound, a coordination complex, or an acid-base complex.



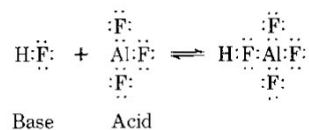
The adducts formed by neutralization reactions like those in Figure 1 can function, in turn, as Lewis acids or bases toward other substances. They also can undergo various displacement reactions in which the original acid-base components of the adduct are replaced by another Lewis acid or base or are interchanged with the components of another adduct. These displacement reactions are summarized in Table II.

It can be seen that Brønsted acids are actually adducts of the Lewis acid, H^+ , and that Brønsted-Lowry displacement reactions, as written in Equation 10 of Part I, are all Lewis base displacements. The more stable the Lewis adduct, the weaker it is as a Brønsted acid and, conversely, the weaker the adduct, the stronger it is as a Brønsted acid. Also, if the solvation of the ions is ignored, all neutralizations of the solvent cation and anion in the solvent system, as well as all interactions of a cation with an anion, can be viewed as being either direct Lewis neutralization reactions or displacement reactions. For example:

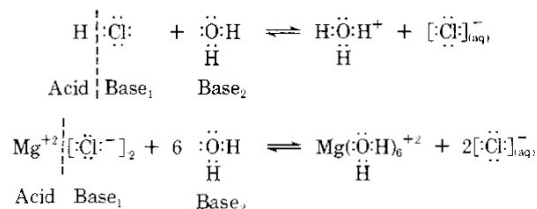


The interpretation of chemical reactions in terms of the Lewis acid-base definitions can be extended further to include the following phenomena:

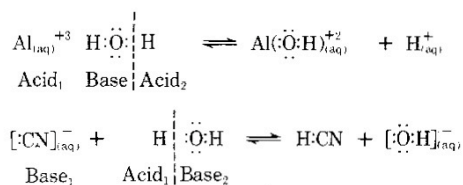
Solubility interactions in which a complex of definite stoichiometry is formed, for example, in the dissolution of AlF_3 in anhydrous liquid HF,



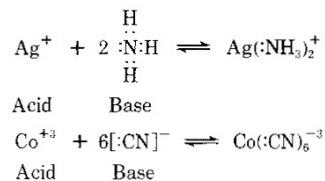
Ionic dissociation in a solvent,



Solvolysis reactions,

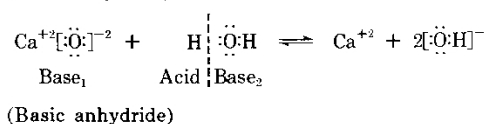
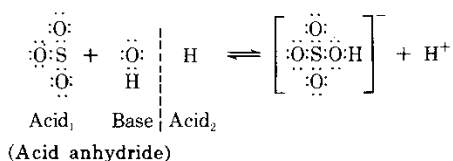


The formation of metal complexes,

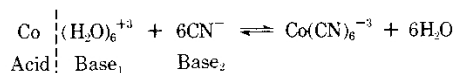


In a dissociation reaction the solvent molecule is able to act as an acid or a base, and is able to cause a displacement reaction in the solute adduct, giving as products charged adducts called solvated ions. In a solvolysis reaction, on the other hand, the solute adduct or, more commonly, one of the products of its dissociation, is a strong enough Lewis acid or base to cause a displacement reaction

in the solvent itself. Still other common examples of solvolysis are the reactions of the so-called acidic and basic anhydrides with water:

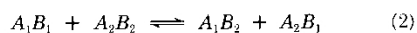


In the case of metal complex formation, the Lewis base is usually called a ligand. When complex formation occurs in water or some other solvent, the reaction really is a Lewis base displacement in which the ligand competes with the solvent for the metal cation or Lewis acid. The reaction between Co^{+3} and CN^{-} in water actually should be written:

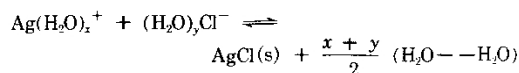


Special cases of these phenomena are also classified as acid-base reactions according to the Arrhenius, Brønsted-Lowry, and solvent system definitions, but only the Lewis definitions are able to correlate all of them.

As seen from the above examples, the solvent itself often plays the role of an acid or base when reactions occur in solution. In fact, simple neutralizations, like Equation 1, seldom occur except in the gas phase or in very inert solvents. When we consider the effects of the solvent for reactions taking place in solution, including both the solvation of the anion as well as the cation for charged species (not illustrated in examples), most of the reactions take the form:



where the solvent functions as either A_2 or B_1 , or both. For example:

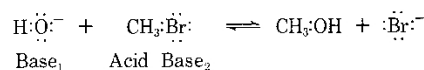


Water and other polar solvents are able to play this joint role because they have both acidic and basic sites on their molecules. The positive end of any polar molecule is electron deficient and, hence, behaves as a weak Lewis acid. The negative end is electron rich

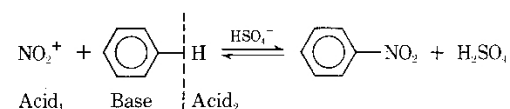
and behaves like a weak Lewis base. Water is able to act as a base via the lone pairs on its oxygen atom and as an acid via hydrogen bonding. Though most of these solute-solvent interactions are ion-dipole or dipole-dipole in nature and weaker than most chemical bonds, they are, nevertheless, important in looking at the total acid-base picture in solutions.

Organic Chemistry

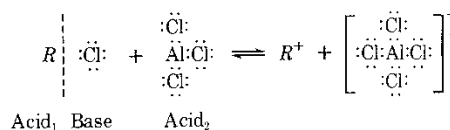
The Lewis definitions are used extensively in organic chemistry where a Lewis acid is called an electrophile (electron lover) and a Lewis base a nucleophile (nucleus lover). Organic nucleophilic reactions are Lewis base displacements:



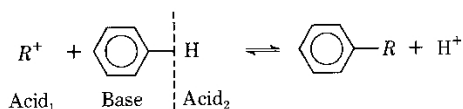
and electrophilic reactions are acid displacements:



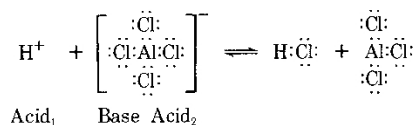
Actually, these reactions as written are really a summary of a number of intermediate steps which, in themselves, are each acid-base reactions. Electrophilic reactions often involve a Lewis acid acting as a catalyst, which is used to prepare the attacking acid or electrophile. AlCl_3 , for example, can be used with an alkyl chloride (R is CH_3 , C_2H_5 , C_3H_7 , and so on) to prepare a carbonium ion (R^{+}):



which then acts as the displacing acid:



The displaced acid, H^{+} , in turn, reacts with the AlCl_4^{-} , regenerating the original catalyst.

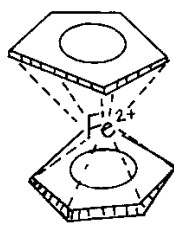


As pointed out in Part I, the ability to function as a catalyst was one of the experimental criteria of acidic behavior.

Several detailed mechanisms for nucleophilic substitutions have also been distinguished and are commonly referred to as the S_N1 and S_N2 mechanisms. Descriptions of them can be found in any standard organic textbook (6). Analogous base displacement mechanisms exist in inorganic chemistry (4).

Other Applications

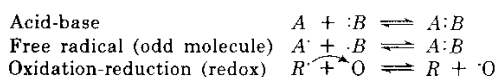
Some authors prefer more general definitions of Lewis acids and bases: A Lewis base is any substance which has electron density that can be shared with another substance in a chemical reaction, and a Lewis acid is any substance capable of accepting electron density from a Lewis base (1). This definition allows us to consider as acid-base reactions those in which the function of individual electron pairs is not obvious. Examples of this would be the formation of such sandwich compounds as ferrocene in which the Fe(II) ion accepts electron density from the π electrons on two cyclopentadienyl ions, $C_5H_5^-$, or charge transfer complexes like that between benzene and iodine, in which the π rings on the benzene are the electron donors. Such bases as benzene and the cyclopentadienyl ion are sometimes called π bases.



Ferrocene

An enormous amount of chemistry can be classified as acid-base. Organic electrophilic and nucleophilic reactions, solvation, dissociation, and solvolysis interactions, and coordination chemistry are all correlated as acid-base reactions by the Lewis definitions. There are, however, other classes of reactions in chemistry, and it is interesting to see how acid-base reactions relate to them.

Commonly, chemical reactions are classified in terms of particle interchanges (synthesis reactions, single decomposition reactions, and so forth), as were Lewis displacement reactions in Table II. However, it is also possible to classify reactions in terms of the type of electron rearrangement occurring in the reaction. We have been using such an electronic classification in grouping the reactions we have been discussing as acid-base. If we consider the other major types of electron rearrangement, to a first approximation, all elementary bimolecular chemical reactions can be electronically classified as (3):



Common chemical reactions can usually be

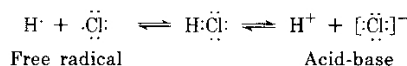
Table II. Classification of Lewis Acid-Base Reactions^a

Name	General reaction	Example
Neutralization	$A + :B \rightleftharpoons A:B$	$BF_3 + :NH_3 \rightleftharpoons F_3B:NH_3$
Base displacement	$A:B_1 + :B_2 \rightleftharpoons A:B_2 + :B_1$	$Cu(:NH_3)_4^{+2} + 2:OH^- \rightleftharpoons Cu(:OH)_2 + 4:NH_3$
Acid displacement	$A_1:B + A_2 \rightleftharpoons A_2:B + A_1$	$CO_2 + H:OH \rightleftharpoons H^+ + HCO_3^-$
Double acid-base displacement	$A_1:B_1 + A_2:B_2 \rightleftharpoons A_1:B_2 + A_2:B_1$	$BF_3H^- + BH_3F^- \rightleftharpoons BF_4^- + BH_4^-$

^a These would traditionally be called synthesis, single decomposition, and double decomposition reactions

shown to be a combination of simpler elementary reactions which fall into one of these categories.

A free radical reaction involves formation of a bond in which both reacting species donate an electron. The resulting bond cannot be distinguished from that formed in an acid-base reaction. Hydrochloric acid, HCl, for example, can be formed either way:



The free radical route is involved in the photochemical reaction of H_2 and Cl_2 and the acid-base route is involved when HCl gas is driven off from a boiling hydrochloric acid solution.

Redox reactions can be considered a limiting case of both acid-base and free radical reactions. To make this clearer, take the case of acid-base reactions and assume the continuum in Figure 2, which represents the extent of electron rearrangement occurring in a reaction between acid, A, and base, B. Notice that this figure is an extension of Figure 1. Most of the continuum would consist of

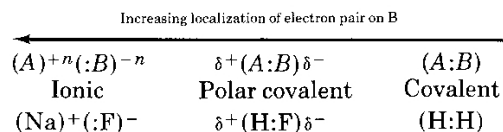
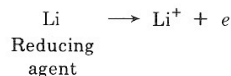


Figure 1. A classification of chemical bonds

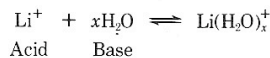
Lewis acid-base reactions in which bonds of varying polarity are formed as the electron density is shifted more and more away from the base and toward the acid. For example, more and more electron rearrangement is needed to form the product from the reactants.

At one extreme, where the base retains most of its electron density, is simple electrostatic attraction of two species, such as ions, involving little or no electron rearrangement. At the other extreme, the electron density of the base is completely transferred to the acid, and the base becomes a reducing agent, as a limiting case and the acid, an oxidizing agent. Some caution is advisable, however. Too little is known about the details of chemical reactions at the present to decide where one class of reactions begins and the other ends, and many reactions can be described formally in several ways. For example, many of the so-called redox reactions which are balanced in terms of net electron loss and gain do not really involve a physical transfer of electrons. They are actually a summary of several simpler steps which are acid-base or free radical in nature (for examples, see ref 5).

But the major point still remains that, for simple, elementary reactions, acid-base and redox reactions are closely related. They are both manifestations of the relative attraction of two species for electrons—a fact which is emphasized by the manner in which they often complement each other in chemical systems. Thus, when a species acts as a reducing agent by giving up electrons to another species, its reaction product often attempts to compensate partially for the lost electron density by acting, in turn, as a Lewis acid. Hence, when Li is oxidized



the resulting Li^+ stabilizes itself by acting as a Lewis acid; for example, by solvating itself:



The converse is true for oxidizing agents. Their reaction product tends to stabilize its newly acquired electron density by partially donating it to another species—that is, by functioning as a Lewis base:

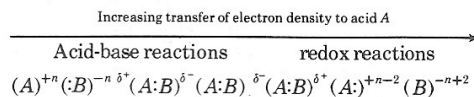
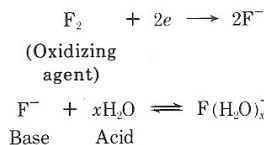
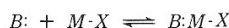
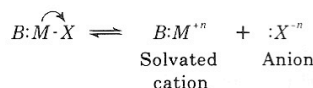


Figure 2. Partial electronic classification of chemical reactions

Similarly many covalent compounds ionize in solution first by coordinating with the solvent. If M is the acidic portion of the solute MX , and if the solvent B can act as a Lewis base, then the reaction is:



The electron density which M gains from B allows it to transfer all of the electron density of the MX bond to X , and the compound ionizes:



In the first step, M obtained electron density by acting as a Lewis acid. In the second step, it disposed of its excess electron density by acting as a reducing agent toward X . This interrelation between acid-base and redox reactions is summarized in Figure 3 (2).

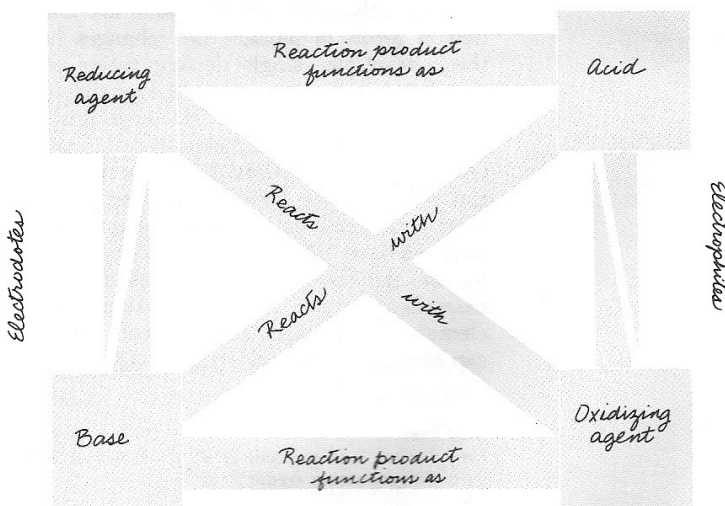


Figure 3. The complementary nature of redox acid-base reactions (2)

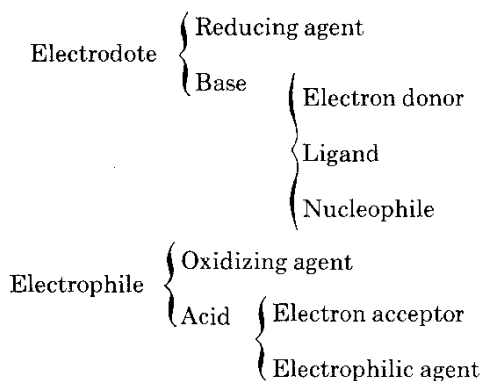


Figure 4. Relationship of various terms

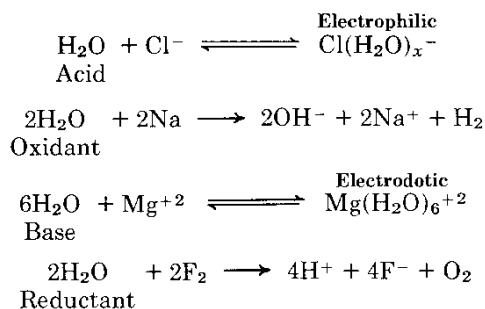


Figure 5. Reactions illustrating the amphoteric nature of water

Some authors have suggested extending the word electrophile to cover all species accepting electron density in a chemical reaction, whether as acids or oxidants, and the word electrodoter or electron giver to all species giving up electron density, whether as bases or as reducing agents (3). Figure 4 shows the relationship between these terms and others commonly used in describing chemical reactions.

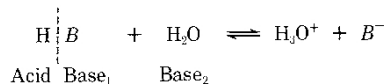
Quantitative Lewis Theory

Obviously it is no longer possible to call something an acid or a base in an absolute sense. All species are in a way electronically amphoteric. That is, whether a species functions as an acid, base, or even as an oxidizing or reducing agent, depends on the chemical system being considered. An excellent example of this is the reactions described for water in Figure 5. To construct an absolute scale of acid-base strengths seems impossible, because the relative nature of Lewis acidity and basicity causes problems. Thus, in water the Lewis acid, H^+ , prefers the base OH^- over the base NH_3 , giving the base strengths $\text{OH}^- > \text{NH}_3$. The Lewis acid Ag^+ , on the other hand, has the opposite preference, giving the strengths $\text{NH}_3 > \text{OH}^-$. However, we can quantitatively describe some Lewis reactions if we limit the conditions being considered.

In aqueous systems such equilibrium constants as

$$K_{\text{ionization}}, K_{\text{solubility}}, K_{\text{hydrolysis}}, K_{\text{instability}}$$

and the Bronsted K_a and K_b scales all treat special Lewis reactions in which excess water is functioning as a reference acid or base. For example, K_a values measure the relative strengths of different bases as they compete with water for the single Lewis acid H^+ :



Because the concentration of the water changes so little in these reactions, it is factored into the equilibrium constant for the reaction:

$$K_a = K'[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]} \quad (3)$$

The larger the K_a , the weaker the base B with reference to water. If two bases, B_1 and B_2 , undergo a displacement reaction in an aqueous system:



the base having the smallest K_a value, as measured by Equation 3, would be expected to obtain the proton.

This special K_a scale is justified by the great importance of the acid H^+ in aqueous and biochemical systems. Similar scales could be constructed for other Lewis acids but, as we have seen, they would not give the same order of base strengths as the K_a scale. In fact, changing the solvent in which they are measured alters the order as well. This inability to be quantified is one of the most serious defects of the Lewis definitions and probably has been the main reason why they haven't been more widely used. Recent developments in inorganic chemistry, however, have altered this situation somewhat and have provided, as will be seen in Part III, some qualitative rules which allow us to make some important predictions about Lewis reactions.

Suggested Reading

- (1) Drago, R. S., Matwiyoff, N. A., "Acids and Bases," 1968, D. C. Heath & Co., Lexington, Mass.
- (2) Gutmann, V., *Monatsh. Chem.*, 1971, 102, 1-21.
- (3) Luder, W. F., Zuffanti, S., "The Electronic Theory of Acids and Bases," 1960, 2nd ed. Chap. 4, Dover, New York, N.Y.
- (4) Sienko, M. J., Plane, R. A., "Physical Inorganic Chemistry," 1963, Chap. 5, W. A. Benjamin, Inc., New York, N.Y.
- (5) Taube, H., *Chemistry*, 1965, 38, 3, 18.
- (6) Vanderwerf, C. A., "Acids, Bases, and The Chemistry of The Covalent Bond," 1961, Reinhold, New York, N.Y.

Lewis Acid-Base Theory

Part III. Hard and Soft Acid-Base Theory

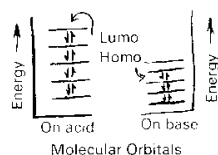


Figure 2. Frontier orbitals

The continuum in Figure 1 was presented in Part II to illustrate the way in which the bond between an acid, *A*, and a base, *B*, could continuously vary between the extremes, classically identified as ionic and covalent. The question was also posed as to whether acids and bases which formed bonds lying to the right of this continuum (primarily covalent bonds) differ in experimental behavior from those acids and bases forming bonds lying to the left (primarily ionic bonds). The answer to this question is yes, and this leads to an important generalization about Lewis acids and bases known as the principle of hard and soft acids and bases (HSAB). But before discussing full implications of this question, it is essential to refine our picture of the bonding between an acid and a base.

Molecular Orbitals and Covalent Bonding

In molecular orbital theory, a traditional coordinate covalent bond forms when two simple species, either ions or atoms, combine and their atomic orbitals fuse forming molecular orbitals which encompass both species. The electron density of the electron pair, originally localized on the base, then flows into one of these molecular orbitals and, thus, is shared by both species. An analogous situation occurs when the two reacting species are more complicated—for example, molecules or complex ions. In this case, their molecular orbitals mix to form new molecular orbitals encompassing both species.

In most reactions, the most important initial mixing occurs between the frontier orbitals (Figure 2). On a base, the frontier orbital is the filled orbital with the highest energy—sometimes called the highest occupied molecular orbital or a HOMO. This orbital contains the electron pair to be shared. On the acid, the frontier orbital is the empty orbital

with the lowest energy, called the lowest unoccupied molecular orbital or LUMO. For these orbitals to mix, however, they must meet at least three requirements: they must overlap in space with one another, have the proper symmetry, and have approximately the same energy.

The symmetry requirement refers to the fact that the behavior of an electron in an atom cannot be described precisely. Instead, probability distributions are needed. The mathematics which describes these electron density distributions or orbitals is analogous to that describing wave systems and, for this reason, electrons are sometimes said to act like de Broglie matter waves. In any case, the resulting electron density distributions look like three-dimensional standing waves and, like real waves, they have nodes (Figure 3). Every time a distribution passes through a node its electron wave changes its mathematical sign—that is, the positive and negative signs on the lobes of the electron distributions in Figure 3 have nothing to do with electric charge. They are mathematical signs that tell how the orbitals on two species fuse when the species react.

The symmetry requirement says that for two overlapping orbitals to mix forming a bond, the net signs on their electron lobes must be algebraically positive. In other words, a positive lobe must overlap with a positive lobe or a negative lobe with a negative lobe as in Figure 4. This net positive overlap tells, in turn, that the equations describing the new system will show a large distribution of electron density between *A* and *B*, causing the two positive kernels to be drawn together, and resulting in a bonding situation. A net negative overlap, on the other hand, will produce a system which has a large electron distribution on either side of the *AB* region, causing the two positive kernels to be drawn apart, and resulting in an antibonding situation (Figure 5).

If the two interacting orbitals do not have approximately the same energy, as in the third requirement, the electrons will prefer to remain in the orbital with the lowest energy. As a result, the pair will remain localized on one of the two species, and little mixing of orbitals or covalent bonding will take place.

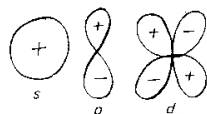
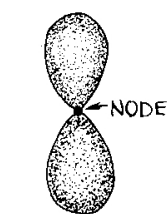


Figure 3. Typical atomic electron distributions or orbitals showing their nodal properties

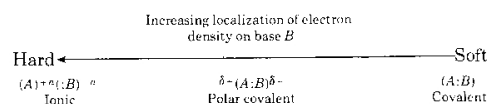


Figure 1

These ideas can be combined to give the continuum in Figure 1 a more sophisticated interpretation. For simplicity, a simple cation, A^+ , is used for a Lewis acid and a simple anion, B^- , for a Lewis base. If the LUMO on A^+ and the HOMO on B^- have sufficient overlap and the proper symmetry, then the extent to which their orbitals mix depends on how closely their energies match. If the energy difference of the frontier orbitals is large, the density of the electron pair remains largely localized on B , and the two species bond primarily by means of their net electrostatic charges. This corresponds to the left of the continuum and to the bonding extreme which we call ionic.

If A^+ and B^- are varied, however, so that their frontier orbitals come closer and closer together in energy, more and more mixing occurs, and a larger percent of the density of the electron pair is delocalized into the region between A^+ and B^- . This decreases the net negative charge on B^- and the net positive charge on A^+ , making the resulting bond less and less polar.

Finally, if the energies of the frontier orbitals match perfectly, the electron density of the pair is then symmetrically distributed in a molecular orbital between A and B , and an ideal covalent bond results (3) (Figure 6). For those readers familiar with the mathematics of simple molecular orbital theory, this picture corresponds to making a molecular orbital from an orbital on acid A^+ and an orbit-

al on base B^- : $\psi_{AB} = a\psi_{A^+} + b\psi_{B^-}$. The value of coefficient a gradually increases from left to right across the continuum. On the far left, $a = 0$, $b = 1$; on the far right $a = b$. Quantum mechanical calculations on ψ_{AB} show that most of the energy of bond AB , when $a = 0$ and $b = 1$, comes from mathematical expressions corresponding to the electrostatic attraction of two ions. Calculations when $a = b$, on the other hand, show that part of the energy of AB bonds on the right comes from quantum mechanical effects called exchange integrals or resonance integrals.

Predicting the Nature of Acid-Base Bonds

It is obvious from the above discussion that if we had a complete description of the energies, spatial distribution, and symmetry properties of the molecular orbitals or atomic orbitals for all Lewis acids and bases, we could predict whether a given acid-base pair would form predominately ionic or covalent bonds. Unfortunately, this information is not always available and, to make such predictions, we must resort to less general criteria which allow us to make some educated, but not always accurate, guesses. It is convenient to consider these criteria separately for acids and bases.

Bases. For bases which have net negative charges, such as anions, or large dipole moments, a very simple model based on polarizability gives some idea whether they will form primarily ionic or primarily covalent bonds. Polarizability expresses the ability of a species' electron cloud to be distorted. If a charged base, B^- , combines with a charged acid, A^+ , the positive charge on A^+ attracts or distorts the electron cloud on B^- into the region between A and B , making B^- less negative, A^+ less positive, and the AB bond less polar. We can associate the amount of distortion with the amount of covalent bonding (Figure 7).

The tightness with which a base holds on to its electrons depends roughly on its size. The further away the valence electrons are from the positive nucleus, the easier it is to polarize them. Hence, we would predict that the electron pairs on S^{-2} will have a stronger tendency to bind covalently than those on O^{-2} . Similarly, we would predict the trend for the halide ions in Figure 8. Obviously, uncharged bases with small dipole moments like CO and C_2H_4 will bond covalently.

Acids. As in the case of uncharged bases, acids such as neutral metals and neutral atoms must form covalent bonds. For charged acids, however, the situation is more complex. It would be expected that the greater the positive charge on the acid, the more effective it will be in distorting the electron cloud of the base, resulting in a more covalent bond. On the other hand, the larger the size of the acid, the more likely it is for the negative charge on the base to repel or push

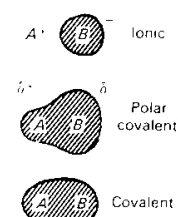


Figure 6. Electron density of the AB bond as a function of the mixing of orbitals on A and B

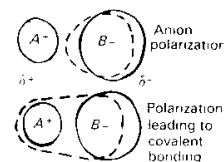


Figure 7. Anion polarization

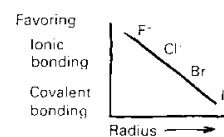


Figure 8

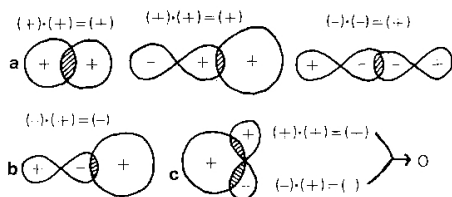


Figure 4. a, net positive overlap of orbitals; b, net negative overlap; c, net zero overlap

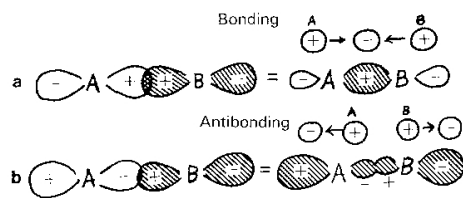


Figure 5

a, Net positive overlap producing a bonding situation
b, Net negative overlap producing an antibonding situation

In the smaller upper drawings the signs refer to the net electrical charges of the electron distributions and the positive kernels. Shading indicates filled orbitals

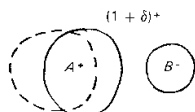
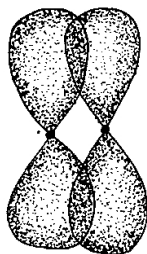


Figure 9. Cation polarization



SIGMA BOND



PI BOND

the acid's electron cloud to one side, thus exposing more positive charge and resulting in a greater distortion of the base or in a more covalent bond (Figure 9). The Al^{+3} ion, forms less polar (more covalent) bonds than Na^+ for the first reason and Cs^+ forms more covalent bonds than Na^+ for the second reason.

It turns out, however, that metal cations having six or more d electrons in their outer shells can maximize both of these effects. The d electrons do not efficiently shield the nuclear charge in these cations, and they behave as if they have a much larger effective positive charge than calculated by counting electrons and protons. The d orbitals are also easy to polarize, creating an even greater effective positive charge. The result is that these acids are able to extensively polarize bases and are able to form strongly covalent bonds. The presence of the d electrons also allows these acids to form pi back bonds with bases. This is illustrated in Figure 10 for a metal carbonyl. In step *a*, the base donates electrons to the metal to form a sigma bond which is a covalent bond along a line joining two atoms. If this sigma bond is short enough, it causes the half-filled d orbitals of the metal to overlap with empty d or p orbitals on the base. The result is step *b*, where the metal donates electron density from its d electrons back to the base, forming a pi bond which is a covalent bond like those formed by electrons moving in orbitals that extend above and below the plane of an organic molecule containing double bonds. This phenomenon appears to give the acid and the base two opportunities to mix their orbitals—once in the formation of the sigma bond and once in the formation of the pi bond (1).

HSAB Theory

Over two decades ago, chemists working in the field of coordination chemistry noticed that, on the basis of experimental behavior in aqueous solutions, Lewis acids and bases tended to group themselves into two large classes. It is now generally agreed that these two classes correspond to those acids and bases which form bonds lying to the right in Figure 1 (covalent) and to those forming bonds lying to the left (ionic).

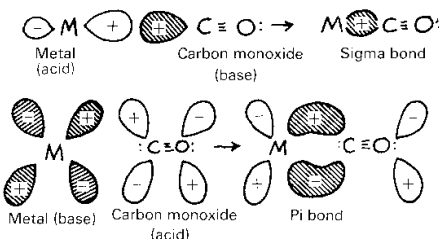


Figure 10. Sigma and pi back bonding in a metal carbonyl

The American chemist, Ralph Pearson, has given these classes the names hard and soft. The term hard is used to describe graphically those cases where the electrons or orbitals remain localized on the reacting species, and the acid and base tend to form ionic bonds. The term soft describes graphically those cases where the orbitals on the reactants are easily distorted or mixed together, and the acid and base tend to form covalent bonds. Pearson has also summarized the experimental behavior of these two classes with the rule: Hard acids prefer to bind to hard bases and soft acids to soft bases (4-10).

Tables I, II, and III list common hard and soft acids and bases. As can be seen, the criteria discussed above can be used to predict into which class many acids and bases fall; thus, I^- is a soft base, Br^- is borderline, and F^- is hard. Likewise, H^+ , Na^+ , and Li^+ are hard acids, whereas Ag^+ , Hg^+ , and Cu^+ are soft.

Notice also that this classification of acids and bases is not absolute. Just as the contin-

Table I. Acids

Hard

H^+ , Li^+ , Na^+ , K^+ (Rb^+ , Cs^+)
 Be^{+2} , $\text{Be}(\text{CH}_3)_2$, Mg^{+2} , Ca^{+2} , Sr^{+2} (Ba^{+2})
 Sc^{+3} , La^{+3} , Ce^{+4} , Gd^{+3} , Lu^{+3} , Tb^{+4} , U^{+4} , UO_2^{+2} ,
 Pu^{+4}
 Ti^{+4} , Zr^{+4} , Hf^{+4} , VO^{+2} , Cr^{+3} , Cr^{+6} , MoO^{+3} ,
 WO^{+4} , Mn^{+2} , Mn^{+7} , Fe^{+3} , Co^{+3}
 BF_3 , BCl_3 , $\text{B}(\text{OR})_3$, Al^{+3} , $\text{Al}(\text{CH}_3)_3$, AlCl_3 , AlH_3 ,
 Ga^{+3} , In^{+3}
 CO_2 , RCO^+ , NC^+ , Si^{+4} , Sn^{+4} , $\text{CH}_3\text{Sn}^{+3}$,
 $(\text{CH}_3)_2\text{Sn}^{+2}$
 N^{+3} , RPO_2^+ , ROPO_2^+ , As^{+3}
 SO_3 , RSO_2^+ , ROSO_2^+
 Cl^{+3} , Cl^{+7} , I^{+5} , I^{+7}
 HX (hydrogen-bonding molecules)

Borderline

Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2}
 Rh^{+3} , Ir^{+3} , Ru^{+3} , Os^{+2}
 $\text{B}(\text{CH}_3)_3$, GaH_3
 R_3C^+ , C_6H_5^+ , Sn^{+2} , Pb^{+2}
 NO^+ , Sb^{+3} , Bi^{+3}
 SO_2

Soft

$\text{Co}(\text{CN})_5^{-3}$, Pd^{+2} , Pt^{+2} , Pt^{+4}
 Cu^+ , Ag^+ , Au^+ , Cd^{+2} , Hg^+ , Hg^{+2} , CH_3Hg^+
 BH_3 , $\text{Ga}(\text{CH}_3)_3$, GaCl_3 , GaBr_3 , GaI_3 , Tl^+ ,
 $\text{Tl}(\text{CH}_3)_3$
 CH_2 , carbenes
 π acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, etc.
 HO^+ , RO^+ , RS^+ , RSe^+ , Te^{+4} , RTe^+
 Br_2 , Br^+ , I_2 , I^+ , ICN , etc.
 O , Cl , Br , I , N , RO , RO_2
 M^0 (metal atoms) and bulk metals

uum in Figure 1 implies a continuous variation in bond types so we would expect a continuous variation from very hard acids and bases to very soft acids and bases. This implies that it is meaningful to talk of NH_3 as being a softer base than H_2O , although both lie to the left in Figure 1 and both fall into the larger category of hard. The problem is that, at present, insufficient experimental data are available to make such a detailed classification of acids and bases, and we must be content with the cruder categories in Tables I and II of hard (left), borderline (center), and soft (right). Table III, however, does give a more detailed breakdown.

We should be careful not to read too much into Pearson's rule. It does not say that a hard acid will not combine with a soft base. Rather, it means that if a hard acid is put in a situation where it can react with two different bases, it prefers to bind to the harder of the two. Hence, we still cannot formulate an absolute scale of acid and base strength but, when given a particular acid-base situation,

Table II. Bases

Hard

NH_3 , RNH_2 , N_2H_4
 H_2O , OH^- , O^{2-} , ROH , RO^- , R_2O
 CH_3COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^-
 F^- , (Cl^-)

Borderline

$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2
 NO_2^- , SO_3^{2-}
 Br^-

Soft

H^-
 R^- , C_2H_4 , C_6H_6 , CN^- , RNC , CO
 SCN^- , R_3P , $(\text{RO})_3\text{P}$, R_3As
 R_2S , RSH , RS^- , $\text{S}_2\text{O}_3^{2-}$
 I^-

Table III. Bases in Order of Decreasing Hardness (5)

Base	Base
1. H_2O	12. I^-
2. OH^- , OCH_3^- , F^-	13. SCN^-
3. Cl^-	14. SO_3^{2-}
4. NH_3	15. $(\text{C}_6\text{H}_5)_3\text{Sb}$
5. $\text{C}_6\text{H}_5\text{N}$	16. $(\text{C}_6\text{H}_5)_3\text{As}$
6. NO_3^-	17. SeCN^-
7. N_3^-	18. $\text{C}_6\text{H}_5\text{S}^-$
8. NH_2OH	19. $\text{S}=\text{C}(\text{NH}_2)_2$
9. $\text{H}_2\text{N}-\text{NH}_2$	20. $\text{S}_2\text{O}_3^{2-}$
10. $\text{C}_6\text{H}_5\text{SH}$	21. $(\text{C}_6\text{H}_5)_3\text{P}$
11. Br^-	

we can, by examining the hardness and softness of the species involved, make an intelligent prediction about which reactions will be favored.

Simple Applications

Let us use the information in Tables I and II and apply Pearson's rule to some simple examples:

1. Which is the weakest Brönsted acid in water— HF , HCl , HI , or HBr ?

The reaction of the acid with water can be expressed (where $B = \text{F}^-$, Cl^- , Br^- , and I^-) as: $\text{HB} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + B^-$. Because H^+ is a hard acid and H_2O is a hard base, the hardest base, B , should be the most successful in competing with the water for the H^+ and should form the least dissociated or weakest Brönsted acid. F^- is the hardest base and, in fact, HF is the weakest of the acids.

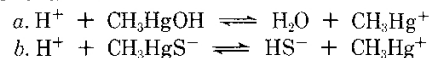
2. Which salt ionizes most in water, NaBr or HgBr_2 ?

Br^- is a softer base than H_2O . Therefore the soft acid Hg^{+2} will prefer the combination HgBr_2 over $\text{Hg}(\text{H}_2\text{O})_y^{+2}$ and will not ionize a great deal. The hard acid, Na^+ , on the other hand, will prefer the hard base, H_2O , and will ionize extensively to form the $\text{Na}(\text{H}_2\text{O})_x^+$ adduct. Another way to look at this effect is to think of polar water surrounding the dissociated ions, masking their electrical charges. This hinders the reassociation of those ions which bind primarily by means of their electrostatic attraction, but not the reassociation of those using primarily covalent bonding.

3. Which complex is more stable in water, $\text{Cd}(\text{CN})_4^{2-}$ or $\text{Cd}(\text{NH}_3)_4^{+2}$?

The soft acid Cd^{+2} must compete for the hard base, H_2O , or the softer bases, NH_3 and CN^- . According to the HSAB rule, it will prefer the softer bases and both complexes will be stable in water. Of the two, however, CN^- is the softer and the cyano complex should be more stable. The $K_{\text{instability}}$ for $\text{Cd}(\text{CN})_4^{2-}$ is 1.4×10^{-19} compared to that of $\text{Cd}(\text{NH}_3)_4^{+2}$ which is 7.5×10^{-8} .

4. Which direction will the following reactions favor?



Reaction *a* goes to the right favoring the combination of the hard acid H^+ and the hard base OH^- . Reaction *b* goes to the left favoring the combination of the soft acid CH_3Hg^+ and the soft base S^{2-} .

5. Explain why, in water, the acid H^+ appears to give the base strengths $\text{OH}^- > \text{NH}_3$, whereas Ag^+ gives the order $\text{NH}_3 > \text{OH}^-$.

Again, the hard acid, H^+ , prefers the harder base, OH^- , and the soft acid, Ag^+ , prefers the softer base, NH_3 .

Some additional problems are given at the end of the article.

Symbiosis

The type of base to which a simple acid bonds alters its electronic structure and, hence, its hardness or softness. This determines its ability to combine further with different bases. In general, a soft base makes an acid even softer by decreasing its net positive charge as the density of the electron pairs becomes delocalized in the newly created molecular orbitals. Therefore, we would expect soft bases to collect together on an acid. This flocking together of birds of a feather has been called the symbiosis effect.

The same effect is observed for hard bases. Thus, the B atom in BF_3 (F^- is a hard base) will prefer to combine with hard bases, whereas the B atom in BH_3 (H^- is a soft base, not to be confused with the hard acid H^+) will prefer to combine with soft bases. Likewise, $Co(NH_3)_5F^{+2}$ (NH_3 , hard; F^- , hard) and $Co(CN)_5I^{-3}$ (CN^- , soft; I^- , soft) are both stable, whereas $Co(NH_3)_5I^{+2}$ (NH_3 , hard; I^- , soft) and $Co(CN)_5F^{-3}$ (CN^- , soft; F^- , hard) are both unstable.

Many ligands such as NO_2^- and SCN^- can coordinate from two different atoms. The relatively soft acid $Co(CN)_5H_2O^{-2}$ prefers to bind to the soft sulfur atom in the SCN^- ion, forming the thiocyanato-S complex. The relatively hard acid $Fe(H_2O)_6^{+3}$, on the other hand, prefers to bind to the harder nitrogen atom, giving a thiocyanato-N complex. The HSAB rule has also been applied to nucleophilic and electrophilic reactions in organic chemistry (6, 11), to catalysis, to the electrochemical series, and to chemical kinetics (10).

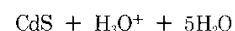
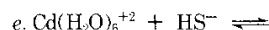
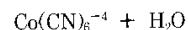
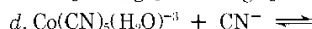
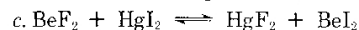
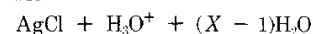
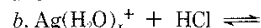
Conclusion

The HSAB principle is, for the present, a useful rule of thumb. Its detailed interpretation, however, is still a matter for research and debate (2). Connecting the principle in a detailed manner with the thermodynamics, kinetics, and especially the quantum mechanics of chemical reactions, may eventually allow chemists to calculate numerical values of hardness and softness and perhaps even allow the quantitative prediction of Lewis acid-base reactions. A quantitative relation between acid-base and oxidation-reduction reactions may also be possible. An even more exciting prospect, however, is that the HSAB rule may be merely a special case of a more general principle which would allow prediction of chemical reactivity as a whole.

Whatever the case, the HSAB rule hints of exciting things to come in inorganic chemistry and reemphasizes the value of the Lewis definitions. We can, then, at least conclude that Lewis' evaluation of the situation, made over 30 years ago, is still valid today, if not more so. As he put it, "To restrict the group of acids to those substances which contain hydrogen interferes as seriously with the systematic understanding of chemistry as would the restriction of the term oxidizing agent to substances containing oxygen."

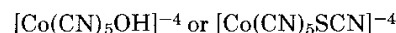
Questions

1. Predict which way the following reactions will go:



2. Would you expect Pt^{+4} to form an S- or an N-bonded complex with SCN^- ?

3. Which of these species is likely to be more stable?



4. Would you expect a metal ion M^{+n} to have the same hard or soft behavior in the gas phase as in an aqueous solution?

Answers

1. a. To the left— Cs^+ is softer than Li^+ (based on size). I^- is soft, F^- is hard.

b. To the right— Cl^- is softer than H_2O ; Ag^+ is soft, H^+ is hard.

c. To the left— Be^{+2} is hard, Hg^{+2} is soft; F^- is hard, I^- is soft.

d. To the right— $Co(CN)_5^{-3}$ is soft, CN^- is soft, and H_2O is hard.

e. To the right— Cd^{+2} is soft, H^+ is hard; S^{-2} is softer than H_2O .

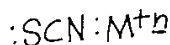
2. An S-coordinated complex, Pt^{+4} is soft, S terminal is softer than N terminal.

3. $[Co(CN)_5SCN]^{-4}$ is more stable. $Co(CN)_5^{-3}$ is soft, SCN^- is soft at S, OH^- is hard.

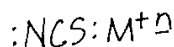
4. No. The reacting species in the gas phase is M^{+n} , whereas in the aqueous phase it is $M(H_2O)_x^{+n}$. In the aqueous phase, hard bases have to compete with the hard base H_2O for any hard acids. In addition, the polar water tends to mask the electrostatic forces characteristic of hard-hard interactions. Soft-soft interactions do not experience these problems to as great an extent. As a result, the contrast between hard and soft behavior is much more significant in the aqueous phase than in the gas phase. Ω

Suggested Reading

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- (9) Pearson, R. G., *Science*, 1966, 151, 172.
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Thiocyanato-N
complex



Thiocyanato-S
complex

Bases able to
coordinate at
two different
sites are
called
ambidentate
bases