THE ELECTRONIC THEORY OF ACIDS AND BASES

W. F. LUDER

Department of Chemistry, Northeastern University, Boston, Massachusetts

Received September 3, 1940

CONTENTS

I. FOREWORD

A. Introduction

From the beginning of the history of chemistry the question as to the nature of acids and bases has been one of great interest. The answer to the question has been revised many times and is at present the subject of considerable controversy.

None of the three current theories of acids and bases satisfactorily explains more than a portion of their experimental behavior. For forty years an increasing amount of data has compelled realization of the fact that acid–base phenomena are far more widespread than is generally acknowledged. Those who have grasped this fact have already abandoned the hydrogen ion–hydroxyl ion theory. Yet neither of the two alternatives is inclusive enough to cover all the data.

The theory of solvent systems conforms to the experimental fact that there are many other substances besides those containing hydrogen which exhibit typical acid properties. But it goes astray in making the definitions of acid and base as rigidly dependent upon the solvent as does the hydrogen ion–hydroxyl ion theory.

The proton theory emphasizes the important fact that acid–base phenomena can be observed in any solvent or even in the absence of a solvent. It also takes into account the experimental fact that there are many other substances besides the hydroxyl ion which exhibit typical basic properties. Yet it does not recognize the complementary data with regard to acids. The followers of Brönsted have maintained that only substances capable of giving up protons can be called acids.

We have, then, two independent and, in important features, contradictory theories of acids and bases. This situation seems to be due to the neglect of two factors very important in contemporary chemistry: first, a portion of the experimental data, and second, the electronic theory of the covalent bond. Probably such neglect was natural and even necessary in the early stages of the development of each theory. Possibly neither would have accomplished as much as it has without some such limitation. However, as a result of this neglect, neither theory gives us much of an insight into the fundamental nature of acids and bases.

The most powerful theoretical tool now available to the chemist is undoubtedly the electronic theory of valency, which we owe to the brilliant intuition of G. N. Lewis (76, 77). It has been used with remarkable results by workers in many fields, yet the only one who has applied it systematically to the problem of the nature of acids and bases has been Lewis himself (77 to 81). When the theory had so well demonstrated its widespread usefulness, one might expect that an attempt by its author to apply it to acids and bases would meet with a favorable reception. But this attempt has been ignored where it has not been actively opposed. Walden has been almost bitter in his ridicule of the ideas of Lewis (102), but he reveals, by his misinterpretations of their consequences, that he has not understood them. Walden's opposition must have had considerable influence in preventing serious consideration of the proposals of Lewis. Yet Lewis' application of his theory to acids and bases explains their properties in the fundamental terms of a simple inherent difference in the electronic structure of the molecules themselves. It also takes into account both portions of the data neglected by the other two theories.

From an experimental standpoint it seems that a substance which exhibits the properties of an acid should be called an acid, regardless of preconceived notions about the dependence of acid properties on some particular element. Those properties have been agreed upon from the beginning. Yet many substances possessing them are not now recognized by most chemists as acids. This situation persists in spite of the fact that some of these substances were once called acids,—when the principal criterion of an acid was its experimental behavior.

In this paper the emphasis is upon experimental behavior. Substances which possess the properties of acids are properly called acids; substances having the properties of bases are properly called bases.

B. Historical development of acid–base theory

Some of the properties by which acids were recognized when the term first came into use were listed by Boyle (102) as follows: they dissolve many substances; they precipitate sulfur from its solution in alkalies; they change blue plant dyes to red; they lose all these properties on contact with alkalies. These were recognized as the properties of aqueous solutions of acids. If the solution of a substance in water had these and other typical acid properties, the substance itself was known as an acid. Thus the gases carbon dioxide and sulfur trioxide were called acids because their solutions exhibited the properties common to all aqueous solutions of acids.

This strictly experimental approach was largely abandoned during the series of controversies which began with Lavoisier's attempt to make oxygen the necessary constituent of all acids. After Davy had shown that some acids do not contain oxygen and that many oxides are not acids, hydrogen became the "acidifying principle." Davy himself wrote in 1814 "that acidity does not depend upon any particular elementary substance, but upon peculiar arrangement of various substances" (38). We shall see how nearly correct Davy was. But Liebig successfully maintained the hydrogen theory against Berzelius by defining an acid as any substance which contained easily replaceable hydrogen atoms.

With the advent of the Arrhenius theory of ionization, an acid was defined as a hydrogen compound ionizing in water solution to give hydrogen ions. A base was a hydroxyl compound which would give hydroxyl ions in water solution. These definitions became quite general, in spite of the efforts of several investigators to show how absurd they were. The exaggeration of the importance of ions in chemical reactions was at its height. A physical chemistry text of the period, as quoted by Folin and Flanders (20), contained the statement that "We have already reached a point where we can say that nearly all, if not all, chemical reactions are due to ions, molecules as such not entering into chemical action." Such an atmosphere was not conducive to a scientific approach, and the work of Collie and Tickle (10), Hantzsch (43, 44), Folin and Flanders (21), and Lapworth (72) was largely ignored.

Collie and Tickle (10), in their paper published in 1899, suggest that oxonium salts are similar to ammonium salts. They refer to "such bases as those of the pyridine series" and even mention a "hypothetical base oxonium hydroxide, OH_3OH". Hantzsch (43, 44) noted the basic action of water, methyl alcohol, and dimethyl ether in anhydrous sulfuric acid.

Folin and Flanders, in a paper published in 1912 (21), reported the titration of a large number of acids in such solvents as benzene, toluene, chloroform, and carbon tetrachloride. They used sodium ethylate and sodium amylate as bases and phenolphthalein as an indicator. They noted that weak acids which cannot be titrated in water give excellent results in organic solvents. Even hydrogen sulfide was titrated. They found their solutions of acids practically non-conducting and concluded that there were very few ions present. This has been supported by the work of Fuoss and Kraus (27, 28, 85). Carbon dioxide could not be titrated in either chloroform or benzene. As we shall see, this seems to agree with Lewis' statement that carbon dioxide is a "secondary" acid (78). The most striking thing about the paper appears in a footnote in which the authors mention that mercuric chloride can be titrated with phenolphthalein and sodium ethylate in the same manner as any other acid, but they failed to draw the logical conclusion that mercuric chloride might be an acid. Lapworth (72) was one of the first to attack the Arrhenius–Ostwald theory of the catalytic activity of acids. However, these and similar investigations failed to make an impression upon the followers of Arrhenius, until the concept of the covalent bond began to relegate ionic reactions to their proper importance in chemistry.

Meanwhile the development of the theory of solvent systems was begun by Franklin in 1905 (22 to 25). Reasoning from formal analogy to the hydrogen ion–hydroxyl ion theory he defined acids and bases in liquid ammonia. According to his theory, if water ionizes into hydronium (or oxonium) and hydroxyl ions, liquid ammonia must ionize into ammonium and amide ions. Substances like ammonium chloride are acids and substances like sodium amide are bases in liquid ammonia. Ammonia solutions of acids and bases neutralize each other just as aqueous solutions do. For example:

$$\begin{array}{cccc} OH_3Cl + & NaOH \rightarrow & NaCl + & 2H_2O \\ NH_4Cl + & NaNH_2 \rightarrow & NaCl + & 2NH_3 \\ \text{acid} & \text{base} & \text{salt} & \text{solvent} \end{array}$$

Other properties of acids and bases, such as the reaction of acids with metals and of bases with non-metals (4), were observed. The similarity between ammonia and water solutions was demonstrated very widely. Even acids like $B(OH)_3$ and $B(NH_2)_3$ were compared, and the latter was called an ammono acid. It appeared that the acid properties of both the hydronium and the ammonium ions must be due to the proton. The question then arose as to whether the idea of the solvent system could be applied to systems in which no protons were present.

Germann (29, 30, 31), Cady and Elsey (9), Jander (57 to 65), Wickert

(105), and Smith (100) have extended the solvent system theory of acids and bases to include aprotonic systems. Germann showed that aluminum chloride in phosgene has typical acid properties. The solution dissolves metals with evolution of carbon monoxide gas and is neutralized by metallic chlorides such as calcium chloride. Germann assumed that the aluminum chloride forms with the solvent a complex which he called a solvo acid. His definitions of acids and bases were formal and complicated, but were simplified by Cady and Elsey (9). They defined an acid as a solute which gives rise to a cation characteristic of the solvent and a base as a solute which gives rise to an anion characteristic of the solvent.

Jander and his coworkers used the same definitions to interpret the results of their work in sulfur dioxide (57 to 65, 104). Smith changed the definitions somewhat in reviewing the work with selenium oxychloride as a solvent (100, 107, 73, 74, 75, 66, 92). He defined an acid as an electron-pair acceptor toward the solvent, and a base as an electron-pair donor toward the solvent. These definitions, suggested in 1938, first show the influence of Lewis' proposals made in 1923 (77).

The extreme of formalism has been reached by Wickert in his definitions of acids and bases in terms of the solvent system (105, 90). He does not hesitate to overlook such experimental behavior as amphoterism in order to state his definitions wholly in terms of ions. Shatenstein also (97) has pointed out one of the several inconsistencies in Wickert's presentation. Wickert defines an acid as an ionic compound the cation of which has an incomplete electronic configuration. Yet he admits that ammonium salts are acids in ammonia. Another contradiction of the experimental facts occurs in that antimony trichloride is correctly listed as an acid, but aluminum chloride is not.

The essential ideas of the theory of solvent systems are summarized in table 1. In the first three examples, it is obvious enough that the acid which has reacted with each solvent is hydrogen bromide. Yet Smith seems to be the only adherent of the solvent system theory who recognizes that in examples 5 and 6 aluminum chloride and stannic chloride are true acids (100). And that is the beginning of the end of the theory.

The strength of the solvent system theory lies in its emphasis upon the fact that acid behavior is not confined to solutions containing proton-donors. The advocates of the theory have demonstrated that their acid solutions have all the typical experimental properties of aqueous solutions of hydrogen acids,—except the presence of the proton. The weaknesses of the theory are two: first, the attempt to limit acid-base phenomena to solvent systems, and second, the undue emphasis upon ionization as the most important factor in acid-base properties. Probably the first followed from the second. At any rate, many investigators have shown (10, 21, 39, 42, 43, 44, 50, 71, 72, 109) that ionization plays a far less important rôle than the followers of the solvent system theory would have us believe. It would appear that the theory merely describes one aspect of the nature of acids and bases: namely, their reactions with amphoteric solvents and the properties of the resulting solutions. We are most familiar with these properties, since they are most easily observed. A reluctance to go beyond them is readily understood, but for many chemists the Brönsted theory has overcome this reluctance, at least with respect to bases.

There are so many excellent discussions of the Brönsted theory (5, 7, 8, 35, 36, 37, 69, 84), that it is only necessary here to point out its one important weakness. The Brönsted theory admits of no acids other than proton-donors. As the proponents of the solvent system theory have shown, this does not correspond to the experimental facts. If the experimental approach is to prevail we cannot go on saying, as Meerwein (91), Shatenstein (97), and others do, that certain substances are "acid-analogous" in their properties, but are not acids simply because they do not contain hydrogen. Brönsted is undoubtedly correct in attributing acid–base properties to the molecules themselves rather than to their solutions. In this respect the Brönsted theory, as far as it goes, is closer to the experimental facts than the theory of the solvent system. Just as important is the conclusion that acids and bases are not necessarily ionic.

TABLE 1

Neutralization reactions according to the theory of solvent systems

NO.	SOLVENT	ACID +	BASE →	SALT +	SOLVENT
1	H_2O	H_3O^+, Br^-	K^+, OH^-	K^+, Br^-	$2H_2O$
2	NH_3	NH_4^+, Br^-	K^+, NH_2^-	K^+, Br^-	$2NH_3$
3	C_2H_5OH	$C_2H_5OH_2^+$, Br^-	K^+, $OC_2H_5^-$	K^+, Br^-	$2C_2H_5OH$
4	SO_2	SO^{++}, Br_2^-	K_2^+, SO_3^{--}	$2K^+$, Br^-	$2SO_2$
5	$COCl_2$	$COCl^+$, $AlCl_4^-$	K^+, Cl^-	K^+, $AlCl_4^-$	$COCl_2$
6	$SeOCl_2$	$(SeOCl)_2^+$, $SnCl_6^{--}$	$2K^+$, Cl^-	K_2^+, $SnCl_6^{--}$	$2SeOCl_2$
7	$SbCl_3$	Sb^{+++}, Br_3^-	$3K^+$, Cl^-	$3K^+$, Br^-	$SbCl_3$

Any attempt to reconcile the two contradictory theories of acids and bases must involve a deeper insight into their fundamental nature. Such an attempt has been made by Usanovich (101, 38) and by Lewis (77 to 81). Usanovich has defined an acid as any substance capable of giving up cations or of combining with anions, and a base as any substance capable of giving up anions or of combining with cations. He also suggests that oxidation-reduction reactions are a special case of acid-base phenomena. Acids combine with electrons as well as with anions, and bases give up electrons to acids. Oxidizing power is a limited phase of acidity, and both are due to attraction for negative particles. Some examples of neutralization according to Usanovich are given in table 2. Sulfur trioxide is an acid because it combines with the anion, O^{--}. Antimony pentasulfide is an acid because it combines with the sulfide ion. Ferric cyanide combines with the cyanide ion. Methyl iodide gives up the cation CH_3^+. Chlorine combines with two electrons from two sodium atoms. This theory is general and covers more of the experimental behavior (e.g., see 16), but objections may be raised to it.

Shatenstein (97) has called attention to certain inconsistencies in the above theory. Among these are the emphasis upon salt formation, and the formal reasoning involved in making ions so important in the scheme. In addition, one might mention the lack of correlation between the definitions and the degree of "coördination-unsaturation" which Usanovich recognizes is of great importance in determining acidity and basicity. Furthermore, the inclusion of oxidation-reduction as a special case of acid-base phenomena does not seem to be justified. The relationship is close, but, as we shall see, is not quite as Usanovich presents it.

TABLE 2

Neutralization reactions according to the theory of Usanovich

NO.	ACID +	BASE →	SALT
1	SO_3	Na_2O	Na_2SO_4
2	Sb_2S_5	$3(NH_4)_2S$	$2(NH_4)_3SbS_4$
3	$Fe(CN)_3$	$3KCN$	$K_3Fe(CN)_6$
4	CH_3I	$(CH_3)_3N$	$(CH_3)_4NI$
5	Cl_2	$2Na$	$2NaCl$

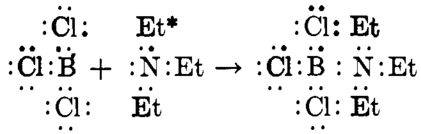
The other attempt to reconcile the proton and the solvent system theories was made by Lewis in 1923 (77). Strictly speaking, it was not an attempt at reconciliation, since both theories were proposed for the first time by Lewis as special cases of his more general and more fundamental theory. Brönsted and Lowry presented their theory independently in the same year, while the general form of the solvent system theory came several years later. The conflict between the two theories has gone on, although the solution to the problem has been at hand since 1923.

C. Outline of the electronic theory of acids and bases

The foundations of an electronic theory of acids and bases have been well laid by Lewis (78). He begins by defining acids and bases in terms of their outstanding experimental property, neutralization. Acids are substances which, like hydrogen ion, neutralize hydroxyl ion or any other base. Bases are substances which, like hydroxyl ion, neutralize hydrogen ion or any other acid. If the definitions are rewarded slightly, they can be based on the experimental facts alone. *Acids are substances which, like hydrochloric acid, neutralize sodium hydroxide or any other base. Bases are substances which, like sodium hydroxide, neutralize hydrochloric acid or any other acid.* Thus worded, the definitions would have applied at any time since the beginning of the classification of acid-base properties. The following experiment, which makes an excellent lecture demonstration, is an interesting example of their generality.

Crystal violet is an indicator which gives the same color change in different solvents. When sodium hydroxide is titrated against hydrochloric acid in water, using crystal violet as the indicator, the solution is yellow when acidic and violet when basic. Pyridine and triethylamine can be titrated in a similar manner against hydrochloric acid, and are therefore bases. If pyridine is dissolved in some comparatively inert solvent, such as chlorobenzene, the same violet color is observed when crystal violet is added. Now if boron trichloride, stannic chloride, or any similar substance soluble in chlorobenzene is added to the basic pyridine solution, the color changes instantly to yellow. Thus boron trichloride and stannic chloride are acids. If triethylamine, acetone, or any other fairly strong base is added, the color changes back to violet. Similar titrations can be performed in other solvents with other indicators and with many other acids and bases none of which contains hydrogen or hydroxyl ions (78). These titrations are strong evidence that there is an inherent difference between the molecules of acids and of bases. This difference is not dependent upon the solvent. It must involve a contrast in atomic structure common to all acids and bases, including hydrogen ion and hydroxyl ion.

The one property common to all acids makes them what Sidgwick (98) calls acceptor molecules. Bases are donor molecules. As Lewis points out, acids and bases coincide completely with Sidgwick's classification of electron-pair acceptors and donors. A base has one or more lone electron-pairs which may be used in coördinate-bond formation. An acid can accept one or more electron-pairs from a base to form coördinate bonds between the acid and base. In terms of the electronic theory: *A base is a base because it can donate an electron-pair to form a coördinate bond. An acid is an acid because it can accept an electron-pair to form a coördinate bond. Neutralization is the formation of the covalent bond between the acid and the base.* For example, when triethylamine neutralizes boron trichloride in chlorobenzene or in the absence of any solvent,



$$BCl_3 + :NEt_3 \rightarrow Cl_3B:NEt_3$$

*Et = C_2H_5

boron trichloride is an acid because it accepts an electron-pair to complete the octet for the boron atom. Triethylamine is a base because the nitrogen atom has an electron-pair which it can offer to form a coördinate bond between the acid and the base. The formation of the covalent bond, —neutralization,—destroys the distinctive properties of both the acid and the base.

The cases of neutralization just discussed take place either in unreactive solvents or in the absence of any solvent. They are less complicated than similar reactions in reactive solvents. Nevertheless, when neutralization and other reactions of these and similar acids and bases in reactive solvents are considered, it is found that they are analogous to corresponding reactions which occur in water in the presence of excess hydrogen ion or hydroxyl ion.

II. THE RÔLE OF THE SOLVENT IN ACID–BASE PROPERTIES

A. Reactions of acids and bases with the solvent

The properties of acids and bases with which we are most familiar from the study of water solutions depend to a great extent upon the presence of the solvent. For example, magnesium reacts slowly with hot water, liberating hydrogen. The reaction is much more rapid in acid solution. The difference must be due to the increased concentration of the solvent cation, the hydrogen ion.[1] At first glance, Lewis' theory seems to have little relation to this large body of experimental behavior with which we are so familiar.

This apparent lack of relationship is the basis of Walden's attack (102) on Lewis' theory. Walden fears that Lewis would destroy the significance of dissociation constants and conductivity measurements. The part played by the solvent would be deliberately eliminated. The oppositeness of acids and bases toward indicators would appear to be purely incidental observations. Unbiased study would have revealed that none of these fears is warranted. We have already seen that the oppositeness of acids and bases toward indicators is by no means a purely incidental observation, and we shall see that Walden's other objections are as groundless, but some justification for Walden's misinterpretation must be ad-

---

[1] The term "hydrogen ion" will continue to be used in place of "solvated proton," "hydronium ion", "oxonium ion", or "hydroxonium ion".

mitted. Lewis understands the significance of his theory so well that he has apparently overlooked the necessity of demonstrating its applicability to the familiar data. A sketchy attempt to do this has been made previously by the present author (87). In this paper a more complete presentation will be given.

Water may be regarded as the product of the neutralization of hydrogen ion by hydroxyl ion. The proton is an acid because it tends to accept an electron-pair from a base to complete the K shell of electrons. The hydroxyl ion is a base because the oxygen atom can donate an electron-pair to an acid. The formation of the coördinate bond between the proton and the hydroxyl ion is neutralization. The question as to whether the product is actually neutral, in the sense that the donor and acceptor properties of the oxygen and hydrogen atoms are balanced, is probably not of great importance. Sidgwick (98) believes that the oxygen is more powerful as a donor than the hydrogen is as an acceptor. What is more important is that the relative acidity of water can be compared with that of other solvents. For example, glacial acetic acid is more acidic and liquid ammonia more basic than water. In terms of the electronic theory this means that the acetic acid molecule has a greater tendency to accept an electron-pair than does water and that the ammonia molecule has a greater tendency to donate an electron-pair.

When an acid is dissolved in a solvent, the reaction between the acid and the solvent depends primarily upon two factors: the strength of the acid (its tendency to accept an electron pair), and the basic strength of the solvent (its tendency to donate an electron pair). The second factor will be considered in part III. In a given solvent, the strength of the acid can be measured, within the limits of the "leveling effect" of Hantzsch, by means of the equilibrium constant of the reaction with the solvent. For example, if glacial acetic acid, a typical covalent liquid which conducts an electric current poorly, reacts with water according to the equation

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

the equilibrium constant,

$$K = \frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2] \times [H_2O]}$$

serves as a semi-quantitative measure of acid strength when compared with similar constants for other acids. This is true only if the acid is not too strong. For strong acids like hydrochloric acid, also a typical covalent compound (possessing only 17 per cent ionic character, according to Pauling (94)), the reaction proceeds completely to the right in a solvent as basic as water.

Similar conclusions apply to other acids. If the reaction occurring when carbon dioxide, a weak acid, is dissolved in water is represented by the equation

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO^-$$

the equilibrium constant,

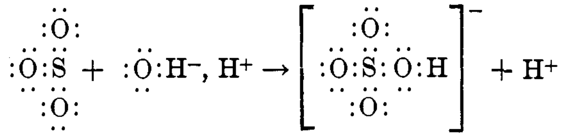
$$K = \frac{[H_3O^+] \times [HCO_3^-]}{[CO_2] \times [H_2O]^2}$$

may serve as a measure of the acid strength of the carbon dioxide. Strong acids like sulfur trioxide act in the same manner as hydrochloric acid. Sulfur trioxide accepts an electron-pair from water just as does the hydrogen in hydrogen chloride, seeking its maximum coördination number of two. The subsequent division into ions is different in that the water molecule is split by the sulfur trioxide, but this is irrelevant to the theory, as we shall see. The reaction

$$SO_3 + 2H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

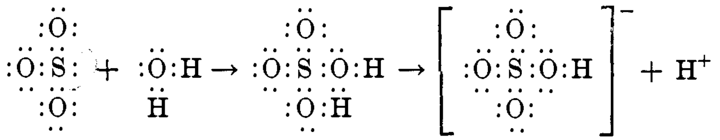
proceeds strongly toward the right. The same considerations hold for acids such as boron chloride, aluminum chloride, or stannic chloride. The boron and aluminum atoms tend to accept an electron-pair to complete their stable shells of eight electrons. The tin atom tends to gain two electron-pairs to complete its stable shell of twelve, as in H_2SnCl_6. There is no valid reason for calling the same type of reaction by two different terms: namely, ionization in the case of hydrochloric acid or acetic acid, and hydrolysis in the case of sulfur trioxide, carbon dioxide, or stannic chloride. The net result is an increase in the concentration of the solvent cations. We shall see that this increased concentration of the solvent cations is responsible for most of the familiar properties of acids and bases in water and similar solvents. It is due to the tendency of an acid to accept electron-pairs from bases in order to complete the characteristic stable electron configuration of the acid.

The actual mechanism may be regarded in either of two ways, as represented by simplified equations for the reaction between sulfur trioxide and water:



$$\begin{matrix} & :\ddot{\mathrm{O}}: \\ :\ddot{\mathrm{O}}: & \ddot{\mathrm{S}} \\ & :\ddot{\mathrm{O}}: \end{matrix} + :\ddot{\mathrm{O}}:\mathrm{H}^-, \mathrm{H}^+ \rightarrow \left[\begin{matrix} & :\ddot{\mathrm{O}}: & \\ :\ddot{\mathrm{O}}: & \ddot{\mathrm{S}}: & \ddot{\mathrm{O}}:\mathrm{H} \\ & :\ddot{\mathrm{O}}: & \end{matrix}\right]^- + \mathrm{H}^+$$

a direct reaction between the sulfur trioxide molecule and the hydroxyl ion; or



$$\begin{array}{c}\overset{\cdot\cdot}{:O:}\\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:\\ \underset{\cdot\cdot}{:O:}\end{array} + \begin{array}{c}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H\\ H\end{array} \rightarrow \begin{array}{c}\overset{\cdot\cdot}{:O:}\\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:S:\overset{\cdot\cdot}{O}:H\\ \underset{\cdot\cdot}{:O:H}\end{array} \rightarrow \left[\begin{array}{c}\overset{\cdot\cdot}{:O:}\\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:\overset{\cdot\cdot}{O}:H\\ \underset{\cdot\cdot}{:O:}\end{array}\right]^- + H^+$$

a direct reaction between the sulfur trioxide molecule and the water molecule, followed by ionization. In either case the result is the same. If the acid is strong enough or if the solvent is basic enough, the concentration of the cation characteristic of the solvent is increased.

The corresponding conclusion holds for bases dissolved in ionizable solvents. The solution contains a greater concentration of anions than is present in the pure solvent. The strength of the base in a given solvent can be estimated from the equilibrium constant. For example, when pyridine is dissolved in water, the pyridine molecule acts as a base in donating an electron-pair to the water molecule:

$$C_5H_5N: + H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H \rightleftharpoons C_5H_5N:H^+ + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H^-$$

The equilibrium constant,

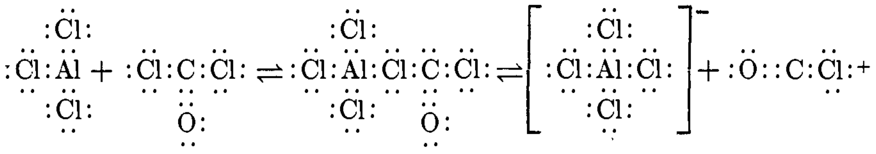
$$K = \frac{[C_5H_5NH^+] \times [OH^-]}{[C_5H_5N] \times [H_2O]}$$

serves to measure the basic strength of the pyridine.

These examples, purposely chosen with water as the solvent, are enough to show that the part played by the solvent is not "deliberately eliminated." Dissociation constants and conductivity measurements still have as much significance as ever. Walden's objections simply do not apply. When a sufficiently strong acid reacts with water, the concentration of the hydrogen ion is increased. When a sufficiently strong base reacts with water, the concentration of the hydroxyl ion is increased. The word "strength" now refers to the tendency of acids to accept electron-pairs and the tendency of bases to donate them, but in a given solvent the strength of an acid or a base, within limits, can be measured by its dissociation constant. There are many examples in the literature to support this conclusion for solvents other than water.

The typically acid properties of aluminum chloride in phosgene (30) are due to this increased concentration of solvent cations. These properties will be considered in section C of this part. Germann found that the conductivity of the aluminum chloride solution was less than that of the calcium salt, $Ca(AlCl_4)_2$, and concluded that the acid was weak.

Aluminum chloride is an acid because it accepts an electron-pair to complete the octet of the aluminum atom. The phosgene is amphoteric and in this reaction is acting as a base. The resulting cation will be solvated, because of the strong tendency of the carbon atom to maintain its octet. The data do not permit certainty as to the mechanism of the reaction between aluminum chloride and phosgene, but if we write the equation as



$$:\underset{..}{\overset{..}{\mathrm{Cl}}}:\overset{:\overset{..}{\mathrm{Cl}}:}{\underset{:\underset{..}{\mathrm{Cl}}:}{\overset{..}{\underset{..}{\mathrm{Al}}}}} + :\underset{..}{\overset{..}{\mathrm{Cl}}}:\underset{\underset{..}{\overset{..}{\mathrm{O}}}:}{\overset{..}{\underset{..}{\mathrm{C}}}}:\underset{..}{\overset{..}{\mathrm{Cl}}}: \rightleftharpoons :\underset{..}{\overset{..}{\mathrm{Cl}}}:\overset{:\overset{..}{\mathrm{Cl}}:}{\underset{:\underset{..}{\mathrm{Cl}}:}{\overset{..}{\underset{..}{\mathrm{Al}}}}}:\underset{..}{\overset{..}{\mathrm{Cl}}}:\underset{\underset{..}{\overset{..}{\mathrm{O}}}:}{\overset{..}{\underset{..}{\mathrm{C}}}}:\underset{..}{\overset{..}{\mathrm{Cl}}}: \rightleftharpoons \left[\ :\underset{..}{\overset{..}{\mathrm{Cl}}}:\overset{:\overset{..}{\mathrm{Cl}}:}{\underset{:\underset{..}{\mathrm{Cl}}:}{\overset{..}{\underset{..}{\mathrm{Al}}}}}:\underset{..}{\overset{..}{\mathrm{Cl}}}:\ \right]^- + :\overset{..}{\mathrm{O}}::\mathrm{C}:\underset{..}{\overset{..}{\mathrm{Cl}}}:^+$$

the equilibrium constant,

$$K = \frac{[\mathrm{COCl}^+] \times [\mathrm{AlCl}_4^-]}{[\mathrm{AlCl}_3] \times [\mathrm{COCl}_2]}$$

will serve as a measure of acid strength when compared with the dissociation constants of other acids in phosgene. According to Germann's conductivity measurements K is small, so aluminum chloride is a fairly weak acid with respect to phosgene. Similar treatment can be given the results of other investigators.

Meerwein (91) has shown that aluminum alcoholates, when dissolved in alcohols, increase the concentration of the solvent cation in the same manner as aluminum chloride does in phosgene:

$$\mathrm{Al(OR)_3} + \mathrm{ROH} \rightarrow \mathrm{HAl(OR)_4}$$

Other acids, such as boron trifluoride, also increase the hydrogen-ion concentration in organic acids. The work of Jander (60) with sulfur dioxide, that of Smith and others with selenium oxychloride, and some of the work in liquid ammonia can be interpreted in a similar way, not only for acids but for bases as well.

The reason for the solvent system definitions of Cady and Elsey is clear. Acids often do increase the concentration of solvent cations; bases often increase the concentration of solvent anions. However, this does not always happen. When acids react with solvents like ether and pyridine, ionization to give a cation characteristic of the solvent is unlikely. Usanovich (101) has shown the similarity in electrical conductivity of solutions of such acids as the arsenic and antimony trichlorides in ether to a solution of sulfuric acid in ether. The conductance of the solutions is greater if the ether is replaced by a stronger base, such as pyridine. Arsenic trichloride reacts with pyridine with liberation of a large amount of heat, forming, after evaporation of the excess pyridine, a crystalline compound $AsCl_3 \cdot C_5H_5N$. It is a familiar fact that pyridine forms crystalline compounds with those salts which, according to Lewis' theory, are fairly strong acids, e.g., zinc chloride. In these cases ionization of the solvent is impossible. The reaction may be represented as follows:

$$C_5H_5N\colon + AsCl_3 \rightleftharpoons C_5H_5N\colon AsCl_3 \rightleftharpoons C_5H_5N\colon AsCl_2^+ + Cl^-$$

The arsenic atom becomes more negative by gaining a share in the lone electron-pair of the nitrogen atom. The electrical stress can be relieved by the ionization of a chlorine atom. A similar situation holds for ether. An oxonium salt is formed in solution. If we regard the ether and pyridine as solvents, we see that no cation characteristic of the solvent is formed.

We might have drawn the same conclusion from the previously considered reaction between pyridine and water:

$$C_5H_5N\colon + HOH \rightarrow C_5H_5N\colon H^+ + OH^-$$

If pyridine is considered the basic solvent and water the acid dissolved in it, there is again no splitting of the solvent to give a cation characteristic of the solvent. The above examples illustrate the inadequacy of the idea that acids and bases can be defined in terms of ions. In certain solvents acids increase the concentration of solvent cations and bases increase the concentration of solvent anions, but in other solvents they do not. These experimental facts do not affect the electronic theory of acids and bases, because it is not stated in terms of ions. It is not even concerned with the mechanism of ionization after neutralization takes place. It recognizes, as does the Brönsted theory, that ionization may not be involved in many reactions of acids and bases.

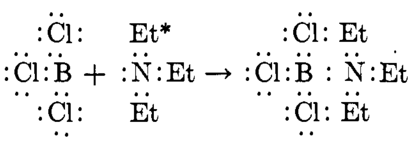
B. Neutralization and the solvent

Neutralization is the formation of the coördinate bond between the acid and the base. The electronic theory gives a real meaning to the word, a meaning of which the Brönsted theory takes no account. The type equation of the Brönsted theory:

$$\text{acid}_1 + \text{base}_2 \rightleftharpoons \text{acid}_2 + \text{base}_1$$

is often assumed to dispose of the concept of neutralization. We shall see in part III that this is not true. The equation may represent the fact that acids or bases will replace weaker acids or bases from their compounds. It does not abolish neutralization.

The acid boron trichloride is neutralized by the base triethylamine when both substances are in the pure liquid or gaseous state:



$$\begin{array}{cccccc} \overset{\cdot\cdot}{:Cl:} & & Et^{*} & & \overset{\cdot\cdot}{:Cl:} & Et \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}} & + & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:Et & \rightarrow & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:Et \\ \underset{\cdot\cdot}{:Cl:} & & Et & & \underset{\cdot\cdot}{:Cl:} & Et \end{array}$$

$^{*}Et = C_2H_5$

The product is usually called a molecular or addition compound. Lewis calls it a pseudo-salt, and remarks in passing that such compounds are incapable of ionization. This would seem to be an oversight. The possibility of ionization of one of the chlorine atoms ought to be considered. It may not occur to a great extent in this particular compound, but where sufficient electrical stress is set up, upon the acceptance of a share in another electron-pair by the acid, one would expect ionization to be favored. Such ionization would, of course, be greatly affected by the dielectric constant of the solvent. Three examples of ionization, of the many which could be given, are the following:

$$C_5H_5N: + H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow C_5H_5N:H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow C_5H_5N:H^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-$$

$$AlCl_3 + COCl_2 \rightarrow ClOCCl{:}AlCl_3 \rightarrow COCl^+ + AlCl_4^-$$

$$SnCl_4 + 2SeOCl_2 \rightarrow (SeOCl)_2SnCl_6 \rightarrow 2SeOCl^+ + SnCl_6^{--}$$

In such cases the product is usually considered a salt. There seems to be no need for the name "pseudo-salt."

Considering only acid-base reactions, solvents may be divided into three classes: (*1*) those that are practically inert toward acids and bases, e.g., benzene, carbon tetrachloride, and chlorobenzene; (*2*) those that are ionizable, e.g., water, ammonia, sulfur dioxide, phosgene, and selenium oxychloride; (*3*) those that do not ionize but do react with acids and bases, e.g., ether and pyridine. If we consider the neutralization of boron trichloride by triethylamine in the three types of solvents, we find that the net result may be the same as when the neutralization occurs in the absence of a solvent.

When the solvent is inert it is merely a diluent and the neutralization product is obtained directly. When the solvent is ionizable, intermediate reactions with the solvent may be observed. If either the acid or the base, or both, are strong enough, they will be at least partially neutralized by the solvent; e.g., if selenium oxychloride is chosen as the solvent,

$$BCl_3 + SeOCl_2 \rightarrow SeOCl^+ + BCl_4^-$$

$$(C_2H_5)_3N + SeOCl_2 \rightarrow (C_2H_5)_3NSeOCl^+ + Cl^-$$

When the two solutions are mixed, neutralization takes place, with the elimination of solvent.

$$SeOCl^+, BCl_4^- + (C_2H_5)_3NSeOCl^+, Cl^- \rightarrow (C_2H_5)_3NBCl_3 + 2SeOCl_2$$

The same product is obtained as when the reaction is carried out directly or in an inert solvent.

When the solvent reacts without ionizing, it reacts with either the acid or the base, but not ordinarily with both. Such solvents are usually not amphoteric. For example, if boron trichloride is neutralized by triethylamine in ether, the boron trichloride would react with the ether, but the triethylamine would not. The oxygen atom in the ether can donate an electron-pair to form an oxonium bond, but the hydrogen atoms in ether have little tendency to form hydrogen bonds (94).

$$BCl_3 + (C_2H_5)_2O \rightarrow (C_2H_5)_2OBCl_3$$

When triethylamine is added, it merely displaces the weaker base and the resulting product is the same as before.

$$(C_2H_5)_2OBCl_3 + (C_2H_5)_3N \rightarrow (C_2H_5)_3NBCl_3 + (C_2H_5)_2O$$

In all four cases the neutralization product is the same.

However, it would be dangerous to generalize from this observation, since the reactions depend upon the relative strengths of the various acids and bases involved. Probably the most that ought to be attempted is the classification of solvents as inert, amphoteric, and non-amphoteric. The reactive non-ionizing solvents should be called non-amphoteric rather than either acidic or basic, because the ionizing solvents may be predominantly acidic or basic while retaining the possibility of amphoteric behavior under proper conditions.

C. Typical reactions of acids and bases

Typical properties of acids and bases are usually taken to be those which are observed in water solutions of acids and bases. Most of these properties are due to the increased concentration of solvent cation or solvent anion caused by the presence of the acid or base. The most familiar reactions dependent upon this effect probably are the reactions between the free elements and solutions of acids and bases, electrolysis, and the reactions of amphoteric substances. The first is the only one which requires further discussion before similar reactions in other solvents are considered.

Active metals like sodium and calcium are oxidized by pure water. Active non-metals like chlorine and sulfur also react with water, but the reactions are more complex. Chlorine reacts to give hydrochloric and hypochlorous acids. Sulfur reacts slowly when heated with water, to give several products (25). These reactions may be considered as due to the presence of hydrogen ions and hydroxyl ions. The hydrogen ions oxidize active metals and become free hydrogen. The reaction of hydroxyl ions with active non-metals is not so simple. This is probably due to the fact that the oxygen atom has a greater attraction for electrons than any other atom except fluorine. Many metals will reduce hydrogen ion, but only one non-metal, fluorine, will oxidize hydroxyl ion under ordinary circumstances. Chlorine and sulfur are unable to remove electrons completely from the hydroxyl ion.

These reactions proceed much more rapidly when the hydrogen-ion or hydroxyl-ion concentration is increased by the addition of an acid or base. This increase in rate seems to be a mass action effect, e.g., in the reaction

$$Mg + 2H_3O^+ \rightarrow Mg^{++} + H_2 + 2H_2O$$

increasing the concentration of the hydrogen ion will have the same effect whether it is done "directly" by adding hydrogen chloride, or indirectly by adding sulfur trioxide to the water. In like manner, it makes no difference how the hydroxyl-ion concentration is increased. It may be brought about by adding the ions directly through the addition of sodium hydroxide or it may be done indirectly by adding triethylamine to the water:

$$(C_2H_5)_3N\!: + H\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!H \rightarrow (C_2H_5)_3N\!:\!H^+ + :\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!H^-$$

It is worth noting at this point that, in these typical reactions, hydrogen ion and hydroxyl ion are not acting strictly as acid and base. The hydrogen ion acts as an oxidizing agent, removing electrons completely from the metals which react with it. The hydroxyl ion acts as a reducing agent toward the only element capable of removing electrons from it:

$$2F_2 + 4OH^- \rightarrow 4F^- + O_2 + 2H_2O$$

Such reactions, as well as those of electrolysis and of amphoteric behavior, have been observed in other solvents. Reactions which occur in ammonia (22 to 25), sulfur dioxide (2, 57 to 65, 104), acetic acid (11 to 15, 36), hydrogen sulfide (106), hydrogen fluoride (26), phosgene (29 to 31), selenium oxychloride (100, 107), alcohols (53, 91), and sulfuric acid (43, 44) are analogous to those which take place in water. Some of them have been interpreted according to the solvent system theory, others according to the proton theory. All of them may be understood more clearly on the basis of the electronic theory of acids and bases. Only a few examples will be discussed here.

A solution of aluminum chloride in phosgene dissolves metals with the liberation of carbon monoxide. According to Lewis' theory, the aluminum chloride is an acid and accepts an electron-pair from the solvent. The resulting electrical stress favors the ionization which increases the concentration of solvent cation. The solvent cation oxidizes the metal, and carbon monoxide is produced:

$$COCl^+ + Ca \rightarrow CO + Cl^- + Ca^{++}$$

or

$$CO(AlCl_4) + Ca \rightarrow CO + Ca(AlCl_4)$$

This behavior is analogous to that of sulfur trioxide when dissolved in water. The sulfur trioxide accepts an electron-pair from the solvent, and the concentration of the solvent cation is greatly increased. The solvent cation oxidizes the metal, and hydrogen is produced.

Similar reactions are observed in the other solvents listed above. Those in selenium oxychloride are particularly interesting since, as with phosgene, no protons are involved. Although the reported value of its solvent conductance (66) seems to be too high, the ion concentrations in pure selenium oxychloride are likely to be relatively great. It would appear also that the solvent cation is a stronger oxidizing agent than hydrogen ion. Yet when an acid like stannic chloride is dissolved in selenium oxychloride (100), the result is as expected. The solution reacts more vigorously with metals than does the pure solvent, because of the increased concentration of solvent cation:

$$SnCl_4 + 2SeOCl_2 \rightarrow (SeOCl)_2^+, SnCl_6^{--}$$

Jander has not yet investigated this effect in sulfur dioxide. One would expect that the same behavior would be observed. Sulfur monoxide should be produced when metals react with acid solutions of sulfur dioxide. One method of preparing sulfur monoxide (95, 20) is by the action of sulfonyl chloride on metals. The effect of strong acids, such as sulfur trioxide and boron trichloride, should be to increase the rate of formation of sulfur monoxide.

Corresponding reactions for bases, i.e., the action of the solvent anion as a reducing agent, are observed in liquid ammonia. Whereas in water fluorine is the only active non-metal which can oxidize hydroxyl ion, in ammonia the other halogens can oxidize the amide ion. Iodine reacts with amide ion, just as fluorine reacts with hydroxyl ion (4, 25):

$$3I_2 + 6NH_2^- \rightarrow 6I^- + 4NH_3 + N_2$$

The reaction is more vigorous in a potassium amide solution than in ammonia alone. Other reactions with non-metals such as sulfur, involving an increased concentration of solvent anion, are more complex.

They are similar to those in water, since, like the hydroxyl ion, the amide ion does not readily lose electrons completely.

When electrolysis reactions in various solvents are considered, the conditions that determine which ion is to be discharged at either electrode are such that no conclusions can be drawn with regard to acid-base phenomena. For example, hydrogen is discharged at the cathode when an aqueous solution of an acid is electrolyzed, but hydrogen is also produced when an aqueous solution of sodium sulfate or of sodium hydroxide is electrolyzed. The most that can be said for the results of electrolysis is that they are consistent with what has just been said concerning cations and anions characteristic of the solvent. Carbon monoxide is discharged at the cathode when a solution of aluminum chloride in phosgene is electrolyzed. Selenium dioxide and selenium monochloride are produced at the cathode upon electrolysis of a solution of stannic chloride in selenium oxychloride.

Interpretation of the work of Bagster and Cooling (2) according to the electronic theory of acids and bases would indicate that they unknowingly produced sulfur monoxide by electrolysis. Their interest in demonstrating the existence of the hydronium ion apparently caused them to overlook indications which might have led to the discovery of sulfur monoxide. When water was added to liquid sulfur dioxide and gaseous hydrogen bromide was passed in, two liquid layers were formed. Electrolysis of the sulfur dioxide layer yielded hydrogen at the cathode and bromine at the anode. Water collected at the cathode in proportion to the amount of silver deposited in a coulometer, but the amount of hydrogen discharged was less than expected, if the only ion being discharged was the H_3O^+ ion. This would indicate that $SO(H_2O)_2^{++}$ ions were being discharged as well as hydronium ions. Bagster and Cooling were not able to account for the smaller amount of hydrogen, but they did siphon off the sulfur dioxide layer from the water layer and try electrolysis of the sulfur dioxide alone. The conductance fell rapidly and sulfur was deposited at the cathode, but no water. This would indicate that the (solvated) SO^{++} ion was being discharged to form sulfur monoxide. Sulfur monoxide decomposes readily to form sulfur and sulfur dioxide.

Amphoteric reactions such as those of the hydroxides of aluminum and zinc also occur in other solvents. When potassium hydroxide is added to insoluble aluminum hydroxide in water, the following reaction takes place:

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$

The $Al(OH)_4^-$ ion is soluble. It is formed because the aluminum hydroxide is acidic, in that the aluminum atom accepts an electron-pair to complete its octet. An analogous reaction takes place in liquid ammonia (3), when insoluble aluminum amide is dissolved by potassium amide.

$$Al(NH_2)_3 + NH_2^- \rightarrow Al(NH_2)_4^-$$

The zinc ion is also a fairly strong acid, and its insoluble compounds with solvent anions are often amphoteric. For example, in water, liquid ammonia (25), and glacial acetic acid (15) the following reactions occur:

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{--} \quad \text{(in water)}$$

$$Zn(NH_2)_2 + 2NH_2^- \rightarrow Zn(NH_2)_4^{--} \quad \text{(in ammonia)}$$

$$Zn(C_2H_3O_2)_2 + 2C_2H_3O_2^- \rightarrow Zn(C_2H_3O_2)_4^{--} \quad \text{(in acetic acid)}$$

The complex anions formed are soluble in each case. Such reactions occur because zinc and aluminum ions are fairly strong acids, having considerable tendency to complete their octets. Thus the electronic theory of acids and bases provides a consistent explanation of all such phenomena.

One other example of typical basic properties will be discussed briefly. Zinc, aluminum, and a few other metals are dissolved in water and in liquid ammonia (3) by bases as well as by acids. In both solvents hydrogen is liberated and the same complex anions are formed as when the insoluble solvent anion compounds are dissolved by bases:

$$Zn + 2KOH + 2H_2O \rightarrow K_2Zn(OH)_4 + H_2$$

$$Zn + 2KNH_2 + 2NH_3 \rightarrow K_2Zn(NH_2)_4 + H_2$$

$$2Al + 2KOH + 6H_2O \rightarrow 2KAl(OH)_4 + 3H_2$$

$$2Al + 2KNH_2 + 6NH_3 \rightarrow 2KAl(NH_2)_4 + 3H_2$$

Bergstrom (3) has suggested that the mechanism of the reaction between aluminum and potassium amide in liquid ammonia is as follows:

$$Al + 3KNH_2 \rightarrow Al(NH_2)_3 + 3K$$

The potassium ion is reduced, in spite of the fact that it has less affinity for electrons than the aluminum atom, because the insolubility of the aluminum amide drives the equilibrium to the right. The aluminum amide then reacts with amide ion to form the complex $Al(NH_2)_4^-$ ion, which still keeps the concentration of aluminum ion very low:

$$Al(NH_2)_3 + KNH_2 \rightarrow KAl(NH_2)_4$$

The reaction between the free potassium and the solvent is one which is ordinarily slow, but it is catalyzed by the aluminum:

$$6K + 6NH_3 \rightarrow 3H_2 + 6KNH_2$$

Bergstrom suggests that the mechanism of similar reactions in water is the same, and cites the fact that the blue color observed when a magnesium rod is dipped into fused potassium hydroxide is an indication of the presence of free potassium from the reaction

$$Mg + 2KOH \rightarrow Mg(OH)_2 + 2K$$

Such reactions probably are not general enough to warrant calling them typical basic reactions.

All the reactions so far discussed in this section have involved amphoteric solvents which, it is assumed, may ionize like water. Most of the reactions involve the same effect of acids and bases on the concentration of solvent cations or solvent anions that is observed in water. They are "typical" reactions only because they resemble those in water, with which we are more familiar. We should expect, therefore, that acid–base properties in inert solvents such as benzene, or in non-amphoteric solvents such as pyridine, would not be "typical." In such solvents there is no possibility of a "typical" increase in solvent cations or anions upon the addition of acids or bases. Ions are produced when acids and bases react with non-amphoteric solvents such as pyridine and ether, but the ions formed are not "characteristic" of the solvent. Little more needs to be said here than in section A of this part, except by way of indicating the possibilities of a wider application of Lewis' theory. Only one example will be given. The conductance curves of silver salts in pyridine (86) and in amines (18, 19) are abnormal. A possible explanation lies in the fact that the silver ion is a fairly strong acid. A familiar indication of this is the formation of the $Ag(NH_3)_2^+$ ion in water. The silver ion can accept two electron-pairs, each involving one molecule of a neutral base, such as ammonia, pyridine, or amines.

As a rule no ions are produced when acids and bases are dissolved in inert solvents. The assumption of "protective coatings" (39) to explain the absence of a reaction between metals and a solution of hydrogen chloride in benzene is unnecessary. In water metals react more rapidly when an acid is present, because of the increased concentration of solvent cations. The metal reacts slowly with water even in the absence of the acid, but no such reaction takes place in benzene because there are no solvent cations with which the metal can react. The statement is sometimes made that acids dissolved in inert solvents do not react with carbonates. The reaction with carbonates is one which does not necessarily depend on solvent cations. It depends on the strength of the acid required to displace the weaker carbon dioxide from its compound. Lewis has shown (78) that a strong acid like boron trichloride will displace carbon dioxide from sodium carbonate in a mixture of carbon tetrachloride and acetone.

The fact that acids are not usually ionized in inert solvents permits a better determination of their relative strength than is possible in water. In water perchloric, hydriodic, hydrobromic, hydrochloric, and nitric acids are all practically 100 per cent ionized, thus appearing to be of equal strength. They all have such a strong tendency to accept an electron-pair that the reaction with water goes to completion. Because of this "leveling effect," as Hantzsch called it, there can be no stronger acid than hydrogen ion in water. Any acid much stronger than hydrogen ion will displace it completely. One way in which the strengths of such acids can be compared is by measuring them in some inert solvent. This has been done by Hantzsch (47, 48, 49), who found a great difference in the strengths of several strong hydrogen acids. Perchloric acid is the strongest, followed in order by hydriodic, hydrobromic, hydrochloric, and nitric acids.

We have seen that Walden's fears that Lewis would deliberately eliminate the important part played by the solvent in acid–base properties were entirely groundless. Lewis' acids and bases, dissolved in suitable amphoteric solvents, have the "typical" properties of acids and bases. These "typical" properties are the properties with which we are familiar from our study of water chemistry. Now that we are beginning to branch out into other fields, we may expect to find increasingly that the electronic theory of acids and bases is the only one so far proposed which is at all adequate.

III. FURTHER IMPLICATIONS OF THE ELECTRONIC THEORY OF ACIDS AND BASES

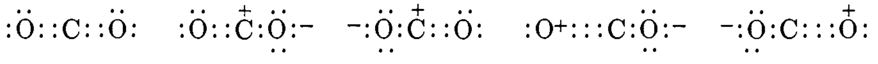
A. The extent of acid–base phenomena

The measure of correlation to be effected by the electronic theory of acids and bases can be surmised by recalling that all the substances that Sidgwick (98) called electron-pair acceptors and donors are really acids and bases (78). There is no need for any other name for them. The list of bases compiled by Brönsted and his followers is identical as far as it goes with that of Lewis, but the clear-cut recognition of the reason for their basicity is denied the followers of Brönsted by their devotion to the "cult of the proton". "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" (78). There is little doubt that the recognition of acids as electron-pair acceptors and bases as electron-pair donors will lead to as great a degree of systematization as did the recognition of oxidizing agents as electron-acceptors and reducing agents as electron-donors. Furthermore, the possibility of correlating the two types of phenomena now appears for the first time. This will be attempted in section D of this part.

Lewis has pointed out that there are only a small number of elements whose atoms can contribute basic properties to a molecule. These are principally the members of the nitrogen, oxygen, and fluorine families. The atoms of the "inert" gases can also act as bases (6, 93), by donating one or more pairs of their outer octets to sufficiently strong acids. On the other hand, all the elements except the rare gases and the heavier members of the alkali and alkaline-earth families can act as acids. Some of them are extremely weak, but even sodium ion has some tendency to accept an electron-pair. The atoms may manifest their acidic or basic tendencies in various ways, as atoms, ions, or molecules. For example, sulfur trioxide is a strong acid because in it the sulfur atom has a great tendency to accept an electron-pair to complete a stable octet (e.g., in becoming a sulfate ion), but the sulfide ion is a fairly strong base. Davy was not so far from the truth when he said that acidity does not depend upon a particular element, but upon the arrangement of atoms (38).

As a rule, consideration of the electronic structure will reveal whether a molecule is acidic or basic and often will give an idea as to its strength as an acid or base. It is found experimentally that these acids and bases, given sufficient difference in strength, combine "without impediment" (78). Lewis calls such acids and bases primary. No heat of activation is required for the neutralization of a primary acid and a primary base. On the other hand, certain substances which experimentally behave like acids, e.g., carbon dioxide and organic acid halides, have electronic formulas which, as usually written, do not show the possibility of their acting as electron-pair acceptors. Neutralization of these substances is always measurably slow (78, 79, 80). Such acids (and bases) are called secondary by Lewis. The neutralization of secondary acids and secondary bases requires heat of activation. Lewis suggests that these secondary acids and bases are not acids or bases in their normal states of lowest energy, as represented by the electronic formulas usually written, but may become acids and bases through excitation. These substances act like acids and bases,—except that their neutralization is slow,—but their electronic formulas do not indicate such behavior. Perhaps some of the difficulty lies in the formulas. This conclusion is supported by the work of Pauling (94).

According to Pauling, resonance in the carbon dioxide molecule occurs among five electronic structures:



$$:\overset{..}{\mathrm{O}}::\mathrm{C}::\overset{..}{\mathrm{O}}: \qquad :\overset{..}{\mathrm{O}}::\overset{+}{\mathrm{C}}:\underset{..}{\overset{..}{\mathrm{O}}}:^{-} \qquad {}^{-}:\underset{..}{\overset{..}{\mathrm{O}}}:\overset{+}{\mathrm{C}}::\overset{..}{\mathrm{O}}: \qquad :\mathrm{O}^{+}:::\mathrm{C}:\underset{..}{\overset{..}{\mathrm{O}}}:^{-} \qquad {}^{-}:\underset{..}{\overset{..}{\mathrm{O}}}:\mathrm{C}:::\overset{+}{\mathrm{O}}:$$

The carbon atom in the second and third arrangements of electrons can accept an electron-pair to complete a stable octet. Consideration of resonance in the carbon dioxide molecule brings the electronic formula into correspondence with the experimental behavior of carbon dioxide as a secondary acid. This is also true of the organic acid halides.

It has been known for some time that the properties of the carbon–oxygen double bond often are not well represented by the usual formula. Lowry suggested in 1923 that, instead of representing the structure of the carbonyl group of aldehydes and ketones as in $R_2C::\ddot{O}:$, the formula $R_2C^+:\underset{\cdot\cdot}{\ddot{O}}:^-$ should be used. Pauling shows that, in the resonance between the two, the latter structure is almost as significant as the former. In the semi-ionic structure the carbon atom can accept an electron-pair, so that the possibility of acidic behavior is indicated. Compounds containing such double bonds should be amphoteric. In terms of the electronic theory, the familiar reactions of aldehydes confirm this conclusion. The organic acid halides exhibit more definite "typical" acid behavior in one respect, because they can react with water to increase the concentration of hydrogen ions.

Another type of "secondary" behavior is evident when amphoteric molecules partially or wholly neutralize each other, or when molecules are neutralized by the solvent in which they are placed. For example, the acid A may be dissolved in the weak base B and be neutralized, in that the stable electron configuration of the acidic atom has been attained by acceptance of electron-pairs from the base. Yet if a stronger base B^1 is added, the stronger base will replace the weaker one in combination with the acid:

$$B^1 + AB \rightarrow AB^1 + A$$

Such reactions usually require activation, but in many cases this is small enough to be ignored (78).

Another extension of the idea of acids and bases involves acidic and basic radicals in organic compounds (78). For example, the familiar ortho–para-directing groups for substitutions in the benzene ring are basic. They have electron-pairs which they can share with a neighboring atom. The meta-directing groups are acidic. They can share an electron-pair possessed by a neighboring atom. The action of the acid and basic radicals in directing substituents is explained in terms of resonance by Ingold (55) and Pauling (94).

As has already been indicated, the treatment of amphoteric behavior is much more satisfactory on the basis of the electronic theory. Amphoterism is widespread. As Hantzsch has shown experimentally (49, 51), even strong acids like nitric acid may be amphoteric. Hydrogen chloride is also amphoteric. It acts as a base toward many strong acids like stannic chloride, in forming such compounds as H_2SnCl_6. This is readily accounted for, since one or more atoms in a molecule may be able to accept electron-pairs while others may donate them. The amphoteric behavior of many solvents has been explained by Sidgwick (98) on this basis. It accounts for the association which is typical of amphoteric solvents. Ether and pyridine are not associated, because they are not amphoteric. Obviously, a very large number of substances can act either as acids or as bases, depending on the conditions under which they react.

These examples are only an indication of the widespread applicability of the electronic theory of acids and bases.

B. Strengths of acids and bases

According to Lewis' theory, the strength of an acid corresponds to its tendency to accept an electron-pair from a base. The strength of a base corresponds to its tendency to donate an electron-pair to an acid. Strong acids and bases combine with each other to form stable compounds. Strong acids and bases may combine with weak ones to form fairly stable compounds, but weak acids and bases do not ordinarily form stable compounds. In general a strong acid, A^1, will replace a weaker one from combination with a base:

$$A^1 + AB \rightarrow A^1B + A$$

A strong base, B^1, will replace a weaker one from combination with an acid:

$$B^1 + AB \rightarrow B^1A + B$$

For example, stannic chloride dissolved in selenium oxychloride combines with the solvent. When a stronger base than selenium oxychloride, such as pyridine, is added, the selenium oxychloride is replaced and a more stable compound is formed (100).

This conception of replacement is often equivalent to the Brönsted formulation,

$$A_1 + B_2 \rightarrow A_2 + B_1$$

but is more exact. Furthermore, it does not require abandoning the concept of neutralization. Neutralization occurs when an acid combines with a base, but a stronger acid will replace the first one. This sequence may be illustrated as follows:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The formation of the coördinate bond between the water molecule and the hydrogen chloride, by means of the "hydrogen bond," results in such great electrical stress that practically all of the molecules thus formed split into ions. Neutralization has occurred through the formation of the coördinate bond. The subsequent behavior is irrelevant. The "acidic" reaction of the solution toward litmus and some other indicators is only relative. The solution is merely acidic with respect to pure water. If a stronger base than water is added, the water will be displaced from its combination with the proton:

$$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$$

$$B^1 + AB \rightarrow AB^1 + B$$

The ammonium ion is more stable than the hydronium ion.

With proper precautions, such replacement reactions can often be used to measure acid or base strength, as we have already seen in section A of part II. An interesting example of this method is given by the work of Sisler and Audrieth on the action of liquid ammonia on sulfur trioxide addition compounds (99). Although they did not think of it as such, their work seems to be an excellent illustration of the replacement of bases by a stronger base. Sulfur trioxide is one of the strongest acids known. It forms compounds even with such weak bases as hydrogen chloride. Compounds of sulfur trioxide with the five bases pyridine, dimethylaniline, dioxane, sodium chloride, and hydrogen chloride were added to liquid ammonia, a stronger base. The reactions were more rapid in the order given, those between ammonia and the sodium chloride–sulfur trioxide and the hydrogen chloride–sulfur trioxide addition compounds being extremely vigorous.

A convenient way of using the replacement method may be to employ an indicator as one of the acids or bases (12, 32, 40, 42, 49, 50, 68, 71). Among methods of estimating acid or base strength are the determination of dissociation constants by other means, such as conductivity measurements (19, 70, 103, and others) and the measurement of catalytic activity (48, 49). By the latter method Hantzsch showed that the order of strength of some hydrogen acids in inert solvents is as follows: $HClO_4 > HI > HBr > RSO_2OH > HCl > HNO_3 > CCl_3COOH$. Kolthoff and Willman (70) have found the same order for perchloric, hydrobromic, hydrochloric, and nitric acids in glacial acetic acid by the conductance method. Another method which may offer promise in some cases involves electromotive force measurements (34, 96). It is interesting to note that the "anomalous" conductance curves cited by Hall and Werner (34) have since been accounted for by the work of Fuoss and Kraus (27, 28, 85).

While in general it seems possible to arrange acids or bases in a sequence of strengths, the situation is far from clarified. Three of the principal sources of confusion are the leveling effect, the existence of specific reactions such as those cited by Lewis (78, 81), and the effect of concentration. The leveling effect makes it impossible to differentiate between the strengths of acids such as perchloric and hydrochloric in dilute aqueous solution. Both are strong enough acids and water is strong enough as a base so that the reactions go to completion in dilute solution. The more basic a solvent is, the greater will be its leveling effect upon acids. For example, in liquid ammonia acetic acid appears to be as strong as hydrogen chloride (96). Ammonia is a strong enough base so that the reaction to form ammonium and acetate ions is practically complete. On the other hand, when the solvent is weak enough as a base the differences begin to appear again. In acetic acid the difference between perchloric acid, hydrogen bromide, hydrogen chloride, and other acids becomes obvious (12, 70). The use of an inert solvent, when possible, may overcome the difficulty arising from the leveling effect. This may not be necessary if work in a particular solvent can be confined within certain limits. The order in strength of many weak acids is the same in water as it is in inert solvents such as chlorobenzene (32).

The only important criticism of Lewis' theory has been made by Shatenstein (97). He maintains that Lewis' emphasis upon specific reactions is inconsistent with his "phenomenological criterion" that an acid or base will replace a weaker acid or base from its compounds. If these exceptions are as widespread as Lewis seems to indicate, this criticism appears to be a valid one, unless some consistent reason for their appearance as exceptions can be found. Perhaps in some instances the effect of concentration has not been properly considered. This seems to be true in one case cited by Lewis as an example of specific behavior.

Lewis states (78) that many heavy-metal ions, like silver ion, are stronger acids toward ammonia than toward "water or hydroxyl ion." He says that these ions have little tendency to combine with hydroxyl ion, but a strong tendency to combine with ammonia. This is said to occur in spite of the fact that hydroxyl ion is a slightly stronger base toward hydrogen ion than is ammonia, as shown by the equilibrium constant of the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Lewis develops the idea, using silver ion as an example, as showing how impossible it is to arrange acids in a single monotonic order. This case is one of the principal reasons given by him for believing that relative strength depends upon both the solvent and the particular acid or base used for reference.

The present author believes that Lewis is mistaken in this instance.

If this is true, it seems that such a mistake may arise from a failure to consider carefully enough the effect of concentration on the equilibria involved. Oxidizing and reducing agents are arranged in a series according to their strength at a given concentration. Looking at the electrochemical series, we say that potassium is a stronger reducing agent than aluminum. Yet in liquid ammonia aluminum may reduce potassium ions. In the equilibrium

$$Al + 3KNH_2 \rightleftharpoons Al(NH_2)_3 + 3K$$

the reaction is practically complete to the right, because the aluminum amide is insoluble so that the concentration of aluminum ions is kept low. Such apparent exceptions to the electrochemical series are fairly common, and many other examples could be given, such as the reaction between silver and hydriodic acid and the reversal of a Daniell cell. If the effect of concentration were not understood, the electrochemical series would have been discarded long ago. The situation seems to be similar with regard to acids and bases.

When the effect of concentration is carefully considered, it would appear that the behavior of the heavy-metal ions toward hydroxyl ion and ammonia does not support Lewis' contention that it is impossible to arrange acids and bases in a single monotonic order. In the first place, Lewis fails to distinguish between the basic strength of water and the hydroxyl ion (78, page 299). He says that in aqueous solution, e.g., in a solution of silver nitrate, the heavy-metal ions which combine with ammonia have little tendency to combine with hydroxyl ions. It is true that some of these ions do not displace hydrogen ions from water by combining with hydroxyl ions to any great extent. This merely indicates that they are not strong acids compared to hydrogen ion. A careful distinction must be made between the reaction of these ions with water and their reaction with hydroxyl ion. Both hydroxyl ion and ammonia are much stronger bases than water. No comparison between ammonia and hydroxyl ion can be attempted unless the concentrations of each are comparable. When this is the case, we find that the tendency of the heavy-metal ions to combine with hydroxyl ion is comparable with their tendency to combine with ammonia. For example, cupric ions form a precipitate with hydroxyl ions. The principal difference lies in the fact that one base is charged and the other is not. The negative charge on the hydroxyl ion usually prevents the cation from coördinating as many hydroxyl ions as it does ammonia molecules.

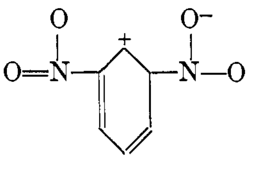
Familiarity with the action of ammonia solution in first precipitating the hydroxides of these heavy-metal ions and then dissolving them upon further addition of ammonia is likely to lead one astray, unless the effects of variation in the concentrations of the various ions and molecules are all taken into account. When this is done, it is found that the metal ions which combine with ammonia are not stronger acids toward ammonia than toward hydroxyl ion. For example, when an ammonia solution is added to a solution of silver nitrate a drop at a time, a brown precipitate forms. This precipitate is probably silver hydroxide, which when dehydrated becomes black silver oxide. Whether its formula is AgOH or not, its precipitation is due to the presence of hydroxyl ion in small concentration, produced by the reaction

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

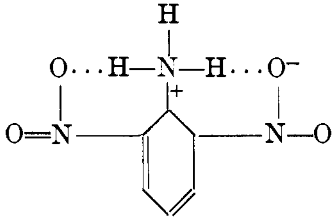
The equilibrium is such that in ordinary use the concentration of ammonia is much higher than the concentration of hydroxyl ion. The formation of the precipitate with the initial addition of ammonia solution shows that hydroxyl ion is a stronger base than ammonia toward silver ion, just as it is toward hydrogen ion. When more ammonia solution is added, the mixture is much more concentrated in ammonia with respect to hydroxyl ion, and the precipitate dissolves to form the silver ammonia complex. This reaction takes place, despite the fact that the hydroxyl ion is a slightly stronger base than ammonia, because the concentration of ammonia has been so greatly increased. It is comparable to the reversal of a Daniell cell or to the reaction between silver and hydriodic acid, which takes place even though silver is below hydrogen in the electrochemical series.

If only a few drops of ammonia solution have been added in excess, addition of a few drops of sodium hydroxide solution brings the precipitate of silver hydroxide back. Even after a large amount of ammonia has been added, the precipitate can be brought back if the proportion of hydroxyl ion to ammonia is made high enough by dissolving solid sodium hydroxide in the solution. When the concentration of hydroxyl ion is maintained by an excess of solid sodium hydroxide, the silver hydroxide precipitate does not dissolve at all. When concentrated ammonia solution is added, vigorous bubbling occurs as the solution is shaken, owing to the escape of some of the ammonia because of the high hydroxyl-ion concentration, and the precipitate turns black; but it does not dissolve so long as the hydroxyl-ion concentration is maintained by an excess of solid sodium hydroxide. After enough water is added to dissolve the sodium hydroxide, the black precipitate redissolves when sufficient ammonia solution is added to make the ammonia concentration large compared to the hydroxyl-ion concentration. Thus it would seem that the behavior of the heavy-metal ions towards hydroxyl ion and ammonia does not support the conclusion that acids and bases cannot be arranged in a single order of strength. When the effect of changing concentration upon such reactions is considered, encouragement is given the feeling that an order of acidic and basic strength which will be at least as reliable as the electrochemical series may be worked out.

The problem seems at present more difficult for acids and bases than for oxidizing and reducing agents. Lewis gives other examples of specific reactions. His examples involving chelation are especially interesting (78, 81). For example, ammonia is a weaker base than triethylamine, yet it behaves as a much stronger one toward *m*-dinitrobenzene. Double chelation is the explanation advanced by Lewis and Seaborg (81):



I



II

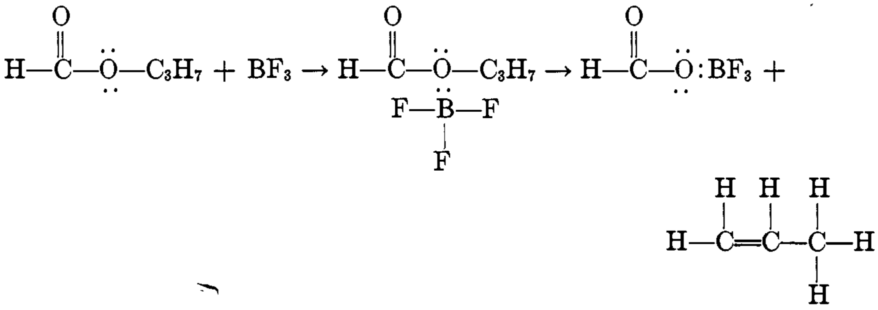
Formula I represents one of the resonating structures of *m*-dinitrobenzene. Formula II represents the compound formed upon the addition of ammonia. Lewis' papers may be consulted for other examples of such effects due to chelation. It also seems to be true that the relative strengths of two bases, one neutral and one charged, e.g., acetate ion and aniline, are affected by changes in solvent, whereas the relative strengths of two bases of the same electrical type are not (42). Another complicating factor for solutions of acids and bases is the influence of the dielectric constant of the solvent. In a solvent of high dielectric constant, dissociation may take place, whereas the same substance in a solvent such as benzene may be highly associated. The degree of dissociation depends upon the difference in strength between the acid or base and the solvent as well as upon the dielectric constant. Perhaps for the time being the problem should be simplified by accepting certain restrictions, such as limiting comparisons to the same charge type.

With these limitations and by proper precautions as to the leveling effect it would seem possible to work out a series of acid and base strengths which would be as useful as the electrochemical series. However, the experimental evidence is not yet complete enough to permit reaching a definite decision at the present time. Perhaps there is no decision to be made. There seems to be little real difference between saying that it is impossible to arrange acids and bases in an exact order because of certain specific reactions, but that in general it can be done for practical purposes, and saying that it is possible if we understand the reason for certain exceptions.

C. Catalysis

One property of acids and bases which has not yet been considered is their catalytic action. Hantzsch (43 to 51) was one of the first to show that acid catalysis does not necessarily depend upon hydrogen-ion concentration, even for hydrogen acids. The Brönsted theory has dealt with a limited phase of acid-base catalysis in terms of mathematics which gives little understanding of the mechanism (8, 82). When we consider the effect of strong acids like the boron and aluminum chlorides on organic syntheses, we realize what a large amount of work remains to be done. Only a few examples of acidic and basic catalysis will be given to show how the mechanism may be better understood by means of the electronic theory.

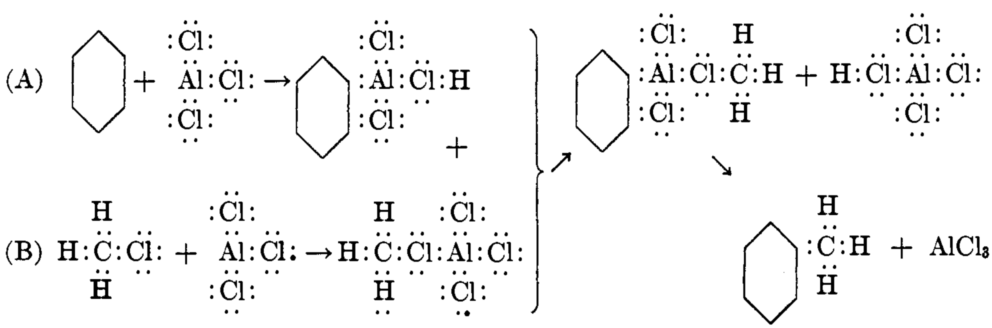
Benzene can be alkylated by esters in the presence of aluminum chloride or boron trifluoride (89). Alcohols are supposed to react with benzene by dehydration and condensation of the olefin into the benzene nucleus. Esters appear to react in a similar manner:



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}C_3H_7 + BF_3 \rightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\cdot\cdot}{\underset{\underset{\displaystyle F{-}\underset{\underset{\displaystyle F}{|}}{B}{-}F}{\cdot\cdot}}{O}}{-}C_3H_7 \rightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{:}BF_3 + H{-}\overset{\overset{\displaystyle H}{|}}{C}{=}\overset{\overset{\displaystyle H}{|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}H}$$

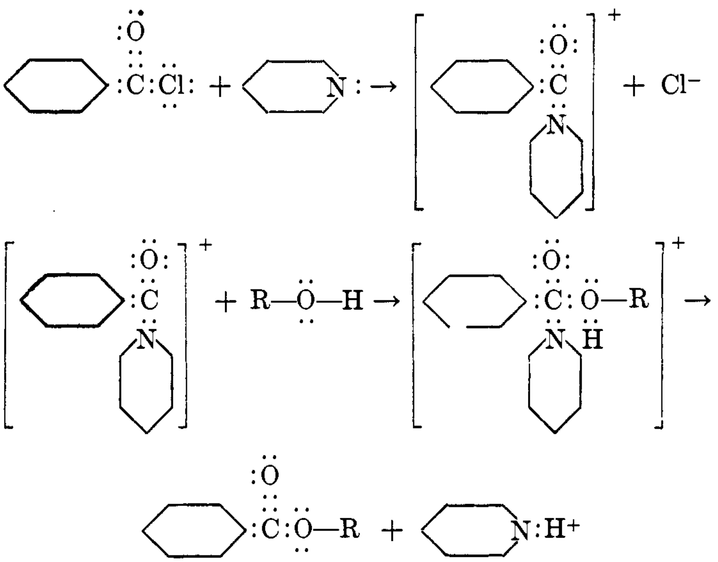
The olefin then reacts with the benzene.

Another example is the formation of toluene from benzene and methyl chloride. One suggested mechanism (17) is as follows:



Reaction A is replacement of the hydrogen by a stronger acid. Reaction B is the combination of a strong acid with a weak base. The resulting electrical stresses lead to instability, and the rearrangements to give toluene follow. The results of Wohl and Wertyporoch (108) indicate that ionization takes place during the reaction.

An interesting example of basic catalysis is given by W. Hückel (53). The reaction between alcohols and benzoyl chloride is much more rapid in pyridine, and conductance measurements indicate ionization. Apparently the reaction between benzoyl chloride (a secondary acid) and pyridine results in ionization, as follows:



Such examples show that the electronic theory of acids and bases can be of great aid in a systematic interpretation of a wide area of catalytic action.

D. Relationship of acid–base phenomena to oxidation–reduction

The experimental relationship between acids and oxidizing agents and bases and reducing agents is close. As has been shown in section C of part II, the "typical" acid effect on metals is due to the oxidizing action of the solvent cation. Usanovich (101) attempted to explain the relationship by including oxidation as a special case of acid behavior. Ingold (54, 55) has classified various reactions as electrophilic and nucleophilic. He was on the verge of discovery, but too close adherence to the "cult of the proton" restrained him. The electronic theory of acids and bases permits a clear-cut solution of the problem. The logical excellence of the theory is perhaps nowhere more strikingly demonstrated than in the greater degree of correlation in all fields of chemistry made possible by an understanding of the relationship between acids and bases and oxidizing and reducing agents. So far as the author is aware, the presentation of this relationship is given here for the first time.

It is an experimental fact that a given substance may under properly chosen conditions act as an acid, a base, an oxidizing agent, or a reducing agent. For example, water acts as an acid toward ammonia, as a base toward hydrogen chloride, as an oxidizing agent toward active metals, and as a reducing agent toward fluorine. Thus a considerable degree of relativity is indicated. This should lead to no difficulty if the terms are used as referring to the experimental behavior of a substance as it acts in the particular reaction under consideration.

TABLE 3

Electrophilic and electrodomic reagents

ELECTROPHILIC REAGENTS: ACIDS AND OXIDIZING AGENTS			ELECTRODOMIC REAGENTS: BASES AND REDUCING AGENTS		
Reagent	Number of electrons accepted		Reagent	Number of electrons donated	
	Shared, acting as an acid	Completely, acting as an oxidizing agent		Shared, acting as a base	Completely, acting as a reducing agent
MnO_4^-		5	Na		1
Cl_2		2	Sn^{++}		2
Fe^{+3}	6, 8(1), 10	1, 3	SO_2	2, 4	2
H_2O	2	2	H_2O	2	2
H_3O^+	2	1	CN^-	2	1
Be^{++}	4	2	S^{--}	2, 4, 6, 8	2
HBr	2		NH_3	2	3
BF_3	2		OH^-	2, 4	2

Ingold (55) called reagents such as chlorine and hydronium ion, which have an attraction for electrons, *electrophilic.* Those reagents which, like ammonia and sodium, have a tendency to give up electrons were called *nucleophilic.* "Electrophilic" seems to be a good word to retain, since it graphically describes the theoretical action of the reagents to which it applies. But it is difficult to picture sodium or other strong reducing agents as actually nucleophilic. A term which indicates the tendency to lose or give up electrons would be more appropriate. *Electrodomic* (Gr. *didomi,* to give) is euphonious and corresponds theoretically to electrophilic.

Both acids and oxidizing agents are electron-acceptors. An acid accepts a share in an electron-pair held by a base, while an oxidizing agent takes over completely the electrons donated by a reducing agent. Both bases and reducing agents are electron-donors. A base donates a share in an electron-pair to an acid, while a reducing agent loses electrons completely to an oxidizing agent. Some electrophilic reagents such as H_3O^+ may act either as acids or as oxidizing agents depending upon the conditions. Others, like boron trifluoride, never act directly as oxidizing agents, while some, like permanganate ion, never act as acids. Some electrodomic reagents, such as sulfide ion, may act either as bases or as reducing agents. Others, such as sodium, never act as bases. Table 3 will help to clarify the various relationships. The reagents are not arranged in the order of their tendency to gain or lose electrons but only so that extremes of behavior will be obvious. Roughly, the order of acid or base strength increases downward in the two columns of reagents.

Acids and oxidizing agents are electrophilic. Electrophilic reagents may accept electrons from electrodomic reagents. Bases and reducing agents are electrodomic. If the reaction between electrophilic and electrodomic reagents involves the complete transfer of electrons, it is oxidation–reduction. If the reaction involves the sharing of electrons which the electrodomic reagent donates to the electrophilic reagent, it is the reaction between an acid and a base, i.e., neutralization.

Thus we see that the electronic theory of acids and bases leads to an even greater degree of systematization in chemistry than Lewis proposed.

IV. CONCLUSION

The electronic theory of acids and bases provides a more logical and more fundamental interpretation than any other. No portion of the experimental facts is ignored by it. It is founded upon experimental behavior, with no preconceived notion as to the dependence of acidity on the presence of a particular element. It provides a general definition which attributes the distinctive properties of acids and bases to the molecules themselves, independently of the solvent. It explains these properties in terms of a simple inherent difference in electronic structure. The other two modern theories are merely limited aspects of the electronic theory of acids and bases.

Brönsted's proton-acceptors accept protons because, like the ammonia molecule, they have a pair of electrons which can be used in forming a coördinate bond with a proton or with any other acid. Experimentally there is no more justification for calling hydrogen chloride an acid than there is for calling sulfur trioxide and aluminum chloride acids.

The solvent system theory is simply a description of the manner in which acids and bases behave in amphoteric solvents. Any acid accepting an electron-pair from an amphoteric solvent causes an increased concentration of solvent cations. Any base donating an electron-pair to an amphoteric solvent causes an increased concentration of solvent anions. Sodium hydroxide in water and sodium amide in liquid ammonia are typical bases, because the concentrations of the solvent anions are increased by direct addition of the ions themselves.

The "typical" properties of acids and bases are largely due to this effect of acids and bases upon amphoteric solvents. These properties are considered typical because we have so long confined our attention to the properties of acids and bases in water, but even these typical properties are better understood in terms of the new theory.

The electronic theory offers great possibilities in the further study of catalysis. It also resolves the difficulty as to the significance of neutralization. One contemporary school of thought holds that neutralization is inseparable from salt formation; the other school maintains that there is no such thing as neutralization, but that an acid and base always react to form a new acid and base. The new theory reconciles the two extremes. Neutralization is the acceptance by an acid of an electron-pair from a base to form a coördinate bond between them. However, the possibility of the replacement of an acid or base by a stronger acid or base still remains.

Acids and bases are identical with Sidgwick's acceptors and donors of electron-pairs. Such an extension of our ideas of acids and bases should lead to at least as great correlation as did the similar extension of ideas of oxidizing and reducing agents. Furthermore, the new concepts result in an even greater degree of systematization by permitting a clear understanding of the relationship between acids, bases, oxidizing agents, and reducing agents. Acidity and oxidizing power are merely different manifestations of the electrophilic tendency of atoms, molecules, and ions. Basicity and reducing power are correspondingly different manifestations of the electrodomic tendency of atoms, molecules, and ions.

REFERENCES

(1) AXELROD, J., AND SWIFT, E. H.: J. Am. Chem. Soc. **62**, 33 (1940).
(2) BAGSTER, L. S., AND COOLING, G.: J. Chem. Soc. **117**, 693 (1920).
(3) BERGSTROM, F. W.: J. Am. Chem. Soc. **45**, 2788 (1923).
(4) BERGSTROM, F. W.: J. Phys. Chem. **30**, 12 (1926).
(5) BJERRUM, N.: Chem. Rev. **16**, 287 (1935).
(6) BOOTH, H. S., AND WILSON, K. S.: J. Am. Chem. Soc. **57**, 2273 (1937).
(7) BRÖNSTED, J. N.: J. Phys. Chem. **30**, 777 (1926).
(8) BRÖNSTED, J. N.: Chem. Rev. **5**, 231 (1928).
(9) CADY, H. P., AND ELSEY, H. M.: J. Chem. Education **5**, 1425 (1928).
(10) COLLIE, J. N., AND TICKLE, T.: J. Chem. Soc. **75**, 710 (1899).
(11) CONANT, J. B., AND HALL, N. F.: J. Am. Chem. Soc. **49**, 3047 (1927).
(12) CONANT, J. B., AND HALL, N. F.: J. Am. Chem. Soc. **49**, 3062 (1927).
(13) CONANT, J. B., AND WERNER, T. H.: J. Am. Chem. Soc. **52**, 4436 (1930).
(14) DAVIDSON, A. W.: J. Am. Chem. Soc. **50**, 1890 (1928).

(15) Davidson, A. W.: Chem. Rev. **8**, 175 (1931).
(16) Dermer, O. C., and Fernelius, W. C.: Z. anorg. allgem. Chem. **221**, 83 (1934).
(17) Egloff, G., Wilson, E., Hulla, G., Van Arsdell, P. M.: Chem. Rev. **20**, 345 (1937).
(18) Elsey, H. M.: J. Am. Chem. Soc. **42**, 2080 (1920).
(19) Elsey, H. M.: J. Am. Chem. Soc. **42**, 2454 (1920).
(20) Emeléus, H. J., and Anderson, J. S.: *Modern Aspects of Inorganic Chemistry.* D. Van Nostrand Company, New York (1939).
(21) Folin, O., and Flanders, F. F.: J. Am. Chem. Soc. **34**, 774 (1912).
(22) Franklin, E. C.: J. Am. Chem. Soc. **27**, 820 (1905).
(23) Franklin, E. C.: Am. Chem. J. **47**, 285 (1912).
(24) Franklin, E. C.: J. Am. Chem. Soc. **46**, 2137 (1924).
(25) Franklin, E. C.: *The Nitrogen System of Compounds.* Reinhold Publishing Corporation, New York (1935).
(26) Fredenhagen, K., and Cadenbach, G.: Z. physik. Chem. **A146**, 245 (1930).
(27) Fuoss, R. M., and Kraus, C. A.: J. Am. Chem. Soc. **55**, 2387 (1933).
(28) Fuoss, R. M., and Kraus, C. A.: J. Am. Chem. Soc. **55**, 3614 (1933).
(29) Germann, A. F. O., and Timpany, C. R.: J. Am. Chem. Soc. **47**, 2275 (1925).
(30) Germann, A. F. O.: J. Am. Chem. Soc. **47**, 2461 (1925).
(31) Germann, A. F. O.: Science **61**, 70 (1925).
(32) Griffiths, D. C.: J. Chem. Soc. **1938**, 818.
(33) Guss, L. S., and Kolthoff, I. M.: J. Am. Chem. Soc. **62**, 1494 (1940).
(34) Hall, N. F., and Werner, T. H.: J. Am. Chem. Soc. **50**, 2367 (1928).
(35) Hall, N. F.: J. Chem. Education **7**, 782 (1930).
(36) Hall, N. F.: Chem. Rev. **8**, 191 (1931).
(37) Hall, N. F.: Chem. Rev. **19**, 89 (1936).
(38) Hall, N. F.: J. Chem. Education **17**, 124 (1940).
(39) Hammett, L. P.: J. Am. Chem. Soc. **50**, 2666 (1928).
(40) Hammett, L. P., and Deyrup, A. J.: J. Am. Chem. Soc. **54**, 2721 (1932).
(41) Hammett, L. P., and Deyrup, A. J.: J. Am. Chem. Soc. **55**, 1900 (1933).
(42) Hammett, L. P.: Chem. Rev. **13**, 61 (1933).
(43) Hantzsch, A.: Z. physik. Chem. **61**, 257 (1908).
(44) Hantzsch, A.: Z. physik. Chem. **65**, 41 (1909).
(45) Hantzsch, A.: Z. Elektrochem. **24**, 201 (1918).
(46) Hantzsch, A.: Z. Elektrochem. **29**, 221 (1923).
(47) Hantzsch, A.: Ber. **60B**, 1933 (1927).
(48) Hantzsch, A., and Weissberger, A.: Z. physik. Chem. **125**, 251 (1927).
(49) Hantzsch, A.: Z. physik. Chem. **134**, 406 (1928).
(50) Hantzsch, A., and Voigt, W.: Ber. **62B**, 970 (1929).
(51) Hantzsch, A.: Ber. **63B**, 1789 (1930).
(52) Hantzsch, A.: Helv. Chim. Acta **14**, 665 (1931).
(53) Hückel, W.: Ann. **540**, 274 (1939).
(54) Ingold, C. K.: J. Chem. Soc. **1933**, 1120.
(55) Ingold, C. K.: Chem. Rev. **15**, 225 (1934).
(56) Jackson, J., and Smith, G. B. L.: J. Am. Chem. Soc. **62**, 544 (1940).
(57) Jander, G., and Wickert, K.: Z. physik. Chem. **A178**, 57 (1936).
(58) Jander, G., and Immig, H.: Z. anorg. allgem. Chem. **233**, 295 (1937).
(59) Jander, G., Knoll, H., and Immig, H.: Z. anorg. allgem. Chem. **232**, 229 (1937).
(60) Jander, G., and Ullman, D.: Z. anorg. allgem. Chem. **230**, 405 (1937).
(61) Jander, G., and Ruppolt, W.: Z. physik. Chem. **A179**, 43 (1937).
(62) Jander, G., and Mesech, H.: Z. physik. Chem. **A183**, 121 (1938).

(63) Jander, G., and Mesech, H.: Z. physik. Chem. **A183**, 255 (1939).
(64) Jander, G., and Mesech, H.: Z. physik. Chem. **A183**, 277 (1939).
(65) Jander, G.: Naturwissenschaften **26**, 779 (1938).
(66) Julien, A. P.: J. Am. Chem. Soc. **47**, 1799 (1925).
(67) Kilpatrick, M., Jr., and Rushton, J. H.: J. Phys. Chem. **34**, 2180 (1930).
(68) Kilpatrick, M., Jr., and Kilpatrick, M. L.: Chem. Rev. **13**, 131 (1933).
(69) Kolthoff, I. M.: Rec. trav. chim. **49**, 401 (1930).
(70) Kolthoff, I. M., and Willman, A.: J. Am. Chem. Soc. **56**, 1007 (1934).
(71) LaMer, V. K., and Downes, H. C.: Chem. Rev. **13**, 47 (1933).
(72) Lapworth, A.: J. Chem. Soc. **107**, 857 (1915).
(73) Lenher, V.: J. Am. Chem. Soc. **42**, 2499 (1920).
(74) Lenher, V.: J. Am. Chem. Soc. **43**, 32 (1921).
(75) Lenher, V.: J. Am. Chem. Soc. **44**, 1664 (1922).
(76) Lewis, G. N.: J. Am. Chem. Soc. **38**, 762 (1916).
(77) Lewis, G. N.: *Valence and the Structure of Atoms and Molecules.* The Chemical Catalog Company, Inc., New York (1923).
(78) Lewis, G. N.: J. Franklin Inst. **226**, 293 (1938).
(79) Lewis, G. N. and Seaborg, G. I.: J. Am. Chem. Soc. **61**, 1886 (1939).
(80) Lewis, G. N., and Seaborg, G. I.: J. Am. Chem. Soc. **61**, 1894 (1939).
(81) Lewis, G. N., and Seaborg, G. I.: J. Am. Chem. Soc. **62**, 2122 (1940).
(82) Livingstone, R.: J. Chem. Education **7**, 2887 (1930).
(83) Lowry, T. M.: J. Chem. Soc. **123**, 822 (1923).
(84) Lowry, T. M.: J. Chem. Soc. **127**, 1371 (1925).
(85) Luder, W. F., Kraus, P. B., Kraus, C. A., and Fuoss, R. M.: J. Am. Chem. Soc. **58**, 255 (1936).
(86) Luder, W. F.: Ph.D. Thesis, Brown University, 1937.
(87) Luder, W. F.: Rept. New Engl. Assoc. Chem. Teachers **41**, 111 (1940).
(88) Maron, S. H., and LaMer, V. K.: J. Am. Chem. Soc. **60**, 2588 (1938).
(89) McKenna, J. F., and Sowa, F. J.: J. Am. Chem. Soc. **59**, 1204 (1937).
(90) McReynolds, J. P.: J. Chem. Education **17**, 116 (1940).
(91) Meerwein, H.: Ann. **455**, 227 (1927).
(92) Muehlberger, C. W., and Lenher, V.: J. Am. Chem. Soc. **47**, 1842 (1925).
(93) Nikitin, B. A.: Compt. rend. acad. sci. U. R. S. S. **24**, 562 (1939).
(94) Pauling, L.: *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, New York (1939).
(95) Schenk, P. W., and Platz, H.: Z. anorg. Chem. **215**, 113 (1933).
(96) Schwarzenbach, G. E.: Helv. Chim. Acta **13**, 870 (1930).
(97) Shatenstein, A. I.: J. Gen. Chem. (U. S. S. R.) **9**, 1603 (1939).
(98) Sidgwick, N. V.: *The Electronic Theory of Valency.* Oxford University Press, New York (1927).
(99) Sisler, H. H., and Audrieth, L. F.: J. Am. Chem. Soc. **61**, 3392 (1939).
(100) Smith, G. B. L.: Chem. Rev. **23**, 165 (1938).
(101) Usanovich, M.: J. Gen. Chem. (U.S.S.R.) **9**, 182 (1939).
(102) Walden, P.: *Salts, Acids, and Bases.* McGraw-Hill Book Company, New York (1929).
(103) Walden, P.: Z. physik. Chem. **A168**, 419 (1934).
(104) Wickert, K., and Jander, G.: Ber. **70**, 251 (1937).
(105) Wickert, K.: Z. physik. Chem. **A178**, 361 (1937).
(106) Wilkinson, J. A.: Chem. Rev. **8**, 237 (1931).
(107) Wise, C. R.: J. Am. Chem. Soc. **45**, 1233 (1923).
(108) Wohl, A., and Wertyporoch, E.: Ber. **64**, 135 (1931).
(109) Wynne-Jones, W. F. K.: J. Chem. Soc. **1930**, 1064.