ACIDS, SALTS, AND BASES[1]

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It is not the purpose of this article to present a complete account of the way in which the concepts of acid, salt, and base have been developed in the course of time. Rather it is its purpose to give a description of the developments these concepts have undergone during the last twenty years, developments to which J. N. Brönsted (8) in particular has made important contributions. In the presentation an effort is made to emphasize the continuity between the old and the new conceptions, and to show how it is possible to use what is good in the new development without giving up the good in the old. It is my hope to help to bring about the more common use and recognition of the new ideas, not only in scientific work, but also in elementary teaching.

ACIDS

Let us begin with the concept of an acid. About 1900, in elementary teaching an acid was described as a hydrogen compound which tasted sour and in aqueous solution colored litmus red (reacted acid). In somewhat more advanced teaching, this description was elaborated by defining an acid as a hydrogen compound which could split off hydrogen ions. By and large, I believe that this presentation is still valid.

Just after the coming out of the ionic theory, there was an inclination to stipulate that the hydrogen compound should be separated into ions before it could be called an acid. Thus it was said that hydrogen chloride was not an acid until it was dissolved in water. From my student days I remember how Biilmann, then an assistant, came up to a group of young students one day and raised the question as to whether hydrogen sulfide was really an acid. At that time it was a little puzzling, the question of whether the hydrogen compound itself should be called an acid, or whether only the part separated into hydrogen ions and anions should have that

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name. The point was soon cleared up, however, at least among the better informed. The power to split off hydrogen ions became the official criterion for an acid. It is quite another matter that the quantity of hydrogen ions in the aqueous solution of the substance in question tells whether the substance is a stronger or a weaker acid.

It has no doubt always been considered self-evident that not only neutral molecules (like hydrogen chloride and acetic acid), but also anions (like the bicarbonate ion, HCO_3^-, and the primary and secondary phosphate ions, $H_2PO_4^-$ and HPO_4^{--}) should be regarded as acids. In the acid salts which contain these acids one has to do with substances which are at the same time acids and salts.

On the other hand, it is only recently that cations which can split off hydrogen ions have been regarded as acids. Of course many people have long realized that the so-called hydrolysis of ammonium salts results from the reaction

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

and that accordingly the weakly acid character of aqueous solutions of ammonium salts is due to the power of the ammonium ion to split off a hydrogen ion (14, 18), but to Brönsted (8) belongs the honor of having drawn from that fact the conclusion that we should regard the ammonium ion as an acid.

Brönsted designates uncharged acids (HCl, CH_3COOH) as neutral acids, negatively charged acids (HCO_3^-) as anion acids, and positively charged acids (NH_4^+) as cation acids.

Using Brönsted's extension of the name "acid" we must reckon as acids not only the ammonium ion and the alkyl substituted ammonium ions in the salts of the amines, but also the hydrated metal ions (aquo ions) which many salts form in aqueous solution, for example, $Cr(H_2O)_6^{+++}$, $Al(H_2O)_6^{+++}$, $Cu(H_2O)_4^{++}$, and so on. As Pfeiffer (18) pointed out in 1906, these aquo ions can split off hydrogen ions, forming the so-called hydroxo compounds. Thus by the splitting-off of hydrogen ions from the hexaaquochromic ion there can be formed the monohydroxo ion, $Cr(H_2O)_5$-$(OH)^{++}$, the dihydroxo ion, $Cr(H_2O)_4(OH)_2^+$, chromic hydroxide, $Cr(H_2O)_3$-$(OH)_3$, and the chromite ion, $Cr(H_2O)_2(OH)_4^-$. The basic compounds which are formed upon the hydrolysis of salts of metals are very often (but by no means always) such hydroxo compounds, formed by the simple splitting-off of hydrogen ions from aquo ions. By regarding the hydrated metal ions as acids, as Brönsted does, one obtains a pedagogically useful, simple explanation of the acid reaction of these salts (their hydrolysis).

The advantage of Brönsted's extended use of the name "acid" is easy to see. Our mode of expression is thereby brought into closer agreement

with the definition of an acid, and is in many cases made simpler and more comprehensible. The extension does not seem to have encountered much opposition. On the contrary, with hindsight it appears so obvious that one involuntarily asks one's self, "How is it that chemists didn't hit upon it sooner?" The extension cannot be explained as the result of new, previously unknown facts. No, the thing which prevented chemists from applying their own definition of an acid to the cation acids is certainly the fact that they have unconsciously required that an acid combine with metal hydroxides to form a salt and water. This requirement the cation acids do not meet. Thus ammonium chloride and sodium hydroxide form not only salt and water, but also ammonia. This requirement is certainly not contained in the official definition of an acid, but has existed and still exists, more or less unrecognized, in chemists' ideas of an acid. It possesses the rights of age. In calling the ammonium ion and ammonium salts acids, one must refuse to recognize this requirement.

My early work with aquo salts and their hydrolysis (2), and with the constitution of the amino acids (3), made it especially easy for me to see the usefulness of Brönsted's extension of the acid concept. And I believe that I may take credit for having seen, even earlier than the originator, the applicability of the new use of the word to the hydrogen ion in aqueous solution. By that time it had become a commonly accepted idea that the hydrogen ion, H^+, is not found free in its solutions, but is always present in solvated form, for example, as H_3O^+ (hydroxonium ion) in aqueous solution. This idea, which can be traced back to the work of Franklin (12), Goldschmidt (15), and Fitzgerald and Lapworth (11) received strong support shortly before 1923 in a paper by Fajans (10). In my work on polybasic acids (4) I start out from the supposition that the hydrogen ion exists in aqueous solution as hydroxonium ion, and in agreement with Brönsted's concept, I regard the hydroxonium ion as a tribasic acid and discuss the values of its three dissociation constants.

While the hydrogen ion is present in water as H_3O^+ (hydroxonium ion), in methyl alcohol it is present as $CH_3OH_2^+$ (methyloxonium ion), in liquid ammonia as NH_4^+ (ammonium ion), and so on. Chemists speaking of hydrogen ions in daily conversation practically always have in mind these solvated hydrogen ions. This is a somewhat dangerous use of words,—especially dangerous when it is necessary to distinguish between free and solvated hydrogen ions. If it is decided to call the free hydrogen ion a hydrogen kernel or proton, the term "hydrogen ion" can still be used for the solvated hydrogen kernel. But I regard it as distinctly more practical to introduce a special common name for these solvated hydrogen ions, and I propose to call them "lyonium" ions (the Greek word "lyo," to dissolve, is used in the prefix of the terms "lyophilic" and "lyophobic" colloids).

When an acid ionizes in a medium, its hydrogen ion is given to the solvent with formation of a lyonium ion. For example,

$$HCl + CH_3OH = Cl^- + CH_3OH_2{}^+$$
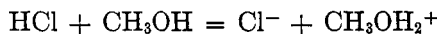
In this reaction the original acid (hydrogen chloride) disappears, but there is formed in its stead a new acid, i.e., the lyonium ion (in our example, the methyloxonium ion). In solutions of strongly dissociated acids we have in fact no longer the original acid, but only the lyonium-ion acid.

Summarizing, it can be said that the new Brönsted phase in the development of the concept of an acid does not bring any change in the commonly used definition of an acid. It merely requires that the definition be taken quite literally, just as it is stated.

<center>SALTS</center>

While the concept of an acid may now be said to have found rational demarcation, the salt concept still suffers from an irrational ambiguity.

We have all been brought up to regard as salts those substances which are formed upon neutralization of acids by bases, and whose formulas can be derived from those of acids (neutral acids) upon replacing the hydrogen atoms of the acid with metal atoms, or with certain compound radicals which behave like metal atoms.

By the side of this official concept, as it might be called, another use of the word "salt" has quietly appeared. Thus it is often said that mercuric chloride and mercuric cyanide are not salt-like substances, there is doubt as to the salt-like nature of anhydrous aluminum chloride, etc. Behind these statements lies the thought that only ionized substances should be spoken of as salt-like. In the same way an effort is made to avoid calling the alkyl derivatives of acids alkyl salts. The term "ester" furnishes an excellent, noncommittal name for them.

It is easy to see the danger of using the word "salt" simultaneously with two different meanings, one which lays emphasis upon the *composition*, metal plus acid residue, and another which lays emphasis upon the *properties* which result from ionization. We should try to agree to use the word "salt" for one of these meanings only. This is surely most easily accomplished if at the same time we introduce a new name for the other meaning.

I believe that it will be most practical to keep the word "salt" for the substances which possess ionic structure, i.e., which are built up from and still contain ions. As the new name for the derivatives of neutral acids in general, without consideration of their ionization, I propose the term "acidate." This word seems to me to serve excellently as a common name for ionized salts, complex metal compounds, and organic esters, in the same way that the word "sulfate" (chloride, etc.) serves as a common name

for substances of all these types derived from sulfuric acid (hydrochloric acid, etc.). If this differentiation between salts and acidates is adopted, it can be said that mercuric cyanide and ethyl acetate are acidates, but not salts. Dry hydrogen chloride is not a salt, but upon dissolving in water it forms a salt solution, since chloride and hydroxonium ions (i.e., a lyonium salt) are formed. Other strong acids behave in the same way. In aqueous solution a weak acid like acetic acid is a mixture of a small amount of ions (a lyonium salt) and a great quantity of undissociated non-salt. Alum is both a double acidate and a double salt. On the other hand, potassium ferrocyanide is a double acidate but not a double salt.

Salt and acidate

Since all anions can combine with the hydrogen ion to form acids, every salt is of necessity an acidate. The salts form a subdivision of the larger class of acidates. The term "salt" is therefore more restrictive than the term "acidate," and it is generally easier to decide whether or not a substance is an acidate, than it is to decide whether or not it is a salt. A knowledge of composition alone as a rule enables one to decide whether a substance is an acidate of a given acid or not. On the other hand, it is frequently difficult to establish the fact that a substance is composed of ions, i.e., that it has the nature of a salt. If the substance is soluble, we have in the power to conduct electricity an excellent criterion for ions. But in the solid state we have no such reliable test, and at the present time doubt exists in many cases. At ordinary temperatures, are the silver halides salts as defined above, or not? Opinion on this point is divided.

Salt and ion

The term "salt" plays in the nomenclature of substances a part similar to that which the term "ion" plays in the nomenclature of molecules. An ion cannot be obtained in the pure state as a substance. If one wishes an ion in the form of a substance which can be collected and weighed, bought and sold, one must take another ion at the same time, i.e., one must deal with a salt.

Salt and electrolyte

The introduction of the new usage does not mean that salt and electrolyte become two names for one and the same thing. An electrolyte is a substance which is dissociated into ions to a demonstrable, but to any arbitrarily small, degree. A salt on the other hand is a substance which is entirely composed of ions.

Acidate and derivative

The term "derivative" is closely related to the term "acidate." Derivatives are frequently understood to be substances derived from hydrogen

compounds upon replacement of hydrogen by something else, and since formally all hydrogen compounds may be regarded as acids (although sometimes extremely weak), all such derivatives are acidates. The term "derivative" is, however, also used in a more inclusive way. Thus acetamide may be derived from acetic acid upon replacement of the *hydroxyl* group by the amino group. It is a derivative of acetic acid, but not an acidate of it.

Salt and acid

That a substance is an acid has nothing to do with the fact that it is possibly a salt as well. A substance which is an acid is not necessarily a salt, but it may be a salt in the same way that a substance which is an acid may also be an alcohol (an oxy acid). Thus the ammonium salts and the so-called acid salts are at the same time acids and salts. Nevertheless, there is always a certain relationship between acid and salt in that those acids which are not themselves ions become ions upon neutralization (i.e., upon splitting off hydrogen ions).

For the understanding of the significance of the new concept of a salt it is very helpful to recall that our chemical substances can be divided quite naturally into three large groups, for each of which there are characteristic criteria: (1) metals, which consist of positive ions together with negative electrons. (2) Salts, which consist of positive and negative ions. (3) The remaining nonmetallic and nonsalt-like substances, which consist of neutral molecules.

Summary

In order to obtain a clear and unambiguous nomenclature, it is proposed to call all substances which can be derived from neutral acids by replacement of hydrogen with metal atoms, or with other radicals, acidates. Many of the acidates, but by no means all, belong to the great class of substances which are characterized by being constructed of ions. It is proposed to restrict the use of the term "salt" to these ionized substances.
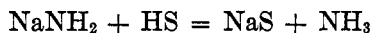
BASES

The use of the word "base" is at the present time particularly vague and ambiguous. We have all been brought up to think of a base as a hydroxyl compound which splits off hydroxyl ions in aqueous solution. Back of this definition lies the idea that a base shall be a substance which, in the first place, can neutralize an acid solution, i.e., rob it of its acid properties, and in the second place, upon neutralization combine with the acid to form a salt (or more generally an acidate) and water. But whether we consider the matter logically or empirically, the power to neutralize and the power to form an acidate and water are not inseparably linked. Since in general

there has been a more or less instinctive tendency to regard the power to neutralize an acid as the more important, there have been constant efforts to extend the concept of a base so as to include, in addition to the hydroxyl compounds, other substances which can neutralize acids.

Thus many chemists have continued to call ammonia and the amines bases, as was done long ago. I can mention Goldschmidt (14) and Fitzgerald and Lapworth (11), for example. Even water and other solvents which can combine with the hydrogen ion to form lyonium ions are called bases by Fitzgerald and Lapworth. Pfeiffer (18) was the first to notice that many metal hydroxides—the hydroxo compounds—can add acids and thereby form aquo salts without splitting off water; he decided for this reason to call the hydroxo compounds pseudo bases. At almost the same time Werner (20) made a distinction between anhydro bases and aquo bases, according as the salt formation takes place without or with the formation of water.

The concept of a base was extended in another way by Franklin (13). Through his work with the solvent liquid ammonia he was led to call metal amides like $NaNH_2$ ammono bases. For in liquid ammonia the metal amides react with acids to form salt plus solvent according to the equation

$$NaNH_2 + HS = NaS + NH_3$$

i.e., in a way quite analogous to the formation of a salt from a metal hydroxide and acid in aqueous solution

$$NaOH + HS = NaS + H_2O$$
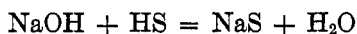
If one generalizes Franklin's idea, in alcoholic solution the alcoholates or alkylates, as I prefer to call them, are to be regarded as bases

$$NaOC_2H_5 + HS = NaS + C_2H_5OH$$
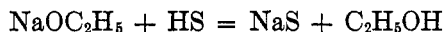
and similarly in glacial acetic acid the acetates should be regarded as bases

$$CH_3COONa + HS = NaS + CH_3COOH$$
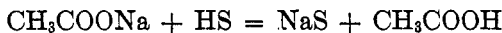
This generalization, however, leads very easily to the masking of what is the essential property of a base. For example, continuing as before one is easily brought to look upon sodium chloride dissolved in dry hydrogen chloride as just as good a base as sodium hydroxide in water.

In 1923 Brönsted (8) attempted to extend the concept of a base in a different way. He advocated the use of the term "base" for molecules which can neutralize acids, and entirely disregarded what is formed in the neutralization. When an acid is neutralized, its hydrogen ion is removed,

and so Brönsted arrived at the simple conclusion that a base should be defined as a molecule which can combine with the hydrogen ion.   Through this extended definition Brönsted evaded a number of difficulties.   Among the bases he included all the molecules which in any way have previously been counted as bases.

The list in table 1 gives some idea of the molecules which are bases according to Brönsted's definition.   Many of them are ions.   All the salt-like substances which contain these ions are to be regarded as bases, and are accordingly included in the table.

Brönsted's definition, like Franklin's generalization, causes every anion (and so every salt) to be classed as a base.   For we know no anion which cannot form undissociated acid molecules with the hydrogen ion.   The perchlorate ion possesses this power to the smallest extent, and is therefore the weakest known anion base.

TABLE 1

Bases according to J. N. Brönsted

MOLECULES OR IONS	SALT-LIKE SUBSTANCES
NH_3 and the amines	
H_2O and the alcohols	
Hydroxo compounds (nonsalt-like metal hydroxides)	
$C_2H_5O^-$ ($C_nH_{2n+1}O^-$)	Ethylates (alkylates)
OH^-, O^{--}	Hydroxides and oxides
HCO_3^-, CO_3^{--}	Bicarbonates and carbonates
CH_3COO^-	Acetates
ClO_4^-	Perchlorates

The useful feature of Brönsted's definition is that it points out the basic nature of the substance in question without reference to a solvent, and at once indicates a way to measure basic strength by measuring the power of the base to combine with the hydrogen ion.
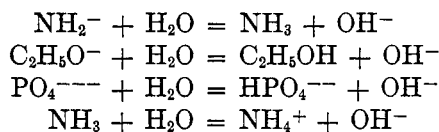
Quite rightly Brönsted is much pleased with his new and elegant definition of a base.   In his easily understood enthusiasm, however, he has been hardly sufficiently aware of the unique position which the hydroxides occupy among bases, and which is the reason that the name "base" was previously reserved for these substances.   If we follow Brönsted and use the name "base" not only for sodium hydroxide but also for sodium carbonate and sodium acetate, substances which all of us have actually employed to neutralize acid solutions, we shall need a new term for the substances which, like hydroxides and oxides in aqueous solution, alkylates in alcoholic solution, and acetates in glacial acetic acid, unite with acids to

form acidates (salts) plus solvent. In preparative chemistry this is a very important property. In distinction to these bases, other bases (bases in the extended sense) form upon neutralization an acidate (salt) and an acid different from the solvent. Thus carbonates in aqueous solution give carbonic acid (carbon dioxide), acetates in aqueous solution give acetic acid, and so on.

The bases to which we are thinking of giving a special name are the solvents' own acidates. I propose to call them "lyates." The ion base characteristic of these substances, which consists of the solvent minus the hydrogen ion, may very well be called "the lyate ion." Just as the concentration of the lyonium ion is customarily written c_H, the concentration of the lyate ion may well be written c_{-H}.

The special character of the lyates and the lyate ions among bases is evident not only in preparative work, where the lyates react with acids to form pure acidate solutions, but is also important in applications of the mass action equations to ionic equilibria in dilute solution. This last is due to the fact that the lyates, as acidates of the solvent, are derived from an acid which in dilute solution acts at nearly constant concentration and active mass.

One more property may be mentioned as a characteristic of lyate ions. In a solvent of acid nature any strong base will react with the solvent to form lyate ion. For example,

$$NH_2^- + H_2O = NH_3 + OH^-$$
$$C_2H_5O^- + H_2O = C_2H_5OH + OH^-$$
$$PO_4^{---} + H_2O = HPO_4^{--} + OH^-$$
$$NH_3 + H_2O = NH_4^+ + OH^-$$

If the base is sufficiently strong the reaction will be practically complete. So in an acid solvent bases which are appreciably stronger than the solvent's lyate ion cannot exist. Similarly, in a basic medium which is capable of forming lyonium ions, acid molecules which are appreciably stronger acids than the lyonium ion do not exist, for these acids will react with the solvent to form lyonium ion.
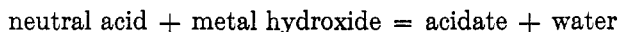
The adoption of Brönsted's extended definition of a base means that the old classical equation
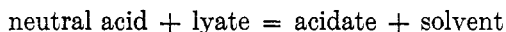
$$\text{acid} + \text{base} = \text{salt} + \text{water}$$
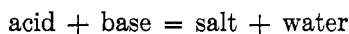
must be abandoned. Nor can the somewhat modernized version of this equation

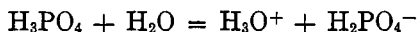$$\text{neutral acid} + \text{base} = \text{acidate} + \text{solvent}$$
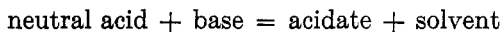
be kept. It is, however, not necessary to give up the equation altogether. We can keep the equation if for *base* we substitute *metal hydroxide*

$$\text{neutral acid} + \text{metal hydroxide} = \text{acidate} + \text{water}$$

or more generally,

$$\text{neutral acid} + \text{lyate} = \text{acidate} + \text{solvent}$$

When a neutral acid is dissolved in a basic medium, as already mentioned, there is formed a smaller or greater amount of lyonium salt. For example,

$$H_3PO_4 + H_2O = H_3O^+ + H_2PO_4^-$$

The lyonium salt formed is neutralized by lyates, just as the original acid is, with formation of acidate and solvent. It does not as a rule do any harm, therefore, to use the word "acid" to represent the sum of the actual neutral acid (HS) and its lyonium salt (in aqueous solution $H_3O^+ + S^-$) present in the solution. On the contrary, this nomenclature is to be recommended as suitable and convenient in many instances.

If a solution of a strong base (the base being completely transformed to lyate salt) neutralizes a solution of a strong acid (the acid being present wholly as lyonium salt), the process of neutralization is of an especially simple character. When the equation

$$\text{acid} + \text{lyate} = \text{salt} + \text{solvent}$$
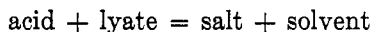
is rewritten in ionic form and simplified, we get for the process of neutralization

$$\text{lyonium ion} + \text{lyate ion} = \text{solvent}$$
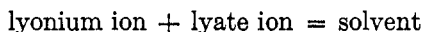
This takes on for aqueous solutions the well-known form

$$H_3O^+ + OH^- = 2H_2O$$

It follows from these equations that dilute solutions of all strong acids and strong bases have the same heat of neutralization in the same amphoteric solvent.

The trouble with the old concept of a base comes from the fact that we have tried to kill two birds with one stone, and combine the concepts of base and lyate. By separating the two concepts we succeed in preserving the good in them both. The lyates are a subdivision of the bases. They occupy a unique position in synthetic and formal chemistry.

I regard it as an advantage that the name "lyate" as defined here includes both oxides and hydroxides without reference to the greater or

smaller water content of these compounds. I have always felt it pedagogically unwise to emphasize the hydroxyl compounds, which are often known only on paper (for example, $Fe(OH)_3$), at the expense of their partial or complete anhydrides ($Fe_2O_3 \cdot H_2O$, Fe_2O_3).

As a matter of fact, the lyate concept is more closely related to the old official concept of a base than is Brönsted's extended concept. There is therefore some reason for continuing to use the word "base" for the substances which in this paper are called lyates. In that event it would be necessary to coin a new word for Brönsted's bases in the extended sense. The term "antiacid" might be suggested. But after long hesitation I have finally come to the conclusion that it is best to try to push through the use of the term "base" for the extended concept, and introduce the new name "lyate" for the acidates of the solvent.

Summary

It is probably satisfactory, in preparatory school, to describe bases as substances which impart a basic reaction (taste, litmus) to water, and which can neutralize (quench) the acid properties of acid solutions. Among the bases should be reckoned, besides the hydroxides of the alkalis and other metals, the oxides of the metals, and ammonia, and the carbonates. In addition it should be pointed out that the hydroxides and oxides are remarkable in that they combine with an acid to give an acidate and water, and that ammonia combines with an acid to give an acidate with no formation of water. To the more advanced student Brönsted's definition of a base should be taught, and the lyate concept should be formulated to cover nonaqueous solutions.

ACID, NEUTRAL, AND BASIC REACTION

In aqueous solution distinction is made between acid, basic, and neutral reaction according as the hydrogen ions (more exactly expressed, the hydroxonium ions) or the hydroxyl ions, or neither, preponderate to a marked degree. The new extension of the concepts of acid and base causes no change here. The reaction of the solution can still be stated quantitatively in terms of the hydrogen-ion concentration, or, to use the system devised in 1909 by Sörensen (19), in terms of the hydrogen-ion exponent, defined as the negative logarithm of the hydrogen-ion concentration, $pH = - \log c_H$. Since 1909 the only important changes which have taken place in stating the reaction of aqueous solutions have been: first, to define the hydrogen-ion exponent pH in a new way, according to which it is not exactly equal to $- \log c_H$, but is more easily calculated from electrometric determinations (9), and secondly, to introduce as a measure of the reaction of a solution the hydrogen-ion activity a_H, measured on a scale which

for very dilute solutions coincides (or almost coincides) with hydrogen-ion concentration (5,7). This requires furthermore the use of $p_aH = - \log a_H$ in place of pH.

The rational use of the concepts of acid, basic, and neutral reaction in a nonaqueous solution is dependent upon the ability of the medium to take up and give off hydrogen ions.

In amphoteric media which, like water, can form both lyonium and lyate ions, it is possible to use the concentration of these ions to distinguish between acid, basic, and neutral solutions, just as in water. On the other hand, if the medium lacks acid character and so cannot form lyate ions, one cannot speak of basic solutions in the same sense as in water. If the medium lacks basic character and consequently cannot form lyonium ions, one cannot speak of acid solutions in the same sense as in water. And finally if the medium is neither acid nor basic, and so can form neither lyate nor lyonium ions, one can speak of neither acid nor basic solutions in the same sense as in water.

The hydrogen-ion exponent pH, defined as $- \log c_H$ (and p_aH defined as $- \log a_H$, where a_H is the hydrogen-ion activity, measured on a scale which at infinite dilution coincides with lyonium-ion concentration), has a definite value only in basic media which can form lyonium ions. There is, to be sure, nothing to prevent the determination of *relative* hydrogen-ion activities in nonbasic media. But the hydrogen-ion activity cannot be given on a lyonium-ion scale. It must be given on the scale of hydrogen-ion activity established for aqueous solutions. The hydrogen-ion activity A defined in this manner, or rather its negative logarithm pA, was proposed by Michaelis and Mizutani (17) as a measure of the degree of acidity of all nonaqueous solutions. Linderström-Lang (16) has agreed to this proposal. Brönsted (8) has suggested calling the hydrogen-ion activity measured on the water scale (A) the acidity of the solution. Correspondingly pA might be called the acidity exponent.

For nonaqueous solutions which can form lyonium ions it is possible to use both c_H and A, both pH and pA, as a measure of the degree of acidity. A great deal can be advanced in support of the use of the different quantities, and probably fields will be found in which each is most convenient. I shall not go into this question at the present time, however.

The extent and position of the scale of reaction

Where only dilute solutions (at the most 1 normal) are concerned, the pH scale in water has a rather definite length. The hydrogen-ion concentration in even the most acid solution (1 normal in acid) cannot be greater than 1, and the pH accordingly not less than 0. On the other hand, the hydrogen-ion concentration in the most strongly basic solution (1 normal

in base) cannot be less than the dissociation constant of water, about 10^{-14}, and consequently the pH cannot be greater than $-\log K = 14$, approximately. There is naturally a close connection between the limited extent of the reaction scale in water and the fact that acids and bases whose strength exceeds certain limits do not exist as such in aqueous solution. Acids like hydrochloric acid, whose strength exceeds that of the hydroxonium ion, will form hydroxonium ion upon dissolving in water. And bases like sodium amide, whose strength exceeds that of the hydroxyl ion, will form hydroxyl ions in water. Since the substances are thereby transformed, and are present only in the transformed state, their greater strength is not manifest in the reaction of the solution.

Since ethyl alcohol is both an acid and a basic medium, and its dissociation constant is of the order of magnitude of 10^{-20}, the pH reaction scale
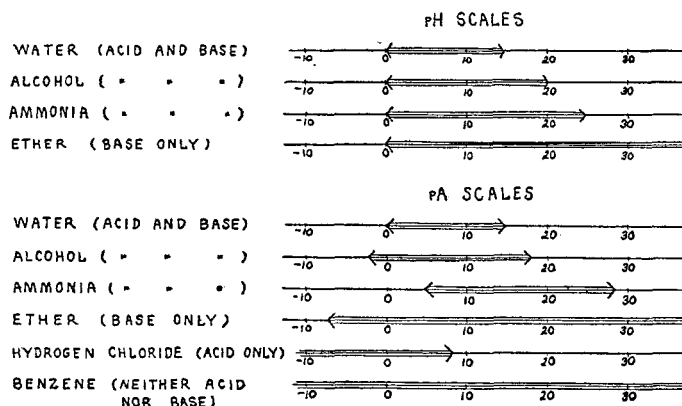

FIG. 1. POSITION OF THE REACTION SCALES IN TYPICAL SOLVENTS

in ethyl alcohol goes from 0 to 20. On the pA scale the most strongly acid solutions in alcohol do not lie at pA $= 0$, but at pA $= -2.5$, and since the pA scale has the same extent as the pH scale, the most strongly basic solutions lie at pA $= 17.5$ in ethyl alcohol. The pA scale therefore extends from -2.5 to 17.5. The value of pA for the most strongly acid solutions (the end of the pA scale on the acid side) is determined primarily, although not exclusively, by the basic strength of the medium. If the medium is a stronger base than water, the pA scale usually begins at positive values. If on the other hand the medium is a weaker base than water, the pA scale usually begins at negative values. In alcohol the pA scale begins on the negative side, and in liquid ammonia on the positive (see figure 1).

In the case of a medium which can take up but cannot give off hydrogen ions (for example, ether $(C_2H_5)_2O$), both the pH and pA scales are without a limit on the basic side.

In the case of a medium which cannot take up hydrogen ions, only the pA scale can be used, and this is unlimited on the acid side. In a medium which cannot take up but can give off hydrogen ions the pA scale is without a limit on the acid side, but limited on the basic. As an example of such a medium hydrogen chloride may be mentioned. If hydrogen chloride should be found upon closer examination to possess some slight power to take up hydrogen ions, the pA scale for this solvent would not be infinitely long on the acid side, but would merely extend far out on this side.

If the medium can neither take up nor give off hydrogen ions (for example, benzene), the pA scale is unlimited on both sides.

In figure 1 is given a diagrammatic representation of the scale of reaction in a number of typical solvents.

THE MEASURE OF ACID AND BASIC STRENGTH

The commonly used measure of the strength of an acid is its dissociation constant. As is well known, the dissociation constant is equal to the hydrogen-ion concentration (lyonium-ion concentration) in a half-neutralized acid solution. (By a half-neutralized acid solution is meant a solution which contains just as many molecules of the acid itself as of the acid minus hydrogen ion.) As a measure of the acid strength one can use, in place of the hydrogen-ion concentration, any other of the numbers which may be employed to give the reaction of the half-neutralized solution (A, pH, pA). Using pH one obtains the pK value of the acid (its dissociation exponent). In general it is most practical to use the same number as that selected for stating the reaction of a solution.

When an acid molecule (S) splits off its hydrogen ion, there is formed an acid residue (B). The acid residue, as Brönsted quite rightly emphasizes, must always be a base, in that it can combine with hydrogen ion to form an acid

$$S \rightleftharpoons B + H^+$$
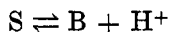
Brönsted calls acids and bases which stand in this mutual relationship to each other "corresponding." It is easy to understand why chemists in the past have not been aware of the correspondence between acids and bases. In the first place, correspondence appears only when Brönsted's extended concept of acids and bases is used. Moreover, the base corresponding to a fairly strong acid is a very weak base, and conversely the acid corresponding to a fairly strong base is a very weak acid. Only when one understands by *acids* and *bases* not only the substances which give to water a decidedly acid or basic reaction, but rather all substances which have the power to split off or take up hydrogen ions, does the correspondence emerge clearly.

As a measure of the strength of bases Brönsted (8) has proposed to use the reciprocal of the dissociation constant of the corresponding acid. It is surely more practical, however, to use the same value for an acid and for its corresponding base, i.e., to use as a measure of strength for both acids and bases the reaction of the half-neutralized solution. Both the strength of the ammonium ion as an acid and the strength of ammonia as a base can be measured by the number which gives the reaction of a solution in which the ammonium ion and ammonia are present at the same concentration. Using the reciprocals for bases merely increases the number of quantities to be remembered and tabulated, and makes more difficult the grasp of the relationship between the reaction and the extent of neutralization in the case of bases. I grant that people are going to be reluctant to express basic strength by a number which increases with decreasing basic strength. But just as we have become accustomed to expressing the degree of acidity in pH values, which undeniably increase with decreasing acidity, we can surely become accustomed to expressing basic strength by a number which increases as basic properties decrease.

In aqueous solution one can use as a measure of the reaction of the half-neutralized solution the lyonium-ion concentration (c_H) or the hydrogen-ion exponent (pH). In nonaqueous, basic media one can use, in addition to these quantities, the acidity A or its negative logarithm, the acidity exponent pA. On the other hand, in nonaqueous, nonbasic media one can use only the last two, the acidity and the acidity exponent (A and pA).

Whether the one or the other of these possible measures is used, care must be taken that the same measure is employed throughout the work in a given solvent. The value of the strength of an acid depends on the medium, whatever scale of reaction is used. It is not even to be expected that the same sequence of acid strength (except very approximately) will be found upon comparing acids in different media. In a paper on the distribution coefficients of ions between different media, Larsson and I (6) have tried to work out the theory of the variation of acid strength with medium, but I shall not go into the matter at this time.

Since free hydrogen ions (hydrogen kernels, protons) are not found at finite, determinable concentrations in any of our solutions, it is not possible to determine the absolute dissociation constants or absolute strengths of acids and bases. The strength of the acid (base) is given in relation to the strength of the lyonium ion (the medium itself) when the strength is stated in terms of the lyonium-ion concentration of the half-neutralized solution. And when the acidity scale is employed, the strength of the acid (base) is compared with the strength of the hydroxonium ion (water). It must not be forgotten, however, that the specific properties of the medium, especially the dielectric constant, have a marked and very varied effect upon the

strength of acids (bases), so that even in the case where the strength is always compared with that of the hydroxonium ion (water), different values may be obtained in different media.

Summary

As a measure of the strength of an acid and the strength of the corresponding base in a given medium, one of the quantities which may be employed to give the reaction of their half-neutralized solution should be used. The choice lies between the lyonium-ion concentration c_H, the acidity A, the hydrogen-ion exponent pH, and the acidity exponent pA. The worker should always select the same quantity which he employs in stating the reaction of his solutions. None of these quantities gives numerical values of acid and basic strength which are independent of the medium, or even proportional to one another in different media (or which in the case of the logarithmic quantities yield the same difference in different media).

THE THEORY OF TITRATION

The theory of titration is not changed by the introduction of the new concepts of acid and base from the form in which I gave it many years ago (1), but because of its close relation to the problems discussed in this paper, I shall make a few remarks about it here, especially about its application to nonaqueous solutions.

The theory of titration furnishes a means of calculating the error made in titrating a solution of one or several acids or bases to the change point of some given indicator. For aqueous solutions the procedure is as follows: The position of the change point of the indicator (p_T) is marked on the scale of reaction, as are the points which give the strengths of the acids and bases present ($p_1, p_2, p_3. . .$). The errors which arise depend altogether upon the position of p_T relative to the points p_1, p_2, $p_3. . .$, and relative to the ends of the scale of reaction (0 and 14). Sharp change of color and consequent accurate titration result when p_T lies far from all these points. If p_T is kept at a distance of at least three units from a p, the error arising from the presence of the acid (base) is less than 0.1 per cent of the amount of the acid (base) in question. If d is the distance between p_T and p, the error is less than 10^{-d} of the amount of the acid (base) corresponding to the p. If the distance between p_T and the ends of the scale is at least four units, the so-called hydrogen- and hydroxyl-ion errors are at most 0.01 cc. of 1 normal titration liquid when the final volume of solution is 100 cc. Generally speaking, this error is at most $v \times 10^{-d}$ cc. of normal titration liquid (v is the final volume and d the distance between p_T and the nearer end of the scale (0 or 14)).

When the procedure is to be transferred to nonaqueous solutions, the only thing to be changed is the ends of the scale, which no longer lie at 0 and 14, but at the numbers which give the reaction of solutions 1 normal in lyonium ion and 1 normal in lyate ion respectively. If the medium does not form lyonium ions, or does not form lyate ions, the scale is unlimited on the corresponding side, and the error arising from too close approach to the end of the scale on this side disappears. In benzene and other media where the scale of reaction is unlimited on both sides, one has to prevent only the too close approach of the titration exponent p_T to the p's corresponding to the acids and bases present.

SUMMARY

I hope that I have succeeded in describing the manner in which the recent extension of the concepts of acid, base, and salt, primarily through Brönsted's useful and clarifying work, has progressed to a point where it will be desirable to introduce the new viewpoint and the new definitions into the elementary teaching of chemistry.

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