QUARTERLY REVIEWS

THE USE OF THE TERMS "ACID" AND "BASE"

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Introduction.—The pursuit of exact verbal definitions of qualitative concepts is rarely of much scientific value, provided that the requirements of convenience and consistency are satisfied. However, the development and clarification of definitions of acids and bases has been closely connected with experimental and theoretical advances in this field, and several new definitions have been directly fruitful in stimulating fresh work. Since the present usage of these terms is by no means uniform, it may be useful to follow the development of the subject.

Like most definitions, the terms acid and base originated in empirical observations of physical and chemical properties, rather than in any theoretical interpretation of these properties. They were first regarded as the constituents which react together to form salts, usually with the liberation of water. Somewhat later Boyle and others (end of seventeenth century) laid more stress on specific properties of acids, *e.g.*, their power of precipitating sulphur from its solutions in alkalis and of changing blue plant-dyes to red. This kind of characterisation was made more definite in the eighteenth century; for example William Lewis (1746) added sour taste and effervescence with chalk as typical properties of acids. Bases (or alkalis) were characterised chiefly by their negative properties of destroying or reversing the effects caused by acids.

The first theory of acidic behaviour which is comprehensible in modern terms was that of Lavoisier (end of eighteenth century), who regarded oxygen as the " acidifying principle " which converted elements like carbon, nitrogen, sulphur, etc., into carbonic, nitric, or sulphuric acid. This view led to the assumption that all acids were formed by the combination of a " radical " with oxygen. Thus a variety of organic acids were supposed to contain hypothetical radicals combined with oxygen, and, in particular, it was assumed that hydrochloric acid (and hence chlorine) contained oxygen. Davy (1810–15) pointed out that it was wrong to assume that chlorine was a compound of oxygen until its compound nature had been demonstrated, and the discovery of hydrobromic, hydriodic, and hydrocyanic acids shortly afterwards cast still further doubt upon the oxygen theory of acids. In spite of this and other evidence, the latter theory was strongly supported by some chemists, notably by Berzelius and Gay-Lussac, up to about 1840.[1]

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[1] For a detailed account of the early history of this subject, see P. Walden, " Salts, Acids and Bases " (New York, 1929).

Davy at first expressed the opinion that " Acidity does not depend upon any particular elementary substance, but upon peculiar arrangement of various substances ", a view which accords well with some current definitions (*v. infra*). However, it soon became clear that all the substances commonly accepted as acids did contain *hydrogen*, and Davy soon recognised hydrogen as the essential element in an acid. Liebig showed that this idea was in harmony with the behaviour of organic acids, and in 1838 he defined acids as " compounds containing hydrogen, in which the hydrogen can be replaced by metals ", a definition which was generally accepted without modification until the advent of Arrhenius's dissociation theory. It should be noted that this definition denies the name acid to the acidic oxides themselves, although their compounds with water are often ill-defined or unknown (*e.g.*, carbonic acid, silicic acid, etc.). Bases were still regarded as substances which reacted with acids to form salts, and there was no theory as to their constitution corresponding to the hydrogen theory of acids.

Acids and Bases in the Classical Electrolytic Dissociation Theory.—The replaceable hydrogen definition of acids give no indication of why combined hydrogen could only seldom be replaced by metals, and the only criterion which it gave of the relative strengths of acids and bases was the often misleading one of the displacement of one acid or base by another. It was shown at an early date that the catalytic effects of acids in certain reactions showed a general correlation with their generally accepted order of strength, but no really quantitative comparison was possible without a knowledge of the laws governing the dissociation of electrolytes.

The work of Ostwald and Arrhenius on electrolytic dissociation (1880–90) showed clearly that only those hydrogen atoms which produce hydrogen ions in aqueous solutions can give rise to acid properties, and the application of the law of mass action to the dissociation equilibrium gives the dissociation constant as a rational measure of the strength of the acid. In fact, one of the chief supports of the Arrhenius theory was the close correspondence between the electrical conductivities of acid solutions, their catalytic effects in various reactions, and the (less accurate) estimates of their strengths obtained from measurements of the distribution of a base between two acids. Similarly, basic properties were associated with the production of hydroxyl ions in solution, and the dissociation of a number of weak bases was shown to conform to the Ostwald dilution law, though here the amount of quantitative information and correlation with other data was originally much less than for acids. The definition of acids and bases as substances giving rise to hydrogen and hydroxyl ions respectively in aqueous solution followed naturally from these considerations, and was generally accepted for the next thirty or forty years. It explained their characteristic properties in solution in terms of the ions produced, and their neutralisation to give salts by the reaction $H^+ + OH^- \longrightarrow H_2O$. A great deal of quantitative work was done on the dissociation constants of acids and bases and their application to other types of ionic equilibria, such as hydrolysis, buffer solutions, and behaviour with indicators. The anomalies of strong electrolytes had relatively little effect on equilibria involving weak acids and bases, and a satisfactory account was rendered of a large mass of data.

The success of these quantitative developments helped to mask some logical weaknesses in the qualitative definitions of acids and bases. For example, it was not clear whether a pure non-conducting substance like anhydrous hydrogen chloride should be called an acid, or whether it became one only in contact with water, though it was usually considered that the anhydrous compound was an acid in virtue of its latent tendency to split off hydrogen ions. Another type of difficulty arose in solvents other than water, where investigation showed that the ions produced by acids and bases were frequently quite different from the hydrogen and hydroxyl ions in aqueous solution. This difficulty appeared in a particularly acute form when it was realised that " typical " acid–base reactions such as neutralisation and titration with indicators could sometimes occur in solvents such as chloroform or benzene where no free ions can be detected by conductivity measurements. There was also a more serious ambiguity in the definition of bases. Most of the substances which would neutralise acids belonged to one of two classes : metallic hydroxides and organic amines. Of these, only the former could be said to split off hydroxyl ions. The dissociation of the amines in water could be written as $NR_3 + H_2O \rightleftharpoons NR_3H{\cdot}OH \rightleftharpoons NR_3H^+ + OH^-$, and there was much dispute as to whether NR_3 or $NR_3H{\cdot}OH$ (for the existence of which there is little direct evidence) should be regarded as a base. No real decision was reached on this point, and in some quarters [2] a distinction was made between " anhydro-bases " like NH_3 which neutralise acids by picking up a hydrogen ion, and " aquo-bases " like KOH which liberate a molecule of water in the process.

Definitions Related to Particular Solvents.—If sodium hydroxide is dissolved in ethyl alcohol, hydroxyl ions are produced, as in water. On the other hand, a solution of still more strongly basic properties is obtained by dissolving sodium ethoxide in alcohol, the solution containing the ion OEt^-, which bears the same relation to EtOH as OH^- does to H_2O. Further, various lines of evidence showed [3] that the proton H^+ could not exist in solution, being converted completely into solvated species such as H_3O^+ in water, $EtOH_2^+$ in alcohol, and NH_4^+ in liquid ammonia.

These led to the idea of " solvent systems " of acids and bases, in which the acid–base definition is modified according to the solvent being used. This view was originated by E. C. Franklin [4] for the solvent liquid ammonia, where the typical acidic and basic anions are respectively NH_4^+ and NH_2^-. A typical neutralisation reaction in this solvent is

$$\underset{\text{Acid}}{NH_4Cl} + \underset{\text{Base}}{NaNH_2} \longrightarrow \underset{\text{Salt}}{NaCl} + \underset{\text{Solvent}}{2NH_3}$$

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[2] *E.g.*, A. Werner, *Z. anorg. Chem.*, 1893, **3**, 267 ; 1897, **15**, 1 ; *Ber.*, 1907, **40**, 4133 ; " Neuere Anschauungen auf dem Gebiete der anorganischen Chemie ", 2nd edition, p. 218 (Braunschweig, 1909).

[3] For references, see R. P. Bell, " Acid–Base Catalysis ", pp. 37–39 (Oxford, 1941).

[4] *J. Amer. Chem. Soc.*, 1905, **27**, 820 ; 1924, **46**, 2137 ; *Amer. Chem. J.*, 1912, **47**, 285 ; " The Nitrogen System of Compounds " (New York, 1935).

or, in terms of ions,

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

analogous to

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

There are many other points of analogy: for example, solutions of ammonium salts in liquid ammonia dissolve metals with the evolution of hydrogen—$2NH_4^+ + Mg \longrightarrow Mg^{++} + H_2 + 2NH_3$—and there is a class of "ammono-acids" such as $B(NH_2)_3$, which can be compared with the hydroxy-acids $B(OH)_3$, etc.

In this and similar cases the transfer of a proton is still involved in all typical acid–base reactions. However, other workers have gone further, and extended the nomenclature acid and base to solvents and solutes containing no hydrogen. Thus H. P. Cady and H. M. Elsey [5] have defined an acid as a solute that 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. This system is exemplified by the work of Jander [6] in liquid sulphur dioxide. Here the solvent is supposed to ionise according to the equation $2SO_2 \longrightarrow SO^{++} + SO_3^{=}$; hence $SOCl_2$ is a typical acid, and K_2SO_3 a typical base. This kind of treatment has been extended to a variety of solvents, including $COCl_2$, $SeOCl_2$, and HCN.[7]

This kind of definition gives a logical account of behaviour in a particular solvent, but has to be modified completely for a change of solvent. It has served a useful purpose in stimulating work in unusual types of solvent, but it does not give a clue to several of the general properties of acids and bases (*e.g.*, catalysis, action on indicators), and it is inconvenient to use such everyday words as acid and base in a sense which varies with change of solvent. Hence, although this type of definition is still used by a few authors, we shall not consider it further here.

The Brönsted–Lowry Definition.—This definition of acids and bases was proposed almost simultaneously by J. N. Brönsted [8] and T. M. Lowry [9] in 1923, and is still the one in most general use. It reads : *An acid is a species having a tendency to lose a proton, and a base is a species having a tendency to add on a proton.* This can be expressed in the scheme $A \rightleftharpoons B + H^+$, where A and B are termed a *conjugate* (*or corresponding*) *acid–base pair.* The definition places no restriction on the sign or magnitude of the charges on A and B, though, of course, A must always be more positive than B by one unit. It is important to realise that the symbol H^+ in this definition represents the bare proton, and not the "hydrogen ion" of variable nature which is formed in solution by the addition of a proton to the solvent molecule (H_3O^+, $C_2H_5{\cdot}OH_2^+$, NH_4^+, etc.): hence the definition is independent of the solvent. Further, it clearly does not include as acids and

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[5] *J. Chem. Education*, 1928, 1425.

[6] G. Jander and H. Mesech, *Z. physikal. Chem.*, 1939, *A*, **183**, 255, and earlier papers.

[7] A. F. O. Germann, *J. Amer. Chem. Soc.*, 1925, **47**, 2275, 2461; *Science*, 1925, **61**, 70; G. B. L. Smith, *Chem. Reviews*, 1938, **23**, 165; G. Jander and G. Scholz, *Z. physikal. Chem.*, 1943, **192**, 163.

[8] *Rec. Trav. chim.*, 1923, **42**, 718.

[9] *Chem. and Ind.*, 1923, **42**, 43.

bases species derived from a solvent not containing hydrogen (*e.g.*, $SOCl_2$ in SO_2).

The Brönsted–Lowry definition of an acid obviously includes those neutral molecules known as acids in the classical dissociation theory, *e.g.*, HCl, H_2SO_4, $CH_3{\cdot}CO_2H$, etc. It also includes negative ions like HSO_4^-, $CO_2H{\cdot}COO^-$, thus falling in line with the description of salts like $NaHSO_4$ as acid salts. On the other hand, the recognition of cation acids such as NH_4^+ represented an extension of the older definition. For example, the acid reaction of a solution of ammonium chloride is most simply related to the tendency of the ammonium ion to lose a proton ($NH_4^+ \rightleftharpoons NH_3 + H^+$), the chloride ion playing no part in the process: similarly, the acidity of solutions of many heavy metal salts can be related to cation acids such as $[Fe(H_2O)_6]^{+++} \rightleftharpoons [Fe(H_2O)_5OH]^{++} + H^+$.[10] These explanations are simpler and more logical than the older interpretations in terms of "hydrolysis".

The change in definition of bases is more radical, since no mention is made of the hydroxyl ion or similar ions. Neutral bases will include ammonia and the amines, in virtue of reaction schemes like $RNH_2 + H^+ \rightleftharpoons RNH_3^+$. The basic properties of the metallic hydroxides are related to the presence of the hydroxyl ion, a typical (but not unique) anion base. A new feature of the definition is the use of the term base for the anions of weak acids in general: *e.g.*, the alkaline reaction of a solution of sodium acetate is related to the basic properties of the acetate ion ($CH_3{\cdot}COO^- + H^+ \rightleftharpoons CH_3{\cdot}CO_2H$).

It should be noted that the scheme $A \rightleftharpoons B + H^+$ used in the acid–base definition is a hypothetical one, in so far as the free proton cannot exist in solution in measurable concentrations. On the other hand, all typical acid–base reactions can be represented in the form $A_1 + B_2 \rightleftharpoons A_2 + B_1$, where A_1–B_1 and A_2–B_2 are two conjugate acid–base pairs. This may be illustrated by some examples (see next page).

It will be seen that the "hydrogen ion" H_3O^+ does not occupy any unique position in the scheme of reactions, but behaves in the same way as any other acid. The conception of dissociation as an acid–base reaction gives the clue to the degree of dissociation of acids and bases in different solvents, which is determined much more by the acidic or basic properties of the solvent than by its dielectric constant. Thus many bases which are weak in water react completely with the strongly acidic solvent anhydrous acetic acid, while the "strong" acids HCl, HBr, $HClO_4$, etc., which dissociate completely in water, give widely differing electrometric titration and conductivity curves in acetic acid, indicating incomplete dissociation.[11]

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[10] A few workers had adopted this point of view much earlier (cf. P. Pfeiffer, *Ber.*, 1906, **39**, 1864; 1907, **40**, 4040), but without suggesting any extension of the definition of acids. Similarly, in Franklin's ammonia system of acids and bases, ammonium salts were regarded as typical acids in liquid ammonia, but would not be regarded as such in other solvents.

[11] See, *e.g.*, J. B. Conant and N. F. Hall, *J. Amer. Chem. Soc.*, 1927, **49**, 3047, 3062; J. B. Conant and G. M. Bramann, *ibid.*, 1928, **50**, 2305; N. F. Hall and T. H. Werner, *ibid.*, p. 2376; J. B. Conant and T. H. Werner, *ibid.*, 1930, **52**, 4436; N. F. Hall and H. H. Voge, *ibid.*, 1933, **55**, 239.

In solvents unable to accept or donate a proton (*e.g.*, hydrocarbons), there will be no dissociation of acids or bases, but typical acid–base reactions can still take place provided that the solution contains more than one acid–base pair, *e.g.*, an acid + a basic indicator.

The quantitative treatment afforded by the classical dissociation theory remains unchanged when the Brönsted–Lowry definition is used. Thus the ordinary dissociation constant of an acid A in a solvent S is proportional to the equilibrium constant for the reaction $A + S \rightleftharpoons B + SH^+$. It therefore serves as a method of comparing the strengths of the acid–base pairs A–B and SH^+–S. Since the concentration of the solvent is usually omitted from the equilibrium expression, this is equivalent to taking the acid strength of the cation acid SH^+ as equal to the concentration of solvent molecules in the pure solvent; thus the acid strength of H_3O^+ in water is taken as 55·5 moles/litre. All the usual expressions for hydrolysis, buffer action, etc., remain unchanged, and their meaning is often simplified when they are regarded as examples of the fundamental reaction $A_1 + B_2 \rightleftharpoons A_2 + B_1$. In particular, it is only necessary to specify one constant for each acid–base pair, and this is most conveniently taken as the conventional dissociation constant of the acid component. For example, the behaviour of ammonia and ammonium salts can be described completely in terms of the acid constant for the ammonium ion, $[NH_3][H_3O^+]/NH_4^+$, which is quite analogous to $[CH_3{\cdot}COO^-][H_3O^+]/[CH_3{\cdot}CO_2H]$. The classical dissociation constant of ammonia, $[NH_4^+]\ [OH^-]/[NH_3]$, is obtained by dividing the ionic product of water by this acid constant. Brönsted himself[12] has proposed that the strength of a base should be represented by the *reciprocal* of the dissociation constant of the corresponding acid. However,

A_1 +	B_2 ⇌	A_2 +	B_1	Description.
$CH_3{\cdot}CO_2H$	H_2O	H_3O^+	$CH_3{\cdot}COO^-$	Dissociation in water *or* buffer action in acetic acid + acetate.
$CH_3{\cdot}CO_2H$	NH_3	NH_4^+	$CH_3{\cdot}COO^-$	Dissociation of acetic acid in liquid ammonia, *or* dissociation of ammonia in glacial acetic acid, *or* neutralisation of $CH_3{\cdot}CO_2H$ by NH_3, with or without solvent.
H_2O	$CH_3{\cdot}COO^-$	$CH_3{\cdot}CO_2H$	OH^-	Hydrolysis of acetate solutions.
NH_4^+	H_2O	H_3O^+	NH_3	Hydrolysis of ammonium salts, *or* buffer action in $NH_3 + NH_4Cl$.
H_2O	$HPO_4^=$	$H_2PO_4^-$	OH^-	Hydrolysis of secondary phosphates.
H_2O	NH_3	NH_4^+	OH^-	Dissociation of ammonia in water.
$H_2PO_4^=$	H_2O	H_3O^+	$HPO_4^=$	Dissociation of primary phosphate *or* buffer action in mixtures of primary and secondary phosphate.

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[12] J. N. Brönsted, *Z. physikal. Chem.*, 1934, *A*, **169**, 361.

this suggestion has not been generally adopted, and it seems more convenient to use the dissociation constant itself. This does, of course, mean that basic strength is represented by a number which decreases with increasing basic strength, but we already have an example of this in the use of pH for representing the acidity of a solution.

The inception of the Brönsted–Lowry definition was closely associated with the discovery of *general acid–base catalysis.*[13] Dawson had shown at an early date that the acetone–iodine reaction was catalysed not only by hydrogen ions, but also by the undissociated molecules of carboxylic acids. In 1923 J. N. Brönsted and K. J. Pedersen [14] showed that the decomposition of nitroamide was catalysed not only by hydroxyl ions and uncharged amine molecules, but also by the anions of weak acids. Shortly afterwards it was shown [15] that the mutarotation of glucose is catalysed not only by all the species mentioned above, but also by positively charged acids like the ammonium ion. These reactions thus show catalysis by all the types of acids and bases included in the Brönsted–Lowry definition. Many similar cases have been investigated since then, and it is also found that catalysis by acids and bases also takes place in solvents, such as benzene, in which there is no ionisation or reaction with the solvent.

The Special Position of the Solvent.—While the solvent system definition of acids and bases certainly exaggerated the importance of the solvent in acid–base phenomena, the Brönsted–Lowry definition tends to underestimate the special position of the solvent from a practical point of view. Thus although the ions H_3O^+ and OH^- are in principle only particular examples of extended classes of acids and bases, they do occupy a particularly important position in the physical chemistry of aqueous solutions. In the same way, the ions $C_2H_5{\cdot}OH_2^+$ and $C_2H_5{\cdot}O^-$ are particularly important in ethyl alcohol, NH_4^+ and NH_2^- in ammonia, and so on. The solvated hydrogen ions are often referred to as "hydrogen ions" in all solvents (though this may cause confusion with free protons), while there is no generic term for the ions OH^-, $C_2H_5{\cdot}O^-$, NH_2^- etc. N. Bjerrum [16] has therefore proposed that the ions derived from the solvent by the addition and subtraction of a proton should be known as the *lyonium* and *lyate* ions respectively. In particular, salts derived from the solvent anion (hydroxides for water, ethoxides for ethyl alcohol, etc.) would be known as metallic lyates. This suggestion has a good deal to recommend it, but it has not been generally adopted, and will not be considered further.

Pseudo-acids and Pseudo-bases.—These terms have been used in a confusing variety of ways, and there is still no general agreement about their exact meaning. The example usually given of a typical pseudo-acid is nitromethane, which has a dissociation constant in water of about 10^{-11}

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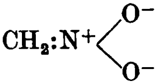
[13] For a full account and references, see R. P. Bell, "Acid–Base Catalysis" (Oxford, 1941), especially Chapter IV.

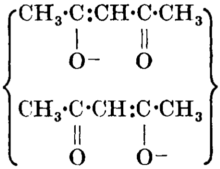
[14] *Z. physikal. Chem.*, 1923, **108**, 185.

[15] J. N. Brönsted and E. A. Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2554; T. M. Lowry and E. A. Smith, *J.*, 1927, 2539.

[16] *Fysisk Tidsskr.*, 1931, Nos. 1—2; *Chem. Reviews*, 1935, **16**, 287.

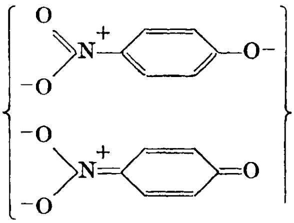
and reacts slowly with hydroxyl ions to give an ion whose structure is presumably  $\mathrm{CH_2:N^{+}\!<\!\begin{matrix}O^-\\O^-\end{matrix}}$. Even very weak acids and bases normally react together instantaneously (as far as can be ascertained), and this slowness of reaction was originally taken as the characteristic property of a pseudo-acid. A. Hantzsch,[17] who discovered this phenomenon, supposed that the slow change was the transformation of the pseudo-acid $\mathrm{CH_3{\cdot}NO_2}$ into the true acid $\mathrm{CH_2{:}NO{\cdot}OH}$, which then dissociated rapidly. However, it has been shown by K. J. Pedersen [18] that there is no need to assume the intermediate formation of $\mathrm{CH_2{:}NO{\cdot}OH}$, and the modern view is that the actual loss of a proton from the methyl group to the hydroxyl ion is a slow process. The reason for this slowness is connected with the reorganisation of electronic structure on the loss of a proton, and this reorganisation provides the best criterion to use in defining the term pseudo-acid, since it is only rarely that a measurably slow reaction occurs. The change of electronic structure is also associated with changes in absorption spectra, which have been used widely by Hantzsch as a criterion for pseudo-acids.

In an extreme case like nitromethane, the charge on the ion resides entirely on an atom other than that from which the proton has been removed. This is so in a number of other molecules, for example acetylacetone, $\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3}$, which has a dissociation constant of about 10^{-9}, gives an ion which is best represented by the mesomeric structure



$$\left\{\begin{array}{c}\mathrm{CH_3{\cdot}\underset{O^-}{\underset{|}{C}}{:}CH{\cdot}\underset{O}{\underset{\|}{C}}{\cdot}CH_3} \\ \mathrm{CH_3{\cdot}\underset{O}{\underset{\|}{C}}{\cdot}CH{:}\underset{O^-}{\underset{|}{C}}{\cdot}CH_3}\end{array}\right\}$$

the charge being distributed between the two oxygens. In other cases the charge may be only partly displaced from the atom originally bearing the proton : for example, phenols having a nitro-group in the ortho or para position give coloured ions which may be written as



In these ions the greater part of the charge probably remains on the phenolic

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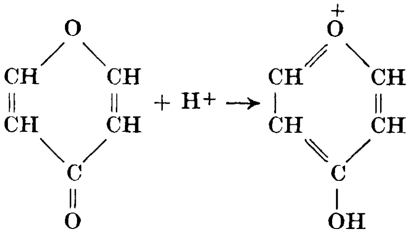
[17] *Ber.*, 1899, **32**, 575.

[18] *Kgl. Danske Vid. Selsk.-Math.-fys. Medd.*, 1932, **12**, No. 1 ; *J. Physical Chem.*, 1934, **38**, 581.

oxygen, but there is no certain method of determining the charge distribution. It is clearly difficult to decide what degree of charge displacement is necessary before the term "pseudo-acid" shall be used. A. Hantzsch [19] concluded from slight optical changes on ionisation that almost all acids (*e.g.*, halogen hydrides, nitric acid, sulphuric acid, carboxylic acids) are pseudo-acids, but his interpretation has been challenged by a number of authors.[20] In any case, such a wide extension of the term would destroy its usefulness, and it is best to reserve it for molecules in which there are strong experimental or theoretical grounds for believing that the charge on the ion is concentrated chiefly on atoms other than that from which the proton has been removed.

From the point of view of the Brönsted–Lowry definition, the anions derived from pseudo-acids will naturally be described as pseudo-bases. There are also examples of uncharged pseudo-bases in the same sense; for example, derivatives of γ-pyrone have strong basic properties, but the positive charge in the cation produced is probably not situated on the oxygen atom to which the proton adds on, *e.g.*:



The change in electronic structure is reflected in a change of absorption spectrum, and similar changes are responsible for the colour change of many plant pigments (anthocyanins and flavones) with pH. The cations of these bases will naturally rank as pseudo-acids.

The original discussions of Hantzsch assumed that every pseudo-acid had a "true acid" corresponding to it, *e.g.*, $CH_2{:}NO{\cdot}OH$ for nitromethane, the enol form of acetylacetone, etc. However, these alternative forms cannot often be isolated, and it is not now believed that they play any part in the typical reactions of pseudo-acids. Further, pseudo-bases would differ from the corresponding "true bases" only in electronic arrangement, and it is now generally held that electronic isomerism of this kind has no real existence.

The above examples illustrate the most logical way in which the terms pseudo-acid and pseudo-base can be used in conjunction with the Brönsted–Lowry acid–base definition. However, these terms have at different times been used in a variety of ways which are at variance with these ideas. The most important of these is the use of the term pseudo-base to describe compounds formed by the addition of hydroxyl ions to certain organic

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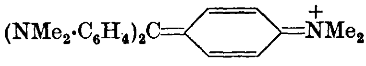
[19] *Z. Elektrochem.*, 1923, **29**, 244; 1924, **30**, 202; *Ber.*, 1925, **58**, 953.

[20] K. Fajans, *Naturwiss.*, 1923, **11**, 179; H. von Halban, *Z. Elektrochem.*, 1923, **29**, 443; H. Ley and H. Hünecke, *Ber.*, 1926, **59**, 510.

cations, accompanied by a structural rearrangement. The best-known examples are the " carbinol bases " of various triphenylmethane dyes. For example, the ion of crystal violet has the structure



where the positive charge and quinonoid structure can be associated with any one of the three benzene rings. This ion reacts slowly with hydroxyl ions to give the carbinol base $(NMe_2{\cdot}C_6H_4)_3C{\cdot}OH$, and the reverse change is brought about by the addition of acid. Similar behaviour is met with in simpler compounds such as the pyrazines and acridines.[21] These carbinol compounds would not be classified as bases at all in the Brönsted–Lowry nomenclature, since they react with acids by splitting off a hydroxyl ion to give water and not by accepting a proton. It seems undesirable to describe them as pseudo-bases, since this term applies more logically to compounds like γ-pyrone.

The names pseudo-acid and pseudo-base have also been applied to molecules which are not themselves acids or bases, but which give acids or bases on dissociation or reaction with the solvent. Thus CO_2 has been termed a pseudo-acid ($CO_2 + H_2O \rightleftharpoons H_2CO_3$), and $NH_4{\cdot}OH$ (if it exists) a pseudo-base ($NH_4{\cdot}OH \rightleftharpoons NH_3 + H_2O$). By an extension of this argument, a covalent halide hydrolysed by water could also be called a pseudo-acid (*e.g.*, $XCl_3 + 2H_2O \rightleftharpoons XOCl + 2H_3O^+ + 2Cl^-$). This usage again seems undesirable.

The Lewis Definition of Acids and Bases.—This definition was first put forward by G. N. Lewis [22] at about the same date as the Brönsted–Lowry definition, but it did not attract much attention until the last ten years or so. It has recently come into a good deal of prominence, especially in the United States, and a recent book on the subject [23] compares its importance in chemistry to that of the theory of relativity in physics. However, opinions have been sharply divided on this subject, and an attempt will be made in this section to give a fair estimate of the position.

Lewis aims at broadening the basis of the acid–base definition from both the experimental and the theoretical standpoint.[24] From the experimental point of view he defines as acids and bases all substances which exhibit " typical " acid–base properties (neutralisation, replacement, effect on indicators, and catalysis) irrespective of their chemical nature or exact mode of action. On the theoretical side he relates these properties to the acceptance (by acids) and the donation (by bases) of electron pairs to form covalent bonds, irrespective of whether the transfer of protons is involved.

The list of compounds classed as bases by Lewis is substantially identical

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[21] A. Hantzsch and M. Kalb, *Ber.*, 1899, **32**, 3116; J. G. Aston, *J. Amer. Chem. Soc.*, 1930, **52**, 5254; 1931, **53**, 1448.

[22] " Valency and the Structure of Atoms and Molecules " (New York, 1923).

[23] W. F. Luder and S. Zuffanti, " The Electronic Theory of Acids and Bases " (New York, 1946).

[24] See particularly G. N. Lewis, *J. Franklin Inst.*, 1938, **226**, 293; also W. F. Luder, *Chem. Reviews*, 1940, **27**, 547.

with the Brönsted–Lowry classification, since those species which can accept a proton contain an unshared pair of electrons, and will also combine with other electron-acceptors. Thus the base NH_3 combines with BF_3 to give $H_3\overset{+}{N}-\overset{-}{B}F_3$. On the other hand, the list of acids is radically altered : Lewis himself writes " . . . any similar valuable and instructive extension of the idea of acids has been prevented by what I am tempted to call the modern cult of the proton." The typical acids of the Lewis definition are molecules like $AlCl_3$, BF_3, SO_3, etc., which do not contain a hydrogen atom, but which are capable of expanding their shell of valency electrons by receiving one or more electron-pairs. These molecules are not acids in the Brönsted–Lowry sense, and most of them are at most " pseudo-acids " in any of the earlier definitions. Classical acid–base reactions as usually written do not reveal any electron-deficiencies, and, in fact, the acids of the older definitions (HCl, H_2SO_4, $CH_3{\cdot}CO_2H$, etc.) can only be included in the Lewis scheme by rather indirect means. Thus reaction between an acid HX and a base B is supposed to be initiated by the formation of a complex XH . . . B, in which the hydrogen accepts extra electrons from the base. Although there is evidence of the existence of hydrogen bonding in a few cases, this bonding is not now believed to involve the formation of a covalent link. As Lewis himself has said :[25] " Evidently what has become known as the hydrogen bond differs not only in degree but in kind from a true chemical bond ", and for this reason the proton acids are sometimes referred to as " secondary acids " by Lewis and his school. They also use the term secondary acid in a different sense to describe some acidic oxides and other substances which, as usually written, cannot expand their electron shell, but which nevertheless give rise to acidic properties (*e.g.*, CO_2, $R{\cdot}COCl$). Thus CO_2 can only be logically termed an acid in the Lewis sense by writing it in the form $O{=}\overset{+}{C}-\overset{-}{O}$.

On the experimental side it is certainly true that the Lewis definition correlates a wide range of phenomena in the qualitative sense. For example, solutions of BF_3 or SO_3 in inert solvents bring about colour changes in indicators very similar to those produced by HCl, and these changes are reversed by adding bases, so that a titration can be carried out. Similarly, the same substances catalyse a large number of organic reactions, some of which are also catalysed by proton-acids. The definition also includes the solvent systems not involving a proton, *e.g.*, $SOCl_2$ in SO_2. However, the wider scope is obtained at the cost of some lack of definiteness. For example, in the Brönsted–Lowry nomenclature, every acid will react with the ammonia molecule to produce the conjugate acid NH_4^+, but on the Lewis scheme the original product $\overset{-}{X}-\overset{+}{N}H_3$ will be different in every reaction, and may or may not dissociate further. Consequently the similar catalytic effects and colours with indicators represent a similarity in electronic displacements rather than a strict parallelism in the nature of the reactions.

The major disadvantage of the Lewis definition compared with those

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[25] G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 1774.

depending on proton transfer is on the quantitative side. In the latter system, the knowledge of one constant for each acid–base pair (for a given solvent and temperature) is sufficient to determine the position of equilibrium in any dilute mixture of acids and bases. (The same kind of prediction can be made to a limited extent about reaction velocities, since there is commonly a quantitative relation between catalytic effect and acid–base strength.) In fact, the most valuable contributions of both the classical and the Brönsted–Lowry concepts have been in the field of quantitative relationships. This kind of quantitative treatment is quite inapplicable in the extended system envisaged by Lewis. Although relatively little quantitative work has yet been done with Lewis acids not containing protons, many facts are already known which show that " the relative strengths of acids and bases depends not only upon the chosen solvent, but also upon the particular acid or base used for reference ".[26]

For example, in the classical sense ammonia is a much weaker base than the hydroxyl ion, but when referred to the Lewis acid Ag^+ the order of strengths is reversed, since AgOH is completely dissociated, while $[Ag(NH_3)_2]^+$ is a stable complex. This absence of any simple system of acid–base strengths is a high price to pay for an increased descriptive scope.

General Conclusions.—The practical point at issue is whether the Brönsted–Lowry definition should be adhered to in scientific writing and teaching, or whether the term acid should be used in the wider sense suggested by Lewis. The latter definition includes more completely those substances showing the qualitative attributes usually associated with acids. On the other hand, the Brönsted–Lowry acids form a group of much greater uniformity obeying quantitative relations confined to this group : moreover, they can only be included somewhat artificially in the electronic definition of acids proposed by Lewis. It therefore seems desirable to distinguish them in some way, and three alternatives are possible : [27]

(*a*) To use the term acid in the most general sense, but to distinguish " proton-acids " or " hydrogen-acids " as a special class. This has the disadvantage of altering a time-honoured usage, and of introducing a cumbrous name for common substances.

(*b*) To use the term acid in the most general sense, and to distinguish by a prefix those acids which cannot give up a proton. Kolthoff (*loc. cit.*) has suggested " proto-acids ", but this seems an unfortunate name for acids which do *not* contain a proton. It would be more satisfactory to describe them as " secondary acids " or " pseudo-acids ". Unfortunately, we have seen that the former of these terms is already employed by Lewis in almost the opposite sense, while the latter also has a variety of uses.

(*c*) To restrict the term acid to those species covered by the Brönsted–Lowry definition, and to use a different name for the Lewis acids. The term *acceptor* or *acceptor molecule* has long been used in this sense [28] and suggests immediately the chemical properties of the molecules concerned.

[26] G. N. Lewis, *loc. cit.*

[27] Cf. I. M. Kolthoff, *J. Physical Chem.*, 1944, **48**, 51.

[28] Cf. N. V. Sidgwick, " The Electronic Theory of Valency " (Oxford, 1929).

In the opinion of the writer, this proposal represents the most satisfactory alternative, since it does not interfere with established usage, and it preserves the distinction between the two classes of molecule. It does not automatically imply the qualitative resemblances stressed by Lewis, but it is quite natural that proton-donors and electron-acceptors should frequently produce similar effects.

The nomenclature of bases offers less difficulty, since a proton-acceptor will always contain an unshared electron-pair which it can donate to acceptors other than the proton. However, it is probably advisable to use the term " base " only in contexts involving the transfer of a proton, since it is only here that the correspondence of acid–base pairs and the quantitative aspects of acid–base strength can be applied. In other contexts the term *donor* forms a natural complement to *acceptor*.

Finally, it should be stressed that the questions involved in the use of the terms acid and base are concerned essentially with convenience and consistency, and not with any fundamental differences in the interpretation of experimental facts. It is therefore misleading to elevate to a matter of principle controversies about these definitions, or to speak of an " electronic theory " of acids and bases. The chief importance of revised definitions lies in their stimulating effect on experimental work. Just as the Brönsted–Lowry definition initiated many investigations of acid–base equilibria and kinetics in different solvents, so the Lewis definition has led to much valuable work on the reactions of acceptor molecules, which will retain its importance even if (as suggested in this review) the Lewis definition is not a convenient one for general use.