

# Quantitative Aspects of Lewis Acidity

By D. P. N. Satchell

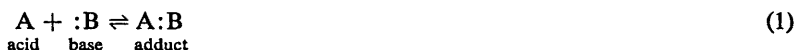
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## 1 Definitions, History, and the Place of Lewis Acids

As all chemists know, G. N. Lewis devised electronic definitions of the terms acid and base. After an examination of typical acid-base phenomena and an analysis of alternative definitions he wrote<sup>1</sup> 'It seems to me that with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and that an acidic substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms. In other words, the basic substance furnishes a pair of electrons for a chemical bond, the acid substance accepts such a pair'. Lewis's fundamental acid-base reaction is the forward step of equilibrium (1), the formation of a co-ordinate covalent bond; its reverse is bond heterolysis.



Related heterolytic processes are (2)–(4). Lewis's viewpoint covers all the phenomena included under the only widely used alternative definitions, the



solvent-systems definitions,<sup>2</sup> and those usually\* accredited to Brønsted<sup>3</sup> and Lowry.<sup>4</sup>

\* It is not generally realised today that Lewis can also claim parentage of these definitions.<sup>1,5</sup>  
<sup>1</sup> G. N. Lewis, 'Valence and the Structure of Atoms and Molecules', Chemical Catalogue Co., Inc., New York, 1923; *J. Franklin Inst.*, 1938, 226, 293; W. F. Luder and S. Zuffanti, 'The Electronic Theory of Acids and Bases', Dover Publications Inc., New York, 1946; 2nd. edn., 1961.

<sup>2</sup> A. F. O. Germann, *J. Amer. Chem. Soc.*, 1925, 47, 2461.

<sup>3</sup> J. N. Brønsted, *Rec. Trav. chim.*, 1923, 42, 718.

<sup>4</sup> T. M. Lowry, *Chem. and Ind.*, 1923, 42, 43.

<sup>5</sup> P. Walden, 'Salts, Acids and Bases: Electrolytes: Stereochemistry', McGraw-Hill Book Co. Inc., New York, 1929.

To see that the Brønsted–Lowry proton transfer formulation comes within Lewis's, compare the typical Brønsted–Lowry acid–base equilibrium (5) with equation (3): the proton in (5) represents the Lewis acid A in (3). In Lewis's scheme, proton donors, the only species recognised as acids by Brønsted, Lowry,



and their followers, often (although not always) participate as adducts of a proton and a base. Thus, despite occasional claims to the contrary, the Brønsted–Lowry formulation can be fitted logically into Lewis's.

That the solvent-systems approach is also covered is perhaps more generally obvious. For instance, reaction (6), occurring in liquid ammonia, between the



solvent-systems acid  $NH_4Cl$  (a species providing the cation characteristic of the solvent) and the solvent-systems base  $NaNH_2$  (a species which provides the solvent anion) is simply another example of equation (3), the sodium and chloride ions playing no essential part in the process. Reaction (6) is written more explicitly in Lewis's terms in equation (7).



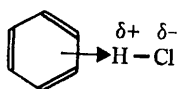
When chemistry textbooks deal with acidity, the various definitions are usually contrasted, and are invariably presented as representing different schools of thought. The inclusiveness of Lewis's scheme, and its correct relationship to other definitions, are almost never properly explained. Certain authors still ignore Lewis altogether, but that attitude is indefensible. Today, critics (like ourselves) of the proton donor–acceptor formulation fault it because of the asymmetry of its definitions (nothing is specified about the atomic structure of the base, which is effectively defined in electronic terms, while the acid must contain hydrogen\*); the solvent-systems scheme is unsatisfactory because no one now believes that acid–base phenomena are restricted to self-ionising solvents. Lewis, arguing along somewhat similar lines, extracted the essential common feature of such schemes: the donation and reception of electron pairs in forming a new acid–base bond. On Lewis's basis, acids are sometimes now divided into vacant-orbital acids (*e.g.*,  $H^+$ ,  $M^{n+}$ ,  $MX_n$ ),  $\pi$ -acids (*e.g.*, trinitrobenzene, tetracyanoethylene), and  $\sigma$ -acids (*e.g.*,  $I_2$ ,  $HCl$ ,  $PhOH$ ), the different class names suggesting the destination of the electron pair donated by the base. Because of the inevitable uncertainty about the details of the bonding in any given case, these names should not be treated too seriously. In Lewis's day, the idea that the electrons donated by the base might enter an orbital covering the whole, or a large part, of the acid molecule, rather than be effectively localised between the acceptor and donor atoms, was unfamiliar. In many cases his picture is still appropriate, but were he writing now he would probably not speak of the lone pair as always

\* Almost all early definitions of acids specify the possession of some particular atomic constitution.<sup>5</sup>

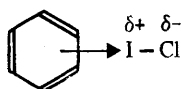
completing the stable group of *one* of the acid's atoms. Such a statement can still stand but is now realised to be over-simple. Lewis's essential idea of donation and acceptance nevertheless remains unaffected by modern developments, and all types of dative covalency are covered by his definitions.

Although these definitions comprise the most important conceptual advance concerning acids and bases made this century, nevertheless more limited definitions still find widespread support, particularly those favoured by Brønsted and Lowry. The most influential contemporary writers in this context are Bell<sup>6-8</sup> and Shatenstein.<sup>9</sup> Their discussions mainly involve brief lists of ways in which the behaviour of Lewis and Brønsted acids are supposed to be importantly and essentially different. We believe these distinctions cannot be accepted today. Bell's discussions have been entirely overtaken by advances in knowledge, and Chapter 8 of the revised (1969) edition of ref. 6 contains errors of fact.

Shatenstein deviates from a strict Brønsted-Lowry orthodoxy in recognising hydrogen-bonding as an acid-base interaction. Fitting hydrogen-bonding into the format of equation (5), with its conjugate acid-base pairs, has always been an embarrassment to Brønsted-Lowry supporters. They must either discredit hydrogen-bonding<sup>6,7</sup>, which is entirely unrealistic<sup>9,10</sup>, or admit it; the way is then opened to analogies like (I) and (II), species which Shatenstein is obliged to view as essentially different.



(I)



(II)

In some media, hydrogen-bonding is the only form of acid-base behaviour available to hydrogen-containing compounds.<sup>10</sup> This causes no difficulties for the Lewis definitions. In hydrogen-bonding (equation 8) the hydrogen-donors are behaving as Lewis acids. When the same compounds engage in complete proton



transfer, as in equilibria like (9), they are behaving as adducts.

<sup>6</sup> R. P. Bell, 'Acids and Bases', Methuen, London, 1952; 2nd. edn., 1969.

<sup>7</sup> R. P. Bell, *Quart. Rev.*, 1947, 1, 113.

<sup>8</sup> R. P. Bell, 'The Proton in Chemistry', Methuen, London, 1959.

<sup>9</sup> A. I. Shatenstein, 'Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds', Consultants Bureau, New York, 1962.

<sup>10</sup> M. M. Davis, 'Acid-Base Behaviour in Aprotic Organic Solvents', N.B.S. Monograph 105, 1968; 'The Chemistry of Non-aqueous Solvents', ed. J. J. Lagowski, Academic Press, London, 1970, chap. 1. This author has now (1970) accepted Lewis's definitions, but we consider that his grounds for regarding them as compatible with Brønsted's are incorrect.

The two most important queries which have been raised by Bell, Shatenstein, and others about the value of Lewis's definitions really concern their practicality. First, it is said that the determination of equilibrium constants for equilibria like (5) provides a convenient method of comparing acid (or base) strengths, that such comparisons disclose a widespread regularity of behaviour, and that such regularity disappears when non-hydrogen acids are included. Secondly, it is urged that the Lewis definitions are too inclusive to be useful; indeed, it is sometimes stated that they include the whole of chemistry. In fact they cover only heterolytic processes; the other *two* general classes of reaction, homolytic (*i.e.*, free-radical) and oxidation-reduction, which fundamentally do *not* involve the movement of electrons in pairs, are excluded.\* Since no one has ever argued that the definition of a free-radical is too inclusive to be useful (and should be restricted, say, to species containing hydrogen) it appears that generality in itself is no disadvantage. Moreover, the vast majority of Lewis acid-base equilibria correspond to reactions like (2), (3), and (4), rather than to (1). Since equation (3) is identical with equation (5), there is obviously no more difficulty in using the equilibrium constants of Lewis acid-base processes as measures of acid-base strength when the concept 'acid' is extended beyond hydrogen acids than when it is not. The only remaining query, therefore, concerns the *scope* of the regularities in quantitative behaviour found under such an extension. Lewis himself believed it would be very limited, and that relative acidity and basicity would depend greatly upon the reference species chosen. This view has been endlessly repeated by advocates of more limited definitions; in this way it became almost axiomatic even before sufficient information existed to test it; it is, however, in any real sense, thoroughly mistaken, as this Review will demonstrate.

## 2 Quantitative Measurement of Lewis Acidity

Apart from Mulliken's provision<sup>12,13</sup> of a quantum-mechanical representation of donor-acceptor bonding, most recent advances concerning Lewis acids have involved the quantitative measurement of their acidity. Until quite recently, quantitative measurements of acid-base equilibria were largely confined to those involving hydrogen acids, or metal ions, in aqueous solution, the main reason being the availability of well-established, comparatively simple techniques for such measurements. However, the current spread of interest to non-aqueous solvents, the widespread importance of Friedel-Crafts catalysts, the description of charge-transfer spectra, and the stimulation of interest provided by Mulliken's

\* Usanovich's little-known acid-base definitions<sup>11</sup> are more inclusive even than Lewis's, and cover oxidation-reduction also. This unfortunate bracketing of electronically distinct processes - *i.e.*, those involving donation and sharing of electron pairs (acid-base) and those involving donation of one or more electrons without sharing (oxidation-reduction) - is surprisingly common; it is deeply imbedded in the literature of oxidation-reduction, where it underlies much confused writing.

<sup>11</sup> M. I. Usanovich, *Zhur. obshchei Khim.*, 1939, 9, 182.

<sup>12</sup> R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, 74, 811.

<sup>13</sup> See also R. E. Rundle, *Rec. Chem. Progr.*, 1962, 23, 195; *J. Amer. Chem. Soc.*, 1953, 85, 112.

theoretical work, have now led to the belated appearance of quantitative information about representatives from most of the possible classes of Lewis acid.

For the quantitative expression of Lewis acidity there is, as we have argued elsewhere,<sup>14</sup> only one widely satisfactory approach: the measurement of equilibrium constants (*i.e.*, of  $\Delta G^\circ$ ). When two acids compete for a given base, the stronger is normally considered to be that which engages the more base. This information is reliably obtained only from  $\Delta G^\circ$  values, and not, for example, from values of  $\Delta H$ . The use of the equilibrium constant as the general measure of acid strength is also in keeping with previous practice for hydrogen acids, and for metal ions studied using aqueous solutions, systems for which results are so plentiful. Only equilibrium constants will be considered in this Review. All the results quoted refer to homogeneous systems.

Simple Lewis acid-base behaviour like (1) is only found in the gas phase, or possibly<sup>15</sup> in very feebly acidic or basic solvents, such as hexane and carbon tetrachloride. A number of such equilibria have nevertheless been studied. The corresponding equilibrium constant is  $K = a_{AB}/a_{AA}a_B \rightleftharpoons C_{AB}/C_A C_B$ . In work with gases, concentrations ( $C$ ) are usually expressed as pressures. In solution, where the distinction between concentration and activity is more important, few of the available results include activity coefficient corrections, except those obtained using dilute aqueous solutions. Apart, therefore, from results quoted for aqueous systems, the constants discussed are very largely based on concentrations alone.

As noted above, equilibria like (1) constitute a minority, and since most experiments involve solvents more basic than they are acidic, the most commonly studied type of acid-base process corresponds to equation (3), or, writing  $B^2 = S = \text{solvent}$ , to equation (10), where AS represents acid co-ordinated to the solvent. The equilibrium constant is now  $K = C_{AB}C_S/C_A S C_B$ . For aqueous



systems, it is conventional to omit the solvent from the definition of  $K$ . Extending this practice generally to equation (10), we have  $K = C_{AB}/C_A C_B$ , which is identical in form to the expression for  $K$  for equation (1).

The foregoing equations have all been written in terms of mono-acidic or mono-basic species. Certain Lewis acids, especially metal ions and covalent metal halides, are poly-basic (*e.g.*, equation 11). Except with chelating bases, the species



B are taken up one at a time, in successive equilibria. We shall be concerned mainly with formation of the 1:1 adducts only.

Apart from studies (and few exist) using low concentrations of anhydrous sulphuric, hydrofluoric, or similar acids, quantitative work with covalent metal halides  $M(\text{Hal})_n$  presents the greatest experimental difficulty in the field as a whole.

<sup>14</sup> D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.

<sup>15</sup> R. Foster, 'Organic Charge-Transfer Complexes', Academic Press, London, 1969.

This is because work is restricted either to the gas phase, or to rigorously dried, non-hydroxylic solvents.<sup>14</sup> Traces of water not only partially neutralise such acids, but often decompose them. In Section 3, we outline the available experimental methods and discuss briefly how method and conditions limit the reliability of the results.

### 3 Experimental Methods

**A. Gaseous Phase Measurements.**—Relatively few gas-phase acid–base equilibria have been studied quantitatively.<sup>14,15</sup> This is true even of hydrogen acids engaging in hydrogen-bonding. Gas-phase techniques involve the determination of equilibrium pressures. Some types of system are therefore completely excluded, and with others when one of the components is relatively involatile its pressure is necessarily low, and the measurement of  $K$  correspondingly inaccurate. These circumstances, and the experimental difficulties inherent in gas-phase work, have combined largely to limit work to completely organic systems or to acids  $MX_n$ , where  $M$  is an element of Group III of the Periodic Table. In favourable cases, accurate values of  $K$  can be obtained.

**B. Liquid-phase Measurements.**—In solution studies, a wide variety of techniques can be used to determine solute concentrations. The commonest methods for aqueous solutions are potentiometry, and u.v. and visible spectrophotometry. With non-aqueous media, techniques include cryoscopy, and n.m.r. and i.r., as well as u.v., spectrophotometry. Occasionally, solubility or other methods are used. The accuracy obtained with potentiometry and u.v. spectrophotometry is normally very good; n.m.r. and i.r. spectrophotometry are more limited by the solute concentration range which it is usually possible to employ; cryoscopy and solubility are comparatively inaccurate methods, with particularly limited temperature ranges. The most widely used method now is u.v. spectrophotometry.<sup>14,15</sup> It has the advantage that very low concentrations of reactants can be used. In work with systems susceptible to interference from adventitious moisture, this advantage can become a danger, for no solvent can be rendered completely anhydrous. Measurements with acids like  $H_2SO_4$  or  $M(Hal)_n$  employed in non-hydroxylic solvents at concentrations  $< 10^{-4}$  mol l<sup>-1</sup> must be expected to involve substantial error. The common use in u.v. techniques of a large excess of one component can also lead to errors if polymeric complexes result, without this fact being realised.<sup>15</sup> Although one or more of the various types of spectrophotometry can normally be employed, a relatively accurate thermal method which provides both  $\Delta H$  and  $\Delta G^\circ$  has recently been developed;<sup>16</sup> its use will sometimes be advantageous.

### 4 Expectations concerning Acid Strength

In this section, and those following, most emphasis is placed upon the covalent

<sup>16</sup> T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 3921.

acids  $\text{MX}_n$ , where M is usually a metal atom,  $n$  its normal valency, and X a halogen atom or an organic radical.

Attention will be confined to equilibria like (11), analogous to equation (1), in which  $\text{MX}_n$  is not decomposed. The following qualitative discussion, given in detail in ref. 14, is based on an essentially valence-bond model.

**A. The Effect of the Electronic Configuration of M.**—Assuming single bonding between any particular base and  $\text{MX}_n$ , thus excluding, temporarily, both chelation effects and double bonds between M and any given atom of the base, three broad principles can be formulated.

(a) The acidity of  $\text{MX}_n$  can arise, when  $n < 4$ , from M's desire to complete an outer electron octet by accepting one (or more) pair of electrons from bases. When two pairs are required, the acidity exhibited is likely, other factors being equal, to be less than when a single pair suffices, owing to (i) the relatively smaller energy gain on receiving the first pair (which does not complete the octet), and (ii) the build-up of negative charge on M if two pairs are received.

Acidic behaviour will also be expected when, although  $\text{MX}_n$  already represents a reasonably stable electronic arrangement, M is an element which can expand its outer electron shell, by using  $d$ -orbitals, to an alternative, stable configuration involving 10, 12, or perhaps 14 electrons. Here the resulting acidity will be expected usually to be less marked, the completion of such large shells normally being energetically less rewarding than the completion of an octet. As for octet completion, the formation of larger configurations is likely to be most favourable energetically when only one electron pair is required.

(b) Other factors being equal, the acidity of M will be expected to fall, within any Group in the Periodic Table, with increasing atomic volume (effectively, with increasing atomic number) owing to the relatively weaker attraction between nuclear charge and the incoming electron pairs (*cf.* Fajan's Rules).

(c) Since, in general, the energies of different atomic orbitals lie closer together with increasing atomic number (thus facilitating hybridisation) and because orbital contraction arising from the electronegativity of the nucleus tends to decrease with increasing atomic number (thus permitting more effective overlap of hybridised orbitals) the use of  $d$ -orbitals, especially outer  $d$ -orbitals, will normally become easier and more effective the heavier is M. In those groups which use  $d$ -orbitals, this effect will counteract, to some extent, the effect of principle (b). Sometimes, increasing size will also be sterically beneficial (see below).

These principles permit much to be understood and predicted. Thus it is reasonable (principle *a*) that few, if any, equilibrium constants for covalent compounds of Group I elements are available, for in these compounds,  $\text{MX}$ , three electron pairs are needed to complete a new octet. In the covalent compounds of Group II (*e.g.*,  $\text{ZnBr}_2$ ,  $\text{CdI}_2$ ), M seeks a normal maximum of two additional electron pairs. By principle (*a*), the observed acidic properties are therefore likely to be only moderate. Principle (*b*) suggests that, towards a

standard base, the sequence of acidity in comparable compounds will be  $Zn > Cd > Hg$ .

Group III elements will be those expected by principle (a) to form the most acidic compounds  $MX_n$ , since M requires only a single electron pair. The common covalent compounds of this Group (*e.g.*,  $BF_3$ ,  $AlCl_3$ ,  $GaBr_3$ , *etc.*) include the majority of the best known Friedel-Crafts catalysts. Principle (b) suggests the sequence of acidity  $B > Al > Ga > In > Tl$  for comparable compounds. In the other sub-Group, the trivalent compounds should display acidities  $Sc > Y > La$ .

Group IV elements in their normal covalent compounds,  $MX_4$ , succeed in completing the octet. Hence a 'saturated' carbon atom will possess no acidic properties under any circumstance (because the First Period elements have no available *d*-orbitals). Similarly, the acidity of  $SiX_4$  compounds will be expected to be weak, and this Group provides a good example of principle (c). In the B sub-Group, the opposing effects of principles (b) and (c) may be guessed to lead to an acidity maximum at derivatives of tin. In the A sub-Group, prediction is difficult, since octet expansion now employs inner *d*-orbitals, and such orbitals are generally closer in energy to the *s* and *p* valence-orbitals than are the outer *d*-orbitals. However, the sequence  $Ti < Zr \approx Hf$  seems sensible since Zr and Hf are of similar size. The use of inner *d*-orbitals for the A sub-Group means that the orders  $Ti > Ge$  and  $Zr > Sn$  will be expected.

Considerations like the foregoing can be applied to the remaining Groups of the Periodic Table,<sup>14</sup> but the above discussion is sufficiently illustrative. Group VII, containing the halogens, is, however, especially interesting from the Lewis acid viewpoint. These elements, normally univalent, will resemble Groups IV (and VI) in that their lower members will be very feebly acidic (F not at all) with the higher members (especially I) being able to undergo octet expansion in suitable circumstances (*e.g.*, when attached to an electron-withdrawing substituent, since such substituents tend to stabilise large outer-electron shells). Thus adducts like  $I_3^-$  and  $C_6H_6 \rightarrow ICl$  are well known; the weak acidic properties<sup>17</sup> of carbon tetrachloride ( $Cl-CCl_3$ ) doubtless arise from similar origins. The sequence of acidity expected for the halogens in comparable compounds is  $F < Cl < Br < I$ , the general level of acidity being low.

The foregoing predictions are obviously tentative. Molecular orbital theory can formulate many acid-base interactions for which valence-bond theory invokes acceptor *d*-orbitals without recourse to these orbitals, and can indeed provide general alternatives to Mulliken's essentially valence-bond approach.<sup>13,16,18</sup> Although there is at present little reason to prefer these molecular-orbital treatments, a rationalisation of relative acidities based partly on *d*-orbital availability, as above, can only be provisional. However, our qualitative model leads to conclusions, and using it we predict<sup>14</sup> the sequence of relative acidity:  $BX_3 > AlX_3 > FeX_3 > GaX_3 > SbX_5 > InX_3 > SnX_4 > AsX_5 > ZnX_2 > HgX_2$ . To

<sup>17</sup> D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149.

<sup>18</sup> J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, 'Valence Theory', Wiley and Sons Ltd., London, 1965, p. 337.



readers with any knowledge of the catalytic powers of covalent halides, this sequence will seem reasonably sensible.<sup>19</sup>

Similar qualitative predictions of acidity can be conducted for other types of acid; for example, for those in which the central metal atom is charged, as in  $[MX_n]^{y+}$ , where X may be any of the ligands  $H_2O$ ,  $NH_3$ , halogen, *etc.* The so-called Irving–Williams series, which comprises the sequence of acidity shown by certain transition metals in their  $M^{2+}$  state in water, can be qualitatively rationalised on the basis of principle (b) alone.<sup>20</sup> By the same principle, one will expect the sequence  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ , and on simple electrostatic grounds, the sequence  $Li^+ < Mg^{2+} < La^{3+}$ . Electronegativities, ionic radii, and ionisation potentials are the measured properties which most closely reflect the qualitative principles we have outlined. For metal ions, provided sufficient variable parameters are included, it is possible to develop empirical equations relating observed equilibrium constants to these properties.<sup>21</sup> Such equations have, however, as yet no rigorous theoretical foundation.

Many classes of Lewis acid either have no single, central acceptor atom (*e.g.*, acids such as trinitrobenzene) or have hydrogen playing this rôle (as in  $H^+$  or  $HX$ ). For these acids the electronic structure of the central atom is either irrelevant or fixed, and the level of acidity is controlled mainly by the substituents attached to the acceptor centre. The substituents X also affect the acidity shown by species  $MX_n$ , and increases resulting from changes in M can be offset by changes in X (and *vice versa*).

**B. The Effect of Substituents.**—(i) *Polar effects.* Since the principal function of M in  $MX_n$  is to receive electron pairs, any substituent X which repels electrons relative to hydrogen will be expected to reduce the acidity of M below its value in the corresponding M–H compound. Conversely, electron-attracting substituents will increase M's acidity. Normally for  $MX_n$  the inductive effects of substituents will be the important ones; tautomeric electron transfer will often be curtailed by the absence of sufficient overlap between the relevant substituent orbitals and suitable metal orbitals.

(ii) *Steric effects.* Trends expected on purely polar grounds can be disturbed by steric effects. If the substituents attached to the acceptor centre of an acid are bulky, and especially if the acceptor centre is small, these substituents may hinder the close approach of the base and/or restrict its rotation in the adduct. A similar effect obtains when any rehybridisation, necessary on forming the adduct, forces substituents into positions in which they interfere with each other. Steric repulsions and additional restrictions on rotation in the adduct render it less stable and therefore reduce the effective acidity of the acid.

**C. The Effect of the Structure of the Base.**—(i) *The electronic state of the base.* It

<sup>19</sup> 'Friedel–Crafts and Related Reactions', ed. G. A. Olah, Interscience Publishers, New York, 1963–1965, vols. I–IV.

<sup>20</sup> H. M. N. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1952, 3192.

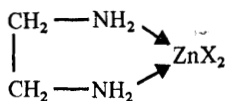
<sup>21</sup> M. Misono, E. Ochiai, Y. Saito, and Y. Yoneda, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2685.

is usually only compounds containing elements of the oxygen, nitrogen, and fluorine Groups which have non-bonding electron pairs available for donation to acids, although unsaturated compounds can also act as bases owing to their  $\pi$ -electron systems. Bases can therefore be classified as  $n$ - or  $\pi$ -donors;  $n$ -donors are the more common, and nitrogen and oxygen are the commonest donor atoms. The availability of the electron pairs will, of course, be affected by substituents attached to the donor atom. The possession by a base of more than one electron pair suitable for donation, and/or of vacant orbitals suitable for electron pair reception from the 'acid', is important in certain contexts, but mostly the formation of a single co-ordinate bond between the acid and base is all that is involved. In such cases, for reactions like (1) and in the absence of steric effects, because the rôle of the acid is simply to accept the proffered electron pair, a given series of bases will be expected to exhibit similar sequences of relative basicity towards any acid, including the proton.

(ii) *Steric effects.* As for acids [Section B (ii)], so for bases the presence of bulky substituents may impede adduct formation and so reduce basicity.

(iii) *Successive co-ordination.* If an acid can form more than one adduct [*e.g.*,  $\text{MX}_4$  acids give 1:1 ( $\text{MX}_4\text{B}$ ) and 1:2 ( $\text{MX}_4\text{B}_2$ ) adducts], the effect of the first base species B to co-ordinate is, so far as the second is concerned, to produce a new acid. Whether or not  $\text{MX}_4\text{B}$  is stronger or weaker than  $\text{MX}_4$  will depend upon the various electronic and steric effects which the addition of B produces. If M and B are singly bonded,  $\text{MX}_4\text{B}$  will be expected usually to be weaker, since some net transfer of charge to M will almost certainly be involved, and steric hindrance, if present, is likely to be greater in  $\text{MX}_4\text{B}$  than in  $\text{MX}_4$ . This particular generalisation is supported by what is known<sup>14,22</sup> of the stepwise co-ordination to acids  $\text{MX}_n$  and to metal ions, and will not be illustrated in detail.

(iv) *Polyfunctional bases.* Suitable acids and polyfunctional bases can form chelated adducts, *e.g.* (III). Clearly, this effect is likely to lead to considerably enhanced stability for such 1:1 adducts compared with the stability exhibited by



(III)

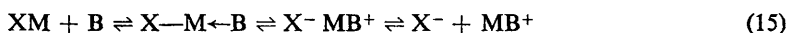
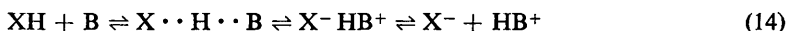
the same acid with similar bases having only one donor centre. This is found<sup>14,22</sup> both for  $\text{MX}_n$  and for metal ions. In the latter context it very often underlies the catalytic activity of these ions (*vide infra*).

<sup>22</sup> F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience Publishers, London, 1962.

**D. Solvent Effects.**—Most acid–base equilibria are studied using a solvent. Solvent effects are of utmost importance for such equilibria, but have been relatively little studied and are not well understood. Almost always a solvent (S) interacts acid–base-wise with either the acid or the base (or with both), *e.g.*, equations (12) and (13). In the absence of solvent co-ordination (equation 1) an



increase in its dielectric constant will favour the more polar side of the equilibrium; this normally means favouring the adduct. For equilibria like (12), the commonest type, an increase in solvent basicity leads to a reduction in  $K$ . Usually, co-ordination effects outweigh those of the dielectric constant.<sup>15</sup> Quite generally, the extent and complexity of processes like (14) and (15), where M is any acceptor centre other than H, is determined by the dielectric constant and acid–base properties of the solvent, and it is an illusion to imagine that hydrogen acids lead to simpler behaviour than do other classes.<sup>9,10</sup>



It can be argued<sup>14</sup> that, for a series of structurally similar bases engaging a standard acid in equilibria like (12), their relative  $K$  values will be similar whatever the nature of  $S \rightarrow A$ . However, for a series of acids with a common base, the relative acidity will depend greatly on S. It has been shown<sup>14,23</sup> that; (a) the overall sequence obtaining in the gaseous phase will normally be found also in solution, and (b) of two solvents, that which leads to the lower general level of acidity (to the smaller  $K$  values) will lead to smaller differences in acidity between acids; *i.e.*, highly co-ordinating solvents lead to a levelling effect. Similar arguments can be applied to equilibria such as (13) which involve acidic solvents.

**E. Extent of Expected Correlations.**—The general tenor of the foregoing sections is that parallelisms in quantitative behaviour are to be expected quite generally between all classes of acid and base. Ultimately, this is because the essentials of acid–base bonding are always the same. Discontinuities in behaviour will, however, be expected; (i) if any special asymmetry is involved within a comparison, so far as bonding opportunity is concerned, and (ii) if environmental effects do not contribute a roughly constant factor.<sup>24</sup> Unequal bonding opportunities can arise from gross discrepancies between the orbitals available, and/or the steric effects obtaining, in different parts of a comparison. Thus, in the comparison of two acids, the same order (indeed much the same magnitude if the environments are similar) of relative acidity should always obtain when reference is to bases of the same structural type. When, however, a change of reference base leads to new

<sup>23</sup> A. Mohammad and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1966, 527.

<sup>24</sup> F. Hibbert and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 573.

possibilities of bonding not equally available to both acids, an important change in relative acidity is inevitable.<sup>14</sup> Relevant here are the phenomena which have led to the division of metal ions into class *A* and *B* acceptors,<sup>25</sup> and to the more general descriptions of soft and hard acids and bases.<sup>26</sup> Class *A* ions, which constitute the great majority, and which include the proton, form more stable adducts with oxygen- and nitrogen-bases than with sulphur- and phosphorus-bases respectively. For class *B* species, the reverse is true. The reasons underlying this dichotomy are still debated, but must be connected with gross differences in orbital availability for the various pairs. One attractive explanation, compatible with the distribution of class *B* metals in the Periodic Table, is that these acids, having well-stocked *d*-orbitals, can form a second co-ordinate bond, in the reverse direction to the primary bond, by donating electron pairs from these *d*-orbitals to vacant, accessible *d*- or *p*-orbitals on the 'donor', when such orbitals exist. The hard-soft terminology, which grew out of the class *A/B* classification, is also based on the observation that some acid-base pairs interact more readily than do other pairs. Thus, in general, polarisable partners, which lead to highly covalent acid-base bonds, tend to react together easily, as do other pairs which lead to relatively ionic bonding. The hard-soft terminology is unfortunately very imprecise (all dative bonds are covalent to some extent, by definition); its main value is its emphasis on well-matched pairs, *e.g.*, Class *B* ions and sulphur-bases.

Ultimately it is the extremities of behaviour which led to the foregoing classifications which provoke queries about the quantitative viability of Lewis's broad definitions; superficially it would appear that regular behaviour throughout the field should be seriously undermined by such preferential interactions. Results now available show, however, that Lewis's own fears on this point were premature,<sup>1</sup> and that nothing quantitative is gained, and that much chemical insight can be lost, by using more restricted definitions of acids and bases.

## 5 Comparison between Prediction and Experiment

**A. Equilibria involving Acids  $MX_n$ .**—Typical results<sup>14,27-30</sup> of measurements of equilibria in aprotic solvents between bases and compounds  $M(\text{Hal})_n$ , where  $M = \text{Zn}, \text{Cd},$  or  $\text{Hg}$ , are in Tables 1—3, together with results for the corresponding protonation equilibria in water. The reactions are all examples of equation (16), where  $S = \text{solvent}$ . The results lead to the following conclusions: (a) apart from bases containing *ortho*- or *N*-substituents, good correlations are exhibited between the various  $pK$  and  $pK_a$  values, and reliable correlation equations



can be set up, (b)  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ , and  $\text{ZnI}_2$  all have similar acid strengths towards a

<sup>25</sup> S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, 12, 265.

<sup>26</sup> R. G. Pearson, *Science*, 1966, 151, 172.

<sup>27</sup> D. P. N. Satchell and R. S. Satchell, *Trans. Faraday Soc.*, 1965, 61, 1118.

<sup>28</sup> R. S. Satchell, *J. Chem. Soc. (B)*, 1967, 1088.

<sup>29</sup> R. S. Satchell and D. P. N. Satchell, *Chem. Comm.*, 1969, 110.

<sup>30</sup> D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 1964, 4296.

variety of anilines and benzamides, (c) towards any given base, the acidity sequence is probably  $ZnX_2 > CdX_2 > HgX_2$ , (d) with anilines,  $CdI_2$  is involved in two equilibria (see Section 6B), both leading to good correlations with proton acidity towards the same bases. The double equilibria could arise because  $CdI_2$  can act as a bifunctional Lewis acid, the iodine atoms, as well as the cadmium atom, being potential acidic sites (see Section 4); (e) the effect on  $K$  of substituent changes in a base is similar for all the acids, (f) compared with anilines (in which the basic centre is nitrogen), benzamides (basic centre oxygen) are relatively much (*ca.*  $10^4$ – $10^5$ -fold) more basic towards the Lewis acids than towards the proton, *i.e.*, for a given  $pK_a$  value,  $pK$  is *ca.* 4 units more negative for benzamides than for anilines.

Conclusions (a)–(e) are entirely in line with the predictions of Section 4. Conclusion (f) is at first surprising and appears to represent an important behavioural discrepancy between  $MX_n$  and the proton. The result has been

**Table 1** Zinc halide – aniline equilibria in acetone at 25 °C

Aniline derivative	$ZnCl_2$				
	$pK_a$	$pK$	$(pK_{calc})$	$pk_1$	$pk_{-1}$
4-Methyl-3-nitro	2.90	– 1.90	(– 1.91)	– 0.30	2.7
3-Nitro	2.50	– 1.69	(– 1.74)	0.14	2.9
6-Methyl-3-nitro	2.32	– 1.88	(– 1.54)	0.92	3.9
4-Chloro-3-nitro	1.93	– 1.37	(– 1.30)	0.72	3.2
4-Nitro	0.99	– 0.74	(– 0.70)	1.32	3.2
	$ZnBr_2$				
4-Methyl-3-nitro	2.90	– 2.40	(– 2.39)	– 0.67	2.8
3-Nitro	2.50	– 1.98	(– 2.07)	– 0.28	2.8
6-Methyl-3-nitro	2.32	– 2.12	(– 1.92)	0.42	3.6
4-Chloro-3-nitro	1.93	– 1.52	(– 1.60)	0.28	2.9
3-Methyl-4-nitro	1.45	– 1.27	(– 1.21)	1.14	3.5
4-Nitro	0.99	– 0.95	(– 0.84)	1.75	3.8
2,6-Dimethyl-4-nitro	0.95	– 0.36	(– 0.81)	3.62	5.1
2-Methyl-4-nitro	0.94	– 1.18	(– 0.80)	2.60	4.9
4-Methyl-2-nitro	0.45	– 0.40	(– 0.40)	2.57	4.1
	$ZnI_2$				
4-Methyl-3-nitro	2.90	– 2.02	(– 2.01)	– 0.83	2.3
3-Nitro	2.50	– 1.88	(– 1.83)	– 0.40	2.6
6-Methyl-3-nitro	2.32	– 1.95	(– 1.63)	0.24	3.3
4-Chloro-3-nitro	1.93	– 1.39	(– 1.39)	0.15	2.6
4-Nitro	0.99	– 0.78	(– 0.78)	1.17	3.1

$K$  refers to the equilibrium  $Zn(Hal)_2S_2 + B \xrightleftharpoons[k_{-1}]{k_1} Zn(Hal)_2BS + S$ , where B = an aniline and S = solvent;  $pK = -\log [Zn(Hal)_2BS] / [Zn(Hal)_2S_2][B] = -\log k_1/k_{-1}[S]$ ; units of  $K$  are  $l\ mol^{-1}$ , and of  $k_1$  and  $k_{-1}$   $l\ mol^{-1}\ min^{-1}$ ;  $pK_a = -\log$  (dissociation constant of  $BH^+$  in water at 25 °C) in all tables;  $pK_{calc} = pK$  calculated from correlation equations of the form:  $pK = apK_a + b$ ; for  $ZnCl_2$ ,  $ZnBr_2$ , and  $ZnI_2$ ,  $a = -0.63$ ,  $-0.81$ ,  $-0.64$ , and  $b = -0.08$ ,  $-0.04$ ,  $-0.15$  respectively.<sup>26</sup>

**Table 2** Equilibria between zinc halides and oxygen- and nitrogen-bases in diethyl ether

Aniline derivative (at 20°C)	$pK_a$	$pK(pK_{calc})$		
		ZnCl <sub>2</sub>	ZnBr <sub>2</sub>	ZnI <sub>2</sub>
4-Bromo	3.91	- 2.20 (- 2.27)	- 2.10 (- 2.12)	—
4-Methyl-3-nitro	2.90	—	- 1.55 (- 1.49)	- 1.30
3-Nitro	2.50	—	- 1.00 (- 1.13)	—
2,4-Dichloro	2.00	- 0.71 (- 0.70)	—	—
2,3-Dichloro	1.83	- 0.47 (- 0.56)	—	—
2,5-Dichloro	1.50	- 0.28 (- 0.29)	- 0.48 (- 0.43)	—
4-Nitro	0.99	—	- 0.08 (- 0.07)	+ 0.20
2-Methyl-4-nitro	0.94	+ 0.75 (+ 0.17)	—	—

Benzamide derivative (at 25°C)	$pK_a$	$pK(pK_{calc})$		
		ZnCl <sub>2</sub>	ZnBr <sub>2</sub>	HgBr <sub>2</sub>
4-Methoxy	- 1.80	- 3.56 (- 3.27)	—	—
2-Methyl	- 1.88	- 3.14 (- 3.20)	—	—
4-Methyl	- 2.01	- 3.17 (- 3.10)	- 3.17	—
<i>N</i> -Methyl	- 2.13	- 2.34 (- 3.01)	—	—
Hydrogen	- 2.16	- 2.96 (- 2.98)	—	—
4-Fluoro	- 2.24	- 2.83 (- 2.92)	—	—
3-Methoxy	- 2.35	- 2.94 (- 2.83)	—	≥ - 1.8
4-Chloro	- 2.47	- 2.72 (- 2.74)	- 2.56	—
3-Bromo	- 2.75	- 2.52 (- 2.52)	—	—
3-Nitro	- 3.07	- 2.21 (- 2.26)	—	—
4-Nitro	- 3.23	- 2.17 (- 2.14)	- 2.17	—

$K$  refers to equation (16);  $pK = -\log [Zn(Hal)_2SB]/[Zn(Hal)_2S_2][B]$ ; units of  $K$  are  $1 \text{ mol}^{-1}$ ; for anilines,  $pK_{calc}$  calculated from  $pK = -0.82pK_a + 0.94$ , and  $pK = -0.70pK_a + 0.62$  for ZnCl<sub>2</sub> and ZnBr<sub>2</sub> respectively; for benzamides and ZnCl<sub>2</sub>, from  $pK = -0.79pK_a - 4.69$ .

**Table 3** Cadmium iodide - amine equilibria in acetone at 25 °C

Amine	$pK_a$	$pK_1 [(pK_1)_{calc}]$	$pK_2 [(pK_2)_{calc}]$	$pK_2$	$pK_{-3}$
4-Methyl-3-nitroaniline	2.90	- 0.97 [- 0.99]	- 1.75 [- 1.76]	0.88	3.76
5-Nitro-1-naphthylamine	2.73	- 0.79 [- 0.83]	- 1.97 [- 1.63]	1.54	4.64
3-Nitroaniline	2.50	- 0.72 [- 0.63]	- 1.46 [- 1.45]	1.56	4.15
6-Methyl-3-nitroaniline	2.32	- 0.93 [- 0.46]	- 1.78 [- 1.30]	3.24	6.15
4-Chloro-3-nitroaniline	1.93	- 0.06 [- 0.11]	- 0.92 [- 0.99]	2.24	4.29
3-Methyl-4-nitroaniline	1.45 <i>ca</i>	+ 0.3 [+ 0.32]	- 0.63 [- 0.62]	2.92	4.08

$K_1$  refers to equation (34), and  $K_2$ ,  $k_2$ , and  $k_{-3}$  to equation (35);  $pK_1 = -\log [(V)]/[CdI_2S_2][B]$ ;  $pK_2 = -\log [(VI)]/[CdI_2S_2][B] = -\log k_2/k_{-3}[S]$ ; units of  $K_1$  and  $K_2$  are  $1 \text{ mol}^{-1}$ ; units of  $k_2$  and  $k_{-3}$  are  $1 \text{ mol}^{-1} \text{ min}^{-1}$ ;  $pK_{calc}$  calculated from equations:  $pK_1 = -0.91pK_a + 1.65$ , and  $pK_2 = -0.89pK_a + 0.53$ .

attributed<sup>14</sup> to the opportunity for double dative bonding between the oxygen and M atoms, arising from participation of both of oxygen's lone pairs, this opportunity not being available for nitrogen-bases. Certain steric considerations also support this view.<sup>14</sup> However, recent comparisons<sup>31</sup> of aqueous  $pK_a$  data with  $pK$  values for hydrogen-bonding equilibria (17) between *p*-fluorophenol and different classes of base in carbon tetrachloride, have revealed an exactly similar phenomenon: oxygen-bases are relatively much stronger than nitrogen-bases



towards hydrogen-bonding than would be expected from their protonation in water. No double-bonding explanation is available here, and the effect arises, not from any important difference between the proton's behaviour and that of other acids, but from a solvent effect. It is probably due to the relatively much greater suppression of oxygen- than of nitrogen-basicity in water, owing to the greater opportunity for solvent hydrogen-bonding (equations 18 and 19); for oxygen bases, the acid (here the proton) has to compete against twice the number of hydrogen-bonding equilibria. This is an example of how solvent co-ordination to



the base can affect relative basicities (*cf.*, Section 4D): a nitrogen- and an oxygen-base of similar  $pK$  in carbon tetrachloride, acetone, or ether exhibit very different  $pK_a$  values in water. Similar phenomena probably underlie the compression of the basicity range normally shown by any series of bases in aprotic, compared with protic, solvents.

Within any class of base, good correlations<sup>31</sup> are found between  $pK$  for hydrogen-bonding in carbon tetrachloride and  $pK_a$  in water, just as they are between  $pK_a$  and  $pK$  for  $\text{M}(\text{Hal})_n$  (see above). Indeed, provided that solvent effects are minimised, hydrogen-bonding results can be used to predict  $pK_a$  values for a wide range of bases.<sup>10,32</sup>

All the foregoing results are evidence for the essential similarity of behaviour of Lewis and Brønsted acids towards bases. The same picture emerges<sup>14</sup> from experiments with oxygen- and nitrogen-bases and acids  $\text{M}(\text{Hal})_n$ , where M is boron, aluminium, or gallium. Excellent correlations between  $pK$  for  $\text{M}(\text{Hal})_n$  and  $pK_a$  are found for equilibria like (20). It is observed also that towards any base the acidity sequence is  $\text{B}(\text{Hal})_3 > \text{Al}(\text{Hal})_3 > \text{Ga}(\text{Hal})_3$ , as predicted in Section 4. The available gaseous-phase equilibrium constants<sup>14,33</sup> for Group III



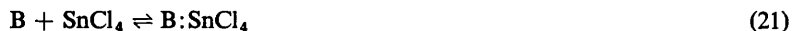
<sup>31</sup> D. Gurka and R. W. Taft, *J. Amer. Chem. Soc.*, 1969, **91**, 4794; R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and K. W. Rakshys, *ibid.*, p. 4801.

<sup>32</sup> E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223; W. Gordy, *J. Chem. Phys.*, 1941, **9**, 215.

<sup>33</sup> F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101.

acids are of only indirect relevance to the present issues, since they mostly concern systems involving important steric hindrance. Indeed, these measurements were largely undertaken to establish the reality of steric hindrance.<sup>34</sup> Brown's implicit assumption (for which the evidence was then very slim<sup>14</sup>) was that, in the absence of steric effects, a parallelism between Brønsted and Lewis acidity *would exist*; it is instructive to realise that this important early work was founded on the assumption of a parallelism whose existence we are still finding it necessary to emphasise today.

Work with Group IV acids  $\text{MX}_4$  has involved mainly compounds in which  $\text{M} = \text{Sn}$ . The pattern of results<sup>14</sup> is very similar to that obtained with Group II and III acids. Typical and particularly interesting measurements referring to equilibria in *o*-dichlorobenzene between  $\text{SnCl}_4$  and anilines<sup>35</sup> and carboxylic acids<sup>36</sup> as bases (B) are in Tables 4 and 5. The extent to which the solvent interacts with the acid is uncertain, and the equilibria may perhaps be written as (21). In the spectroscopic determination of  $K$  for the anilines it was found that the adducts of



the stronger bases exhibit spectra very similar to those given by the corresponding

**Table 4** Stannic chloride – aniline equilibria in *o*-dichlorobenzene at 20 °C

Aniline derivative (B)	$\text{p}K_{\text{a}}$	$\text{p}K$	$\text{p}K_{\text{calc}}$
4-Methyl-3-nitro	+ 2.90	– 3.60	– 3.81
3-Nitro	+ 2.50	– 3.60	– 3.63
6-Methyl-3-nitro	+ 2.32	– 3.35	– 3.54
4-Nitro	+ 0.99	– 3.18	– 2.92
2-Methyl-4-nitro	+ 0.94	– 2.38	– 2.89
4-Methyl-2-nitro	+ 0.45	– 2.50	– 2.66
3,5-Dinitro	+ 0.22	– 2.37	– 2.55
2-Nitro	– 0.29	– 2.30	– 2.31
6-Methyl-2-nitro	– 0.71	– 0.80*	– 0.85
2-Chloro-4-nitro	– 0.94	– 0.70*	– 0.72
4-Chloro-2-nitro	– 1.03	– 0.70*	– 0.67
5-Chloro-2-nitro	– 1.54	– 0.34*	– 0.40
2,5-Dichloro-4-nitro	– 1.78	+ 0.15*	– 0.27
6-Chloro-2-nitro	– 2.43	– 0.06*	+ 0.08
<i>N</i> -Phenyl-4-nitro	– 2.48	– 0.96*	+ 0.11
<i>N</i> -Phenyl-2-nitro	– 2.96	+ 0.26*	+ 0.37
2,6-Dichloro-4-nitro	– 3.20	+ 0.53*	+ 0.50

$K$  refers to equilibrium (21);  $\text{p}K = -\log[\text{B}:\text{SnCl}_4]/[\text{B}][\text{SnCl}_4]$ ;  $\text{p}K_{\text{calc}}$  obtained from correlation equations on p. 187; units of  $K$  are  $\text{l mol}^{-1}$ ; \* adduct shows charge-transfer absorption.

<sup>34</sup> H. C. Brown, *J. Chem. Soc.*, 1956, 1248.

<sup>35</sup> D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 1964, 4134.

<sup>36</sup> D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, **61**, 1132.



**Table 5** Equilibria involving stannic chloride and carboxylic acids in *o*-dichlorobenzene

<i>R</i>	<i>K</i> (at 28°C)	<i>K<sub>H</sub></i> (at 25°C)	<i>K<sub>a</sub></i>
Bu <sup>t</sup>	112	64	8.9 × 10 <sup>-6</sup>
Bu <sup>m</sup>	82	73	1.5 × 10 <sup>-5</sup>
Bu <sup>l</sup>	70	57	1.4 × 10 <sup>-5</sup>
Et	43	—	1.3 × 10 <sup>-5</sup>
Me	20	83	1.8 × 10 <sup>-5</sup>
PhCH <sub>3</sub>	16	63	4.9 × 10 <sup>-5</sup>
ClCH <sub>2</sub> CH <sub>2</sub>	1.8	129	1.0 × 10 <sup>-4</sup>
ClCH <sub>2</sub>	0.14	200	1.4 × 10 <sup>-3</sup>
Cl <sub>2</sub> CH	< 0.01	—	5.1 × 10 <sup>-2</sup>
Ph	52	65	6.3 × 10 <sup>-5</sup>
2-MeC <sub>6</sub> H <sub>4</sub>	174	114	1.2 × 10 <sup>-4</sup>

$K = [\text{SnCl}_4(\text{RCO}_2\text{H})_2] / [(\text{RCO}_2\text{H})_2][\text{SnCl}_4]$  and refers to equation (21), where  $B = (\text{RCO}_2\text{H})_2$ ;  $K_H = [\text{BH}^+][\text{SnCl}_4\text{RCO}_2\text{HRCO}_2^-] / [B][\text{SnCl}_4(\text{RCO}_2\text{H})_2]$  and refers to equation (22), where  $B = o$ -nitrodiphenylamine;  $K_a$  = dissociation constant of  $\text{RCO}_2\text{H}$  in water at 25 °C.

anilinium ion  $\text{BH}^+$ . The weaker bases (Table 4), however, lead to adducts exhibiting additional long-wavelength charge-transfer absorption. The charge-transfer effects are analogous to those found in systems involving molecular halogens or organic  $\pi$ -acids.<sup>15</sup> Adducts possessing charge-transfer absorption occur too for certain anilines with  $\text{SnCl}_4$  in ether, and also with zinc, aluminium, and gallium halides in this solvent.<sup>30,37</sup> The widespread notion that charge-transfer effects are restricted to certain special classes of weak acid-base interaction is mistaken. Adducts having charge-transfer absorption are also formed by a number of other powerfully acidic species  $\text{MX}_n$  in equilibria with aromatic hydrocarbons.<sup>38</sup> Here the analogy with more conventional charge-transfer systems is closer.

The results in Table 4 lead to good  $\text{p}K_a$ - $\text{p}K$  correlations, the bases giving charge-transfer effects falling, however, on a different line from that representing those whose adducts show only anilinium ion spectra. The equations are  $\text{p}K = -0.54\text{p}K_a - 1.23$  and  $\text{p}K = -0.47\text{p}K_a - 2.45$  respectively.

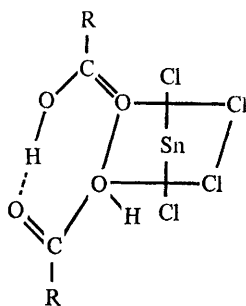
The equilibria with carboxylic acids (Table 5) are interesting because only adducts containing the acid dimer can be detected, these being much more stable than those involving the monomer owing to chelation, as in (IV). A good correlation between  $\text{p}K$  and  $\sigma^*$  exists for the substituted acetic acids.<sup>39</sup>  $\text{p}K_H$  in Table 5 refers to equilibrium (22), where  $B = o$ -nitrodiphenylamine, and the values<sup>40</sup> show that, in spite of the considerable variation in the conventional

<sup>37</sup> A. Mohammad and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1967, 726.

<sup>38</sup> J. J. Myher and K. E. Russell, *Canad. J. Chem.*, 1964, **42**, 1555; P. R. Hammond and R. R. Lake, *Chem. Comm.*, 1968, 987.

<sup>39</sup> J. L. Wardell, Ph.D. Thesis (London), 1965.

<sup>40</sup> D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, **61**, 1127.



(IV)

strengths of the free acids  $\text{RCO}_2\text{H}$ , the acidities of the adducts  $\text{SnCl}_4(\text{RCO}_2\text{H})_2$ ,



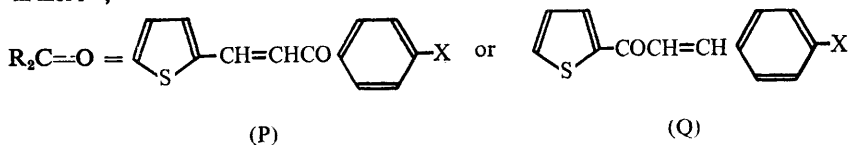
although very great, are all similar. This result suggests that this acidity is largely determined by the co-ordination to  $\text{SnCl}_4$ , and has important implications for

**Table 6** Equilibria between antimony pentachloride or ferric chloride dimer and chalcone analogues in benzene

(P)	pK		$(\text{p}K)_{\text{CCl}_3\text{CO}_2\text{H}}$
	$\text{Fe}_2\text{Cl}_6$	$\text{SbCl}_5$	
X = $\text{NO}_2$	- 2.95	—	- 1.32
X = Cl	- 3.82	- 2.92	- 1.40
X = H	- 4.20	- 3.17	- 1.58
X = $\text{C}_6\text{H}_5$	- 4.36	- 3.11	- 1.48
X = $\text{CH}_3$	- 4.50	- 3.32	- 1.65
X = $\text{OC}_2\text{H}_5$	- 4.61	- 3.91	- 1.80
X = $\text{OCH}_3$	- 4.53	- 4.02	- 1.94

(Q)	$\text{Fe}_2\text{Cl}_6$	$\text{SbCl}_5$	$(\text{p}K)_{\text{CCl}_3\text{CO}_2\text{H}}$
X = Cl	- 3.78	- 2.78	- 1.36
X = H	- 4.18	- 3.11	- 1.50
X = $\text{C}_6\text{H}_5$	- 4.41	- 3.20	- 1.46
X = $\text{CH}_3$	- 4.30	- 3.45	- 1.59
X = $\text{OCH}_3$	- 4.48	- 3.72	- 1.84

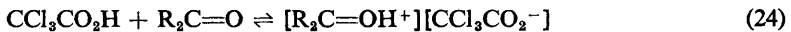
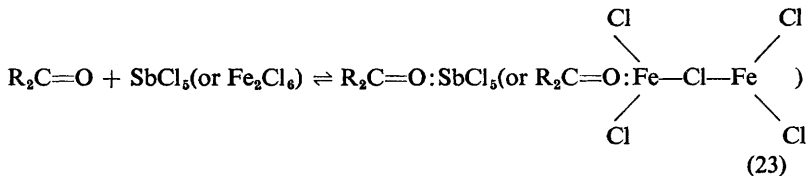
$K$  and  $(K)_{\text{CCl}_3\text{CO}_2\text{H}}$  refer to equations (23) and (24) respectively;  $\text{p}K = -\log[\text{adduct}]/[\text{R}_2\text{C}=\text{O}][\text{MCl}_n]$ ;  $(\text{p}K)_{\text{CCl}_3\text{CO}_2\text{H}} = -\log[\text{adduct}]/[\text{R}_2\text{C}=\text{O}][\text{CCl}_3\text{CO}_2\text{H}]$ ; concentrations in  $\text{mol l}^{-1}$ ;



studies involving co-catalysis. A similar effect will be involved for the frequently used systems containing  $\text{BF}_3$  (or  $\text{ZnCl}_2$ ) and carboxylic acids, although no quantitative results are yet available. The enhancement of the acidity of water on co-ordination to metal ions is well-known.<sup>41</sup>

Other results<sup>14</sup> for the Group IV acids  $\text{MX}_4$  justify the acidity sequences  $\text{SnCl}_4 \gg \text{SnBr}_4 > \text{SnI}_4$ ;  $\text{Si} < \text{Ge} < \text{Sn} \gg \text{Pb}$ ; and  $\text{Ti} < \text{Zr} \leq \text{Hf}$ , sequences entirely in keeping with our expectations (Section 4).

Consider, as a final example of the way acids  $\text{MX}_n$  reflect the behaviour of hydrogen acids, the results<sup>42</sup> in Table 6. These show that, in benzene solution, there is a fair correlation between the  $\text{pK}$  values for the 1:1 equilibria (23) and (24). Evidence that the behaviour of acids  $\text{MX}_n$  can parallel that of classes other



than hydrogen acids is in Table 7. It can be seen that both the nickel acid

**Table 7** Equilibrium between pyridines and diacetyl(bisbenzoylhydrazone)nickel(II) and iodine

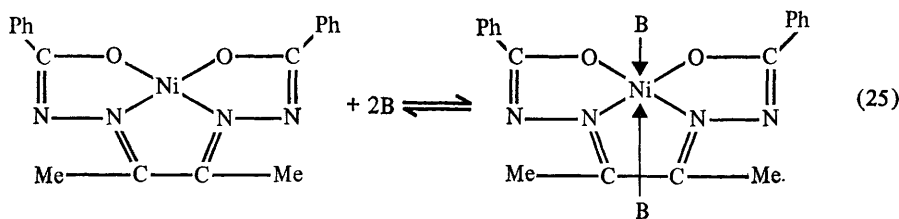
Pyridine derivative	$\text{pK}_a$	$\text{pK}_1(\text{pK}_{\text{calc}})$ (25°C, $\text{CCl}_4$ )	$\text{pK}_2(\text{pK}_{\text{calc}})$ (25°C, $\text{C}_6\text{H}_6$ )
3-Chloro	2.84	- 1.22 (- 1.23)	—
3-Bromo	2.84	- 1.24 (- 1.23)	—
Hydrogen	5.21	- 2.04 (- 2.13)	- 3.78 (- 3.87)
3-Ethyl	5.56	- 2.39 (- 2.26)	—
3-Methyl	5.63	- 2.32 (- 2.29)	- 3.90 (- 4.06)
2-Methyl	5.97	—	- 0.48
4-Methyl	5.98	- 2.33 (- 2.42)	- 4.45 (- 4.22)
4-Ethyl	5.99	- 2.39 (- 2.43)	—
3,5-Dimethyl	6.15	- 2.58 (- 2.49)	—
2,5-Dimethyl	6.40	- 2.48 (- 2.58)	- 0.54
3,4-Dimethyl	6.46	- 2.62 (- 2.60)	—
2,6-Dimethyl	6.75	- 1.66 (- 2.72)	- 1.05
Isoquinoline	5.40	—	- 3.78 (- 3.95)

$K_1$  refers to the equilibrium  $\text{B} + \text{I}_2 \rightleftharpoons \text{B} \rightarrow \text{I}_2$ , where B is a substituted pyridine;  $K_2$  refers to equation (25);  $\text{pK}_1 = -\log[\text{BI}_2]/[\text{B}][\text{I}_2]$ ;  $\text{pK}_2 = -\log[\text{adduct}]/[\text{NiX}_4][\text{B}]^2$ ; units of  $K_1$  and  $K_2$  are  $\text{l mol}^{-1}$  and  $\text{l}^2 \text{mol}^{-2}$  respectively;  $\text{pK}_{\text{calc}}$  calculated from equations  $\text{pK}_1 = -0.38 \text{pK}_a - 0.15$  and  $\text{pK}_2 = -0.46 \text{pK}_a - 1.47$ .

<sup>41</sup> M. M. Jones, 'Ligand Reactivity and Catalysis', Academic Press, New York, 1968.

<sup>42</sup> O. F. Boberov, V. N. Tolmachev, and V. F. Laurushin, *Dopovidi Akad. Nauk, Ukrain. R.S.R.*, 1966, 1315.

(equation 25) and iodine behave analogously towards unhindered pyridines.<sup>43,44</sup> As expected, steric effects are more severe in the nickel equilibria.



A complete survey<sup>14</sup> of the quantitative behaviour of acids  $\text{MX}_n$  shows: (i) that towards any series of bases throughout which the donor centre is of the same type, acids  $\text{MX}_n$  and hydrogen acids exhibit parallel behaviour regardless of the solvents involved in the comparison. The equilibrium constants fit equations of the form  $\text{p}K_{\text{MX}_n} = a\text{p}K_{\text{HX}} + b$ , where  $a$  normally lies between 0.7 and 1.0, (ii) that relative acidities of species  $\text{MX}_n$  are almost invariably compatible with expectations based on the electronic structure and size of  $M$ , the nature of the ligands  $X$ , and on the assumption of single bonding between  $\text{MX}_n$  and the reference base, (iii) that the nature of the reference base has little effect on sequences of acid strength. How true this will remain when results for sulphur-, phosphorus-, and carbon-bases are more plentiful is, of course, not known. It is encouraging to remember, however, that the Irving-Williams series is maintained for a wide range of hard and soft ligands.

**B. Correlations involving other Lewis Acids.**—Although many equilibrium measurements have been made with other classes of Lewis acid, in particular with metal ions,<sup>45</sup> with molecular iodine,<sup>15</sup> and with certain  $\pi$ -acids,<sup>15</sup> the results are nevertheless fragmentary. It is surprisingly difficult to extract comparisons like those of Section A above. Inspection of the results available shows, however, that for metal ions a substantial fraction involve chelating bases. For such bases, the relevant proton basicity constant is a matter for conjecture.<sup>46</sup> With  $\pi$ -acids, part of the difficulty arises from the fact that many of the measured equilibria involve steric complications. Below we present typical examples of such useful comparisons as are available; probably not all of these are really free from steric disturbance.

(i) *Metal ions as acids.* Relevant measurements are summarised in references 21 and 46—48. It appears that: (a) normally for any metal ion and a series of bases (ligands) of given structural type,<sup>48</sup> the association constant obtained in aqueous

<sup>43</sup> L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 1958, 848.

<sup>44</sup> W. J. McKinney, M. K. Wong, and A. I. Popov, *Inorg. Chem.*, 1968, 7, 1001.

<sup>45</sup> L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes', *Chem. Soc. Special Publication No. 17*, London, 1964.

<sup>46</sup> J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 1958, 2001.

<sup>47</sup> Y. T. Chen, *Z. phys. Chem. (Leipzig)*, 1962, 220, 231.

<sup>48</sup> W. J. Peard and R. T. Pfaum, *J. Amer. Chem. Soc.*, 1958, 80, 1593; R. J. Bruehlmann and F. H. Verhoek, *ibid.*, 1948, 70, 1401.

solution is rectilinearly related to the acid dissociation constant of the base (just as for acids  $MX_n$ ), (b) sequences of relative acid strength (e.g.,  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$  and  $Cu^{2+} > Zn^{2+} \approx Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$ ) are largely independent of the base. As explained in Section 4, these sequences can be predicted from simple principles. Anomalies arising from class *B* behaviour do not as yet occupy a prominent place among these equilibrium measurements seen as a whole. This is partly because much of the quoted evidence for class *B* behaviour involves  $\Delta H$  rather than  $\Delta G^\circ$ . There seems every reason to think that the general behaviour of acids  $M^{n+}$  towards structurally related bases parallels that shown by the proton and by species  $MX_n$ . The normal restriction of correlations to structurally related bases is expected. Such restrictions apply throughout the field, and are not absent,<sup>10,31</sup> as is sometimes thought, for comparisons among hydrogen acids.

The behaviour of  $Ag^+$  is compared with that of yet other classes of acid in Table 8. An interesting correlation<sup>49</sup> involving the acid  $I^+$  is shown in Figure 1.

**Table 8** Equilibria between substituted benzenes and various acids

Substituted benzene	$Ag^+$ (MeOH- H <sub>2</sub> O) 25°C	$I_2$ (CCl <sub>4</sub> ) 25°C	TCNE (CH <sub>2</sub> Cl <sub>2</sub> ) 22°C	HCl (toluene) -78.5°C	SO <sub>2</sub> (CCl <sub>4</sub> ) 25°C	HF 20°C
H	0.97	0.48	0.26	0.61	0.35	0.09
CH <sub>3</sub>	1.04	0.51	0.48	0.92	0.59	0.63
<i>o</i> -(CH <sub>3</sub> ) <sub>2</sub>	1.25	0.87	0.91	1.13	1.23	1.1
<i>m</i> -(CH <sub>3</sub> ) <sub>2</sub>	1.19	0.99	0.79	1.26	1.11	26
<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub>	1.00	1.00	1.00	1.00	1.00	1.00
1,3,5-(CH <sub>3</sub> ) <sub>3</sub>	0.70	1.85	2.26	1.59	1.57	13,000
1,2,4,5-(CH <sub>3</sub> ) <sub>4</sub>	0.77	2.10	7.10	—	—	140
1,2,3,4,5-(CH <sub>3</sub> ) <sub>5</sub>	1.00	3.02	16.1	—	—	29,000
1,2,3,4,5,6-(CH <sub>3</sub> ) <sub>6</sub>	0.55	4.81	34.4	—	—	97,000

All equilibria are of the type  $A + B \rightleftharpoons AB$ , where  $A$  = acid and  $B$  = substituted benzene; numerical values expressed as  $K (= [AB]/[A][B])$  relative to  $K$  for *p*-xylene; all results from ref. 50; TCNE = tetracyanoethylene.

(ii) *Molecular Halogens.* Results for equilibria involving molecular iodine with



pyridines<sup>44</sup> are in Table 7. Apart from the 2,6-dimethyl derivative, a good correlation equation with  $pK_a$  can be constructed. Quantitative parallelisms are also found between the halogen acids and other classes in equilibria with  $\pi$ -bases (Table 8, Figure 2). Correlations with typically hard acids are, however, likely to be disrupted by the presence of sulphur-bases. The sequence of acid strength

<sup>49</sup> R. P. Bell and E. Gelles, *Proc. Roy. Soc.*, 1952, A210, 310.

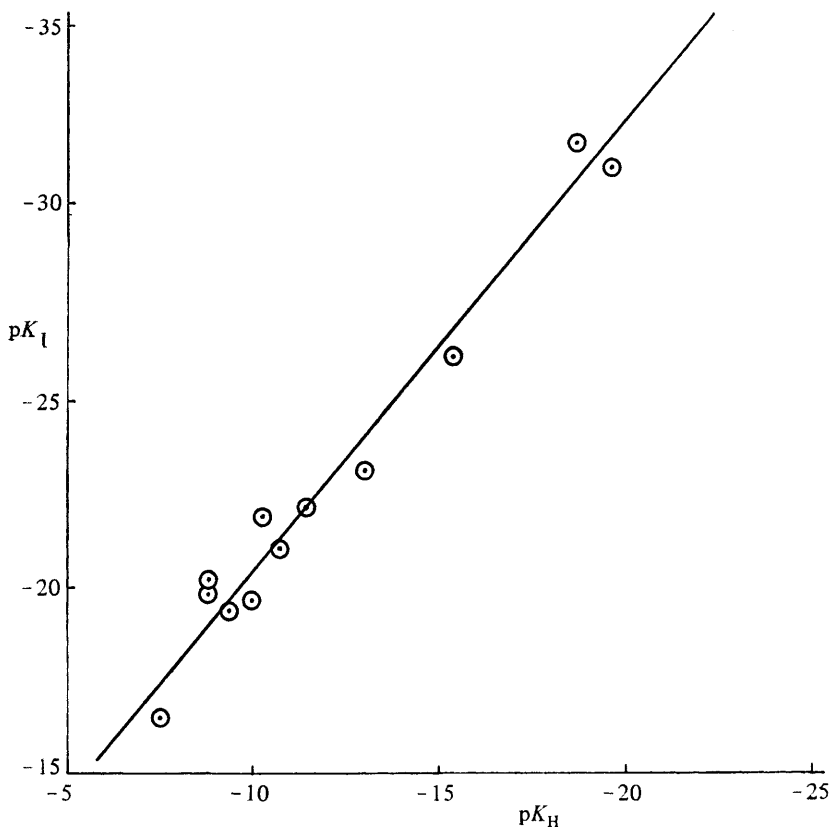


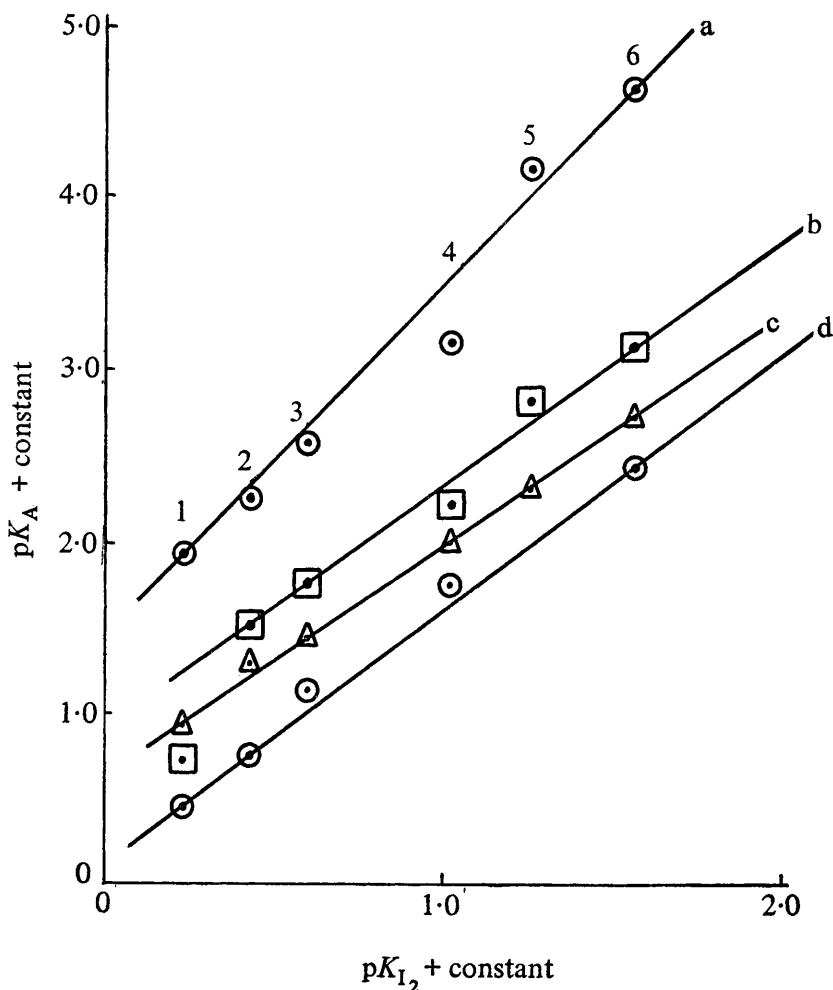
Figure 1 Behaviour of  $H^+$  and  $I^+$  towards carbanions ( $R^-$ ) in water at 25 °C.  $K_H = [RH]/[R^-][H^+]$ ;  $K_I = [RI]/[R^-][I^+]$ ; units of  $K$  are  $l\ mol^{-1}$ ;  $RH$  represents ketones, esters, and nitroparaffins.

$ICl > IBr > I_2 > Br_2 > Cl_2$  is apparently independent<sup>15,50</sup> of the reference base (aromatic hydrocarbons,  $I^-$ , nitriles, amines) and meets expectations based on the nature of the acceptor atom and its attached substituent (see Section 4). In summary, halogen acids can hardly be said to behave in a manner less regular than, say, hydrogen acids.

(iii)  $\pi$ -Acids. Representative results<sup>15,50</sup> are in Table 8 and Figures 2 and 3. Regularities are again apparent. The reason that the equilibria involving HF do not parallel the others is that  $\sigma$ - and not  $\pi$ -adducts are formed with HF (*i.e.*, a different class of basicity is involved).

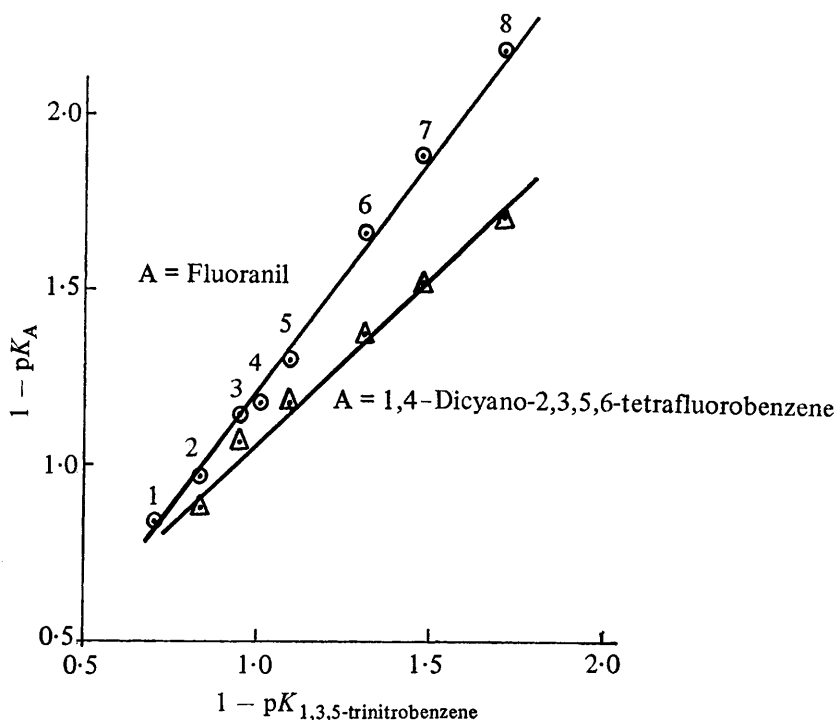
**C. Summary.**—The results outlined demonstrate unequivocally that, as predicted

<sup>50</sup> L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry', Holden-Day Inc., San Francisco, 1964.



**Figure 2** Equilibria between various acids (A) and  $\pi$ -bases (B).  $K_A = [AB]/[A][B]$ ; units of  $K_A$  are  $l \text{ mol}^{-1}$ ; figure adapted from ref. 50, p. 103; (a) = tetracyanoethylene in  $\text{CH}_2\text{Cl}_2$  at  $22^\circ\text{C}$ ; (b) = chloranil in hexane at  $20^\circ\text{C}$ ; (c) = iodine monochloride in  $\text{CCl}_4$  at  $25^\circ\text{C}$ ; (d) = 1,3,5-trinitrobenzene in  $\text{CCl}_4$  at  $20^\circ\text{C}$ ;  $K_{I_2}$  refers to  $\text{CCl}_4$  at  $25^\circ\text{C}$ . 1 = Benzene; 2 = Toluene; 3 = Xylene; 4 = Mesitylene; 5 = Pentamethylbenzene; 6 = Hexamethylbenzene.

in Section 4, extensive regularities in quantitative behaviour permeate the whole field of acidity. Anomalies are usually attributable to steric factors. Genuine anomalies are still largely isolated results. While sequences of acid (or base) strength remain mostly unchanged in different contexts nevertheless the absolute magnitude of relative acidity and basicity does vary (often considerably). This is



**Figure 3** Equilibria between  $\pi$ -acids (A) and  $\pi$ -bases (B) in carbon tetrachloride at 33.5 °C.  $K_A = [AB]/[A][B]$ ; units of  $K_A$  are  $\text{kg mol}^{-1}$ ; values from ref. 15, p. 194; 1 = Benzene; 2 = Toluene; 3 = p-Xylene; 4 = m-Xylene; 5 = Mesitylene; 6 = 1,2,4,5-Tetramethylbenzene; 7 = Pentamethylbenzene; 8 = Hexamethylbenzene.

hardly a ground for abandoning Lewis's definitions, since relative acidity and basicity involving hydrogen acids can vary just as much once consideration is not limited to water-like media.<sup>9,10,51</sup> If attention is restricted to water-like media and to hydrogen acids, then relative acidity and basicity will obviously show little variation from system to system, being disturbed by steric hindrance in certain severe cases only.<sup>52</sup> However, exactly the same can be said for *any* class of acid in a fixed environment. For instance, sterically uncomplicated equilibria involving silver acids in water-like solvents will display much the same degree of self-consistency in behaviour as do those involving hydrogen acids. It is not generally appreciated how artificial are the restrictions imposed by the Brønsted viewpoint. Nothing quantitative is really gained, and a great many instructive chemical parallels can all too easily be overlooked by focusing only upon hydrogen.

<sup>51</sup> N. A. Izmailov, *Zhur. fiz. Khim.*, 1956, 30, 2164; and earlier papers.

<sup>52</sup> V. Gold in 'Progress in Stereochemistry', ed. P. B. D. de la Mare and W. Klyne, Butterworths, London, 1962, vol. 3, p. 169.



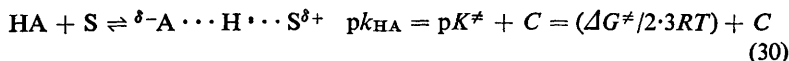
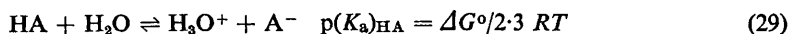
## 6 Acid Catalysis and Thermodynamic Acidity

**A. Hydrogen Acids.**—As is well known, there often exists a relationship, under conditions of fixed temperature, solvent, *etc.*, between the catalytic power of a hydrogen acid in some reaction and that acid's thermodynamic acidity constant ( $K_a$ ) determined in water. If  $k_{HA}$  is the rate constant of the catalysed process, then:

$$k_{HA} = G(K_a)^\alpha_{HA} \text{ or } p k_{HA} = \text{constant} + \alpha p(K_a)_{HA} \quad (27)$$

$$k_B = G'(1/K_a)^\beta_{BH^+} \text{ or } p k_B = \text{constant} - \beta p(K_a)_{BH^+} \quad (28)$$

Equation (27) is called the Brønsted relation.<sup>8</sup> The parameters  $G$  and  $\alpha$  normally remain reasonably constant provided that the strengths of the acids do not vary too much, and that they are all of the same structural type (*e.g.*, are all carboxylic acids). An analogous relationship is found for base catalysis (equation 28). The existence of a Brønsted relation implies that, as  $A$  is altered, similar systematic changes in the free energy are involved for the protonation equilibrium (29) and for formation of the transition state of the catalysed reaction, *e.g.*, (30) where  $S$  is some substrate. In practice,  $\alpha$  (and  $\beta$ ) appear invariably to be less than unity, although there is no clear reason for this,<sup>27</sup> unless all the protonations are



assumed to be tunnel processes.<sup>53</sup> For other classes of acid we find  $\alpha > 1$ . (The idea that  $\alpha$  is necessarily related to the extent of proton transfer in the transition state appears to be based upon a fallacy.) Hydrogen-bond equilibrium constants, referring to a standard base and conditions, could well replace the  $K_a$  values in relationships like (27). The requirement that all the acids (or bases) be of similar structural type arises from the need (*i*) to keep constant the free-energy contributions from solvent co-ordination, and (*ii*) to minimise changes in the base's polarisability. Anomalies due to soft-hard behaviour are thus excluded. Such anomalies otherwise intrude,<sup>26,54</sup> but the knowledge of their existence has not led to any discarding of the Brønsted relation. In the same way there is no reason to discard the Lewis definition of acids because of a few hard-soft anomalies.

Although  $K_a$  and  $k_{HA}$  usually refer to different processes, the relationship also holds if all the constants refer to the same equilibrium. For equilibria like (31)



we have  $k_1 = GK^\alpha$  and  $k_{-1} = G'(1/K)^\beta$ . Since here  $K = k_1/k_{-1}$ , therefore

$$G = G' \text{ and } \beta = (1 - \alpha).$$

<sup>53</sup> J. J. Weiss, *J. Chem. Phys.*, 1964, **41**, 1120.

<sup>54</sup> M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

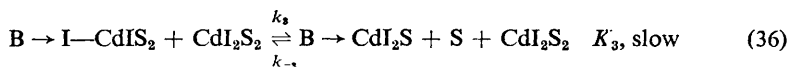
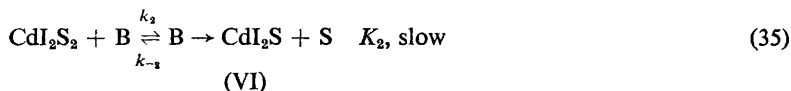
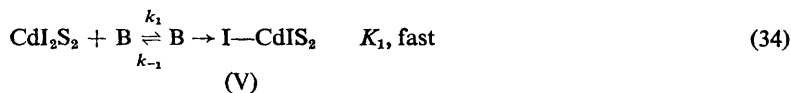
**B. Acids  $MX_n$ .**—Clearly, in view of the parallelisms of Section 5, relationships similar to Brønsted's should exist for all classes of acid. Unfortunately, relevant kinetic work on catalysis by other than hydrogen acids is sparse. Acids  $MX_n$  are frequently used as catalysts in the laboratory, but reliable kinetic studies of such catalysis are few, and none provide data for testing a Brønsted-like relation.<sup>19</sup> Instead there have been many qualitative comparisons of catalytic efficiency (frequently based only on product yield determined after a fixed interval). The sequences of efficiency so obtained have often been used,<sup>19</sup> in lieu of better data, as measures of the acidity of the catalysts; *i.e.*, a Brønsted-like relation has been *assumed*. The general import of the many available qualitative sequences is fairly well in keeping both with what can be predicted, and with what has subsequently been determined,<sup>14</sup> concerning the thermodynamic acidity of acids  $MX_n$ . Individual sequences, however, often contain anomalies, the principle reason being that to legitimately invoke the Brønsted relation it is necessary to limit comparison to processes of the same kinetic order in catalyst; unfortunately, even superficially quite similar species  $MX_n$  often lead to different kinetic orders in a given reaction.<sup>55</sup> The qualitative comparisons available take no cognisance of this.

A clear indication that acids  $MX_n$  do obey Brønsted-like relations, is the behaviour of  $ZnCl_2$  towards a series of anilines (B) in acetone.<sup>27</sup> The system takes the form (32), where S = solvent (*cf.* equation 31 *et seq.*). In diethyl ether, equilibria like (32) are set up rapidly, but in acetone both the position and the



$$K = \frac{k_1}{k_{-1}[S]} = \frac{[ZnCl_2BS]}{[ZnCl_2S_2][B]} \quad (33)$$

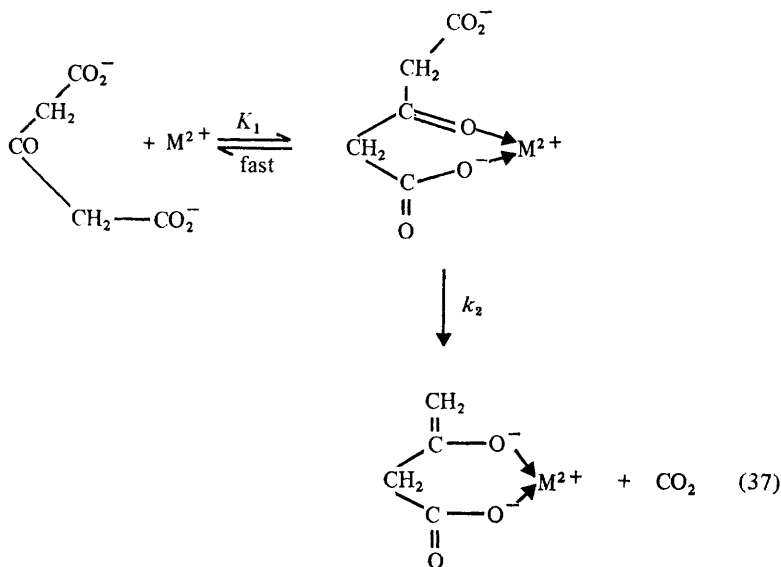
rate of establishment of equilibrium can be studied. Values of  $k_1$ ,  $k_{-1}$ , and  $K$  (Table 1) show that for unhindered bases  $k_1 = GK^{1.5}$  and  $k_{-1} = GK^{0.5}/[S]$ . Similar studies have been made<sup>28</sup> with  $CdI_2$ . Here (Section 5, Table 3) two equilibria, (34) and (35), are found, one being rapidly, and the other slowly established. Species (VI) is the normal 1:1-adduct. The precise structure of species (V) is not known. It can be regarded either as involving I as the acceptor



<sup>55</sup> F. R. Jensen and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039; R. M. Evans and R. S. Satchell, *J. Chem. Soc. (B)*, 1970, 1667 and earlier papers.

atom, as in (34), or as a less-defined outer-sphere complex. Perhaps these descriptions are here synonymous. There is evidence that there are two routes to (VI), one direct, *via* equation (35), with  $k_2 = GK_2^{1.66}$ , the other *via* (V), as in equation (36). The close analogy with substitutions at metal ions in hydroxylic media is instructive. There too an acid-base effect (hydrogen-bonding) between resident and incoming ligands plays an important part in outer-sphere complex formation.<sup>56</sup> The substitutions themselves are often currently considered to involve the slow conversion of an outer- to an inner-sphere complex by replacement of solvent.<sup>57</sup> It may be that double equilibria like (34) and (35) underlie much adduct formation by acids  $MX_n$ , the effect going undetected in most cases. Iodine, being a stronger acceptor centre than the other halogens, renders the phenomenon spectroscopically visible with  $CdI_2$ .

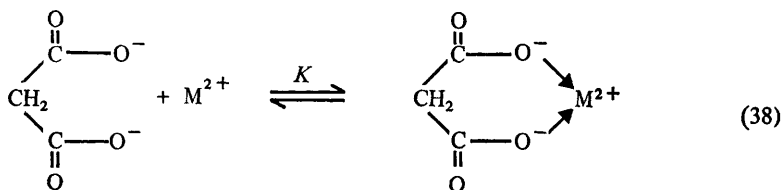
**C. Acids  $M^{n+}$ .**—It is noteworthy that acid catalysis by species  $M^{n+}$  involves almost always either a chelating substrate or the bringing together of two substrates by virtue of their both being attached to the metal.<sup>41,58</sup> In the absence of these (or other) specially favourable circumstances, catalysis by  $M^{n+}$  ions is seldom found. The probable reason is that  $M^{n+}$ , normally studied in water, will usually be co-ordinated to the solvent, or to other non-substrate species, as well as to the substrate. Its ability to polarise the substrate will therefore be less than



<sup>56</sup> M. T. Beck, *Co-ordination Chem. Rev.*, 1968, 3, 91.

<sup>57</sup> See *e.g.*, H. P. Bennetto, R. Bulmer, and E. F. Caldin in 'Hydrogen-Bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor and Francis Ltd., London, 1968, p. 335.

<sup>58</sup> M. L. Bender in 'Advances in Chemistry Series', American Chem. Soc., Washington, 1963, No. 37.



would superficially appear from its formal charge. Evidence<sup>41</sup> suggests that, for the most part, protonation of a substrate produces a much greater effect on that substrate's electron distribution than does adduct formation with a species  $\text{M}^{n+}$ .

There have been very few systematic kinetic studies of metal ion catalysis. Available results suggest, however, that Brønsted-like relations between catalytic rate constants and relevant stability constants exist. Thus  $\text{pk} = \alpha\text{pK} + \text{constant}$  for reactions (37) and (38), where  $k = K_1k_2$ ,  $\alpha \approx 1.3$ , and M can be a variety of metals.<sup>59</sup> Other similar examples are known,<sup>60</sup> and normally  $\alpha > 1$ .

**D.  $\pi$ -Acids.**—The study of the catalysis of reactions by  $\pi$ -acids and bases is in its infancy, and interest still centres mainly on its detection rather than its quantitative study.<sup>61</sup>

## 7 Indirect Measurements of Lewis Acid Strength

Because the measurement of equilibrium constants is often difficult, other more convenient quantitative estimates of Lewis acidity have sometimes been proposed, particularly for acids  $\text{MX}_n$ . The principal short-cut methods have involved<sup>14</sup> (i) the estimation of i.r. frequency shifts (usually of some carbonyl group) upon interaction with  $\text{MX}_n$ , (ii) the use of (usually qualitative) catalytic rate constants for some arbitrary reaction, and (iii) the determination of changes in a chemical shift, or in some other n.m.r. parameter, upon complex formation between the acid and a standard base.

There are theoretical and experimental reasons for believing method (i) to be unreliable.<sup>14,62</sup> Method (ii), as explained in Section 6B, although potentially reliable owing to the probable widespread existence of Brønsted relations for species  $\text{MX}_n$ , has nevertheless rarely, as yet, been properly applied. Method (iii) can, with suitable reference bases, lead to reliable acidity sequences,<sup>29</sup> and, if the change in the n.m.r. parameters is calibrated against sufficient independently measured equilibrium constants, can lead to rapid estimation of unknown K values by interpolation. Unfortunately, most existing work on shifts of all types

<sup>59</sup> J. E. Prue, *J. Chem. Soc.*, 1952, 2331.

<sup>60</sup> See e.g., E. Gelles and A. Salama, *J. Chem. Soc.*, 1958, 3683.

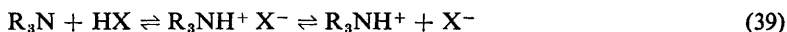
<sup>61</sup> E. M. Kosower, *Progr. Phys. Org. Chem.*, 1965, 3, 81.

<sup>62</sup> A. Mohammad, R. S. Satchell, and D. P. N. Satchell, *J. Chem. Soc. (B)* 1967, 723.

has assumed, without proof, that such shifts quantitatively reflect thermodynamic acidity. To establish a trustworthy short-cut there can be no escape from the direct measurement of at least some equilibrium constants.

## 8 General Conclusions

It is no exaggeration to say that, in so far as reactions of the general type (1)–(4) display quantitative regularities, either kinetic or thermodynamic, amongst themselves, these regularities are little dependent upon the type of acid involved. Similar phenomena are found throughout the field. That this would be so has often been implicitly assumed in the past. All the well-known correlation equations (*e.g.*, those of Brønsted, Hammett, and Taft) concern one aspect or another of equations (1)–(4). The obvious reason for the general homogeneity of behaviour is the fundamental electronic similarity of the reactions. However sophisticated one may be about the quantum mechanics of the bonding, this common denominator remains, and provides an underlying unity. The merit of Lewis's definitions has always been evident: they help to link together, and therefore to provide insights into, an enormous range of reactions. Moreover, we have argued, we believe justly, that contrary to previous belief, no meaningful quantitative penalties are attached to relinquishing Brønsted's definition of acids; and when, in the late 1960's, in justification of the separate treatment of hydrogen and non-hydrogen acids, it is still suggested<sup>6,10</sup> that hydrogen acids (*i*) do not catalyse reactions of species RCl, and (*ii*) are the *only* acids which can enter into



reactions of the general type (39), then we feel that the time has come for a return to the facts and for a general reassessment of the evidence.