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## The Lewis Acid-Base Definitions: A Status Report

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### Contents

I. Introduction	1
II. Historical Perspective	1
A. Original Lewis Definitions: 1923–1938	1
B. Secondary Acids and Bases	3
C. Quantum Mechanical Developments	4
D. Summary and Conclusions	6
III. Lewis Definitions as a Systematizing Tool	6
A. Generalized Lewis Definitions	6
B. The Relative Nature of Reactivity	8
C. Limitations and Qualifications	9
D. Applications	10
E. Summary and Conclusions	11
IV. Empirical Reactivity Approximations	12
A. General Considerations	12
B. Donor and Acceptor Numbers (DN-AN)	12
C. The E & C Equation	14
D. The HSAB Principle	15
1. Linear Free Energy Relations (LFER)	16
2. Aqueous Stability Constants	16
3. The HSAB Rules	17
E. Problems of Interpretation	17
1. Gas-Phase-Noncoordinating Solvents	17
2. Coordinating Solvents	19
F. Comparisons and Conclusions	19
V. References and Notes	21

### I. Introduction

This is not so much a proper review, in the sense of being a detailed survey of current experimental work, as it is a retrospective essay on the current status of the Lewis acid-base definitions as a systematizing tool in chemistry. Indeed, as the main concern is with the nature of the Lewis definitions themselves, their range of application, their limitations, the clarification of interpretive or semantic problems, etc., this essay might be most accurately characterized as a review of monographs and reviews which, in turn, deal with the raw experimental data.

The Lewis definitions are now over a half-century old. To what extent has the work on organometallic compounds, for example, or on new nonaqueous or molten salt solvent systems, or the addition of new bonding concepts to the traditional two-center, two-electron bond and octet rule available to Lewis tended to repudiate or confirm the value of the Lewis definitions? It is hoped that this review will convince the reader that the devel-

opments of the last fifty years have not only confirmed the usefulness of the Lewis concepts, but have actually broadened their meaning and applications, that the phenomena covered by such concepts as coordinate bond formation, central atom-ligand interactions, electrophilic-nucleophilic reagents, cationoid-anionoid reagents, EPD-EPA agents, donor-acceptor reactions, charge-transfer complex formation, etc., are in reality merely aspects of generalized Lewis acid-base chemistry, that this, in turn, is best characterized as the chemistry of closed-shell-closed-shell interactions, and, finally, that it is useful, both for purposes of discussing general reactivity trends and the development of empirical reactivity approximations, to distinguish between such closed-shell interactions and those which involve open-shell species (free radical reactions) or complete electron transfers (redox reactions in the narrow sense).

Some may object to such a classification on the grounds that it includes too much. However, it is the premise of this review that such a broad classification is necessary in order to obtain an accurate overview of periodic trends in chemical reactivity and that more limited classifications, however more manageable from an experimental standpoint, can only lead to a parochial view of the factors determining chemical reactivity.

The review is divided into three major parts, the theme of each being convergence: the historical convergence of reactivity and bonding concepts, the convergence of phenomena, and the convergence of empirical reactivity approximations.

A larger amount of historical material has been included than is normal in reviews of this type. This is because a number of outdated concepts still appear in the literature, especially at the textbook level, and because a lengthy debate has been running in the literature for some time over which set of acid-base definitions is best and which of several empirical reactivity approximations is most correct. In considering this debate it is best to remember that the Lewis concepts are not a theory in themselves. They are rather a set of classificatory definitions which has been arbitrarily superimposed on the electronic theory of reactivity and bonding which forms the basis of modern chemistry. For this reason most of the problems raised in the debates are of a semantic rather than a fundamental nature and it is felt that the use of historical perspective is one of the most effective ways of clarifying the situation.

### II. Historical Perspective

#### A. Original Lewis Definitions: 1923–1938

In 1923 the American Chemical Society published a monograph by G. N. Lewis<sup>1</sup> entitled "Valence and the Structure of

Atoms and Molecules". In this small volume, which has since become a classic, Lewis reviewed and extensively elaborated the theory of the electron-pair bond, which he had first proposed in 1916.<sup>2</sup> It is little known that in this book Lewis also independently proposed both the proton and generalized solvent-system definitions of acids and bases. Lewis wrote:

"...the definition of an acid or base as a substance which gives up or takes up hydrogen ions would be more general than the one that we used before (i.e., the Arrhenius definitions) but it will not be universal. Another definition of acid and base in any given solvent would be the following: An acid is a substance which gives off the cation or combines with the anion of the solvent; a base is a substance which gives off the anion or combines with the cation of the solvent."<sup>1</sup>

The proton definitions were independently proposed in the same year as Lewis' monograph appeared by Brønsted<sup>3</sup> in Denmark and Lowry<sup>4</sup> in England. The solvent-system definitions, on the other hand, have a more complex history. In their most generalized form they involve a recognition that the solvent cation-anion concentrations can be altered either by the mechanism of solute dissociation or by solute induced solvolysis. This is certainly the import of Lewis' definitions, though their first explicit statement in this form is usually attributed to a 1928 paper by Cady and Elsey.<sup>5</sup>

Lewis' purpose in stating these alternative definitions was to show how they could, in turn, be classed as subsets of yet a still more general set of definitions, a set which involved the major theme of this book—the structure of atoms and molecules. Though the acid-base properties of a species are obviously modified by the presence or absence of a given solvent, their ultimate cause should logically reside in the molecular structure of the acid or base itself, and—in light of the electronic theory of matter—not in a common constituent, such as H<sup>+</sup> or OH<sup>-</sup>, but in an analogous electronic structure. Lewis continued,

"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 acid 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."<sup>1</sup>

Lewis' initial presentation of his electronic definitions failed to excite any interest. Virtually no mention of them can be found in the literature for the 15 years following their publication, this period seeing instead an extensive development of the proton and solvent-system definitions. Ironically, in this interim, several workers independently put forward electronic classifications of chemical reactants which were essentially identical with Lewis' definitions, though based on viewpoints seemingly unrelated to the traditional acid-base concepts which were Lewis' starting point. In 1927, for example, Sidgwick<sup>6</sup> noted that in classical coordination complexes the transition metal atom generally completed a stable electronic configuration by accepting electron pairs from the ligands. In honor of this fact he named the process coordinate bond formation and coined the terms "donor" and "acceptor" for the reactants.

Similar classifications evolved out of prequantum mechanical attempts to electronically rationalize the reactivity of organic compounds. The earliest precursor in this area was probably Lapworth's<sup>7,8</sup> division of reactants into electron-poor or cationoid (cation-like) reagents and electron-rich or anionoid (anion-like) reagents, which he proposed in 1925. As later formulated by Robinson,<sup>9</sup> the category of cationoid reagents included not only actual cations but neutral molecules with incomplete octets and oxidizing agents. Likewise, anionoid reagents included both neutral molecules with lone pairs and reducing agents as well as conventional anions. A virtually identical classification was

developed by Ingold<sup>10,11</sup> between 1933 and 1934. He suggested that earlier electronic interpretations of redox reactions by such workers as H. S. Fry and J. Stieglitz be generalized to include not only complete electron transfers, but intermediate degrees of transfer as well, due to the partial donation or sharing of electron pairs. Ingold proposed the name electrophile for such generalized oxidizing agents or electron acceptors and the term nucleophile for generalized reducing agents or electron donors. He also recognized that Brønsted's acids and bases constituted a subset of his more general electrophilic and nucleophilic reagents.

Like Lewis' original definitions, these classifications had little immediate impact on inorganic chemistry. The imaginary boundaries separating the organic and inorganic chemist were still strong enough to prevent such an exchange of ideas. Even Sidgwick's donors and acceptors failed to be fully exploited. Although he had shown how they might be applied to such areas as solvation phenomena, organic chemistry, and main group chemistry, the average introductory text and descriptive inorganic text did not systematically apply the concepts except in discussing the coordination chemistry of the transition metals. Most of the coordination chemistry of the proton and of the alkali metal and alkaline earth ions was not recognized as such and continued to be treated as separate phenomena, justifying the special categories of "acid-base" and "salt formation".

There are at least three probable reasons for the neglect of Lewis' definitions in the period between 1923 and 1938. Of these, two are still important in the sense that they often determine a person's opinion of the value of the Lewis concepts. The first reason undoubtedly lies in the manner in which Lewis originally presented the definitions. Indeed, he did little more than state them, almost as a passing thought, in the middle of a book whose major theme appeared to bear little relation to the subject of acid-base chemistry. In so doing, he failed to provide the necessary examples to support his contention that the electronic definitions actually were more general, and, more importantly, that their use had advantages over the other definitions.

The second, and certainly the most important reason, is that over 100 years of chemical tradition stood behind the proposition that some form of labile hydrogen was the cause of acidity. The proton definitions were the logical culmination of this line of thought. In addition, it proved possible to quantify them in terms of competitive protonation equilibria, as well as to account in a semiquantitative manner for the resulting data with relatively simple electrostatic models.

The third reason is more subtle and requires the exercise of a certain amount of historical hindsight. It has to do with the fact that by tying his definitions to the concept of the chemical bond, Lewis unwittingly linked their usefulness to contemporary views on the nature of the chemical bond itself. The implications of this identification can be seen in the debates which occurred during this period over the problem of bond types.

As a result of the successes of the theory of ionic dissociation and the discovery of the electron in the 1890's, a large number of electrostatic bonding models began to appear in the chemical literature after the turn of the century. Though these models worked quite well for inorganic salts, it gradually became apparent that they were incapable of providing a satisfactory description of organic compounds. By 1913 this defect was forcing a growing number of chemists, including Lewis, to the unpleasant conclusion that two distinct types of chemical bonds existed: polar and nonpolar.<sup>12</sup> The cause of the first was apparently the electrostatic attraction of ions. The cause of the second was unknown.

Hence, when Lewis deduced the shared electron-pair bond from his model of the cubic atom three years later, he was delighted to discover that not only had he found a rationale for the mysterious nonpolar bond, but a way of deducing the logical existence of the polar link from the same premises. His model

suggested that as the electrochemical natures of the two atoms sharing an electron pair began to differ more and more, the pair should become more and more unequally shared, eventually becoming the sole property of the more electronegative atom and resulting in the formation of ions. The defects of the earlier electronic models were thus resolved. Ionic and nonpolar bonds appeared as differences of degree rather than kind, being the logical extremes of a continuum of intermediate bond types. Lewis considered this conclusion the single most important result of his model, one which, in his opinion, removed that duality of bond types "so repugnant to that chemical instinct which leads so irresistibly to the belief that all types of chemical union are one and the same".<sup>1</sup>

Similar views were presented from 1923 onwards by Fajans.<sup>13</sup> Rather than starting from neutral atoms, Fajans began with ionic compounds and examined the progressively increasing polarization of each ion as the nature of its companion ion was varied. In extreme cases this polarization was envisioned as leading to a merging of the electron clouds of the two ions and to covalent bonding.

Lewis' electron-pair bond was largely popularized by Langmuir, who chose to ignore Lewis' views on bond types. Instead he used the electron-pair bonding mechanism, along with the ionic bonding mechanism, to stress the old dichotomy between polar and nonpolar links, implying that all bonds were either of one kind or the other. To emphasize the difference between the two bond types Langmuir<sup>14</sup> introduced the terms electrovalence and covalence.

Langmuir's view of two types of bonds, differing in kind, was further propagated by Sidgwick in his widely read books on valence theory. In support of this view, Sidgwick<sup>15</sup> cited experimental data showing radical discontinuities in the melting points, boiling points, degrees of ionic dissociation in solution, etc., for various series of binary compounds in which the component atoms exhibited progressively decreasing differences in their electronegativities. These discontinuities he attributed to a discontinuous change from ionic to covalent bonding. He also derived theoretical support from the new wave mechanics, which appeared to cast doubts on many of the qualitative conclusions deduced from the less sophisticated atomic models of Lewis and Fajans. Basing his evidence largely on London's work on the hydrogen molecule, Sidgwick pointed out that wave mechanics attributed the covalent bond to a new kind of quantum mechanical exchange force, unrelated to the classic electrostatic forces of ionic bonds. This made it highly improbable that the two bonds differed only in degree. Even more important was the fact that London's calculations seemed to indicate that the force uniting two atoms was "practically entirely of one kind or the other" and, therefore, that intermediate bond types or transition types containing a mixture of these forces were also improbable.

Thus Lewis' views on the chemical bond tended to give his acid-base definitions a wide applicability which cut through many traditional classes of compounds. Differences were attributable to variations in the degree of electron-pair donation, the same fundamental donor-acceptor mechanism underlying all of the systems. On the other hand, the views of Sidgwick and Langmuir, and consequently those of many chemists of the period, would have severely restricted the use of Lewis' definitions as a systematizing tool. The conclusion that there were several types of bonds differing in kind rather than degree gave support to the idea that the traditional distinctions between salts, acids and bases, coordination compounds, and organic compounds were of a fundamental nature.

As the true relationship between wave mechanics and the empirical bonding model of Lewis became better understood, largely through the work of Pauling and Mulliken in the 1930's, it became apparent that many of Lewis' original ideas were still usable. Contrary to London's early conclusions, both MO and VB

theory support Lewis' contention that, for classification purposes at least, a continuum of bond types exists. For a series of simple AB species this idea can be expressed by altering the  $a:b$  ratio (as the nature of A and B vary) in electron wave functions of the types:

$$\text{MO} \quad \Psi(\text{AB}) = [a\Psi_A + b\Psi_B]^2 \quad (1)$$

$$\begin{aligned} \text{VB} \quad \Psi(\text{AB}) &= a\Psi_{\text{AB}} + b\Psi_{\text{A}+\text{B}-} \\ &\quad \text{(covalent)} \qquad \qquad \qquad \text{(ionic)} \\ &= a[\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)] + b[\Psi_B(1)\Psi_B(2)] \end{aligned} \quad (2)$$

Moreover, it is now recognized that London's exchange forces are essentially mathematical fictions which arise because of our poor choice of approximate wave functions. The only important forces known to operate in chemical phenomena are electrostatic forces.<sup>16</sup> Although the process of covalent bond formation involves a complex and highly directional interplay of the electron cloud's kinetic and potential energies,<sup>17</sup> the resulting bonds, as Lewis anticipated, differ from ionic bonds only in the way in which the charges are localized within the molecule.

Likewise, most of the experimental evidence cited by Sidgwick involved the implicit assumption that the physical properties measured were a direct function of bond type only. In reality they are a composite of several factors, including both bond type and structure. Thus, in 1932 and again in 1939, Pauling<sup>18,19</sup> concluded that the discontinuity in melting points for a series of fluorides cited by Sidgwick was due to a discontinuity in structural type rather than bond type. This conclusion is supported by the recent work of Phillips<sup>20</sup> on  $\text{A}^N\text{B}^{8-N}$  binary solids. For this important class of semiconductors he has shown that one can derive a definition of bond ionicity which is a continuously increasing function of the electronegativity difference between A and B. However, despite the fact that bond ionicity increases as a continuous function, there is a critical ionicity at which these compounds undergo a discontinuous change in structure from local tetrahedral coordination to local octahedral coordination.

The process of ionic dissociation is also a complex phenomenon, not necessarily indicative of bond type. Among other things, it depends on the ability of the solvent to both heterolytically cleave the solute and to electrostatically separate the resulting ion pairs. With the proper choice of solvent it is even possible to make a molecule like  $\text{I}_2$  undergo ionic dissociation.<sup>21</sup>

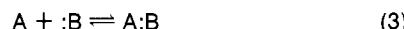
## B. Secondary Acids and Bases

It was not until 1938 that Lewis<sup>22</sup> again returned to the topic of acids and bases and published a paper containing the supporting data and examples so conspicuously absent in his original presentation. In this paper Lewis attempted to show that his definitions were not just formal theoretical analogies, but that they, in fact, accurately identified species exhibiting the experimental behavior of acid-base systems. In order to operationally define what was meant by the term acid-base behavior, Lewis specified four phenomenological criteria for acid-base systems; criteria typified by aqueous proton systems: (1) when an acid and base react, the process of neutralization is rapid; (2) an acid or base will replace a weaker acid or base from its compounds; (3) acids and bases may be titrated against one another by use of indicators; and (4) both acids and bases are able to act as catalysts.

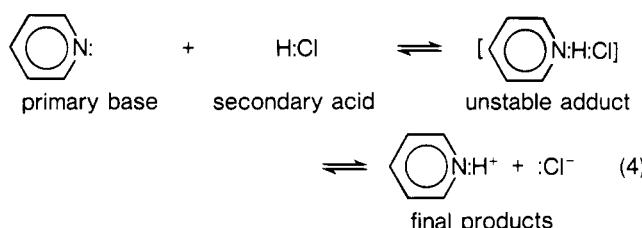
After first remarking that there was complete agreement between the proton and electronic definitions as to which species were basic, Lewis proceeded to show that experimental acidic behavior was not confined to the proton alone, but was exhibited by electron-pair acceptors in general. Particularly striking in this regard were the reactions between metal halides and organic amines in nonaqueous solvents. They could even

be titrated against one another, displaying the same indicator color changes given by Brønsted acids and bases in aqueous solutions. The reason the acid behavior of these species had been overlooked, Lewis reasoned, was the fact that most of these molecular acids were decomposed by the chemist's most common solvent—water.

So rapid and striking were many of these neutralizations that Lewis went on to propose that that criterion 1 (i.e., rapid kinetics) was the salient feature of acid-base behavior, suggesting further that a fundamental subdivision of acids and bases be made on this basis. Acids and bases which underwent neutralization reactions of the general form



and which showed essentially zero activation energy were termed primary, whereas those having measurable activation energies were termed secondary. This last division could be further broken down into two separate classes. The first of these involved species, such as  $\text{CO}_2$ , in which the slow kinetic behavior was apparently due to the necessity of the species undergoing some sort of internal activation before its primary acid or base properties became apparent. The second class involved those species in which the finite activation energy was due to the breaking of one or more auxiliary bonds upon neutralization, causing the initial AB complex to dissociate into several smaller fragments. Hence, Brønsted acids like HCl and  $\text{HNO}_3$  were still acids, though now of the secondary variety, and their neutralizations could be thought of as initially resulting in an unstable hydrogen-bridged adduct which then underwent further decomposition. For example, see eq 4.



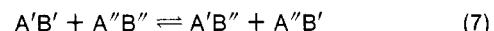
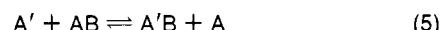
From both the standpoint of the phenomenological criteria and of the octet rule this classification made sense. Lewis' definitions seemed to imply that the driving force of acid-base reactions was the tendency of the acid to complete a "stable" electronic configuration. However, the dot structures of  $\text{CO}_2$  and of both the Brønsted acids and general AB adducts participating in base displacements failed to reveal any incomplete octets (or duplets in the case of hydrogen). There seemed to be no reason why these species should react with bases unless one created the necessary electron deficiencies, either by exciting an electron as in the case of  $\text{CO}_2$ , or by loosening a bond. Consequently these species appeared to be latent acids, their potential acceptor properties becoming active only after the necessary activation energy was supplied (albeit very little in the case of strong Brønsted acids).

Ingold<sup>11</sup> introduced a similar classification by subdividing his electrophiles into the categories of associative and dissociative. The latter had complete valence shells and generally underwent displacement reactions, whereas the former had incomplete valence shells and generally underwent addition reactions.

Proponents of the Brønsted definitions were understandably upset with this nomenclature. The traditional terms of acid and base were being appropriated for a new class of substances and the traditional substances were being renamed. They argued that it was the primary Lewis acids rather than the Brønsted acids that should be given the qualifying terminology, and a number of names were suggested for this purpose, including the terms antibase,<sup>23</sup> acid analogous, proto acid,<sup>24</sup> pseudo acid, and secondary acid.<sup>25</sup>

It is tempting to suggest that yet a fourth reason for the slow adoption of the Lewis definitions can be found in this terminology tangle. Just as a catching name can often give an idea more publicity than its conceptual content merits, so the choice of a controversial name can retard the recognition of a worthwhile concept. The fact that most of the criticism leveled at the Lewis definitions was of a semantic, rather than fundamental, nature suggests that Lewis might have been better advised had he adopted a terminology similar to that of Sidgwick's donors and acceptors and remained content with pointing out that the traditional categories of acid and base represented a familiar example of donor-acceptor displacement reactions.

In retrospect Lewis' kinetic criterion and its accompanying primary-secondary nomenclature appear to be unnecessary complications. Today we recognize that Lewis addition reactions (eq 3) are the exception rather than the rule and that most Lewis acid-base phenomena are of the forms:



From an organizational standpoint it is simpler to regard these as "primary" acid-base displacement reactions rather than as direct neutralizations of special "secondary" acids and bases. In addition, we now take a much broader view of the kinetics of donor-acceptor reactions, the rapid kinetics characteristic of protonic systems being considered as only one extreme of the reactivity spectrum open to generalized acids and bases. Nevertheless, there is a certain amount of quantum mechanical justification for Lewis' distinctions, as will be seen in section III.

Lewis remained fascinated with the first class of secondary acid-base behavior and attempted to account for the mechanism of electron activation in a series of later papers.<sup>26</sup> His results, however, were equivocal to say the least, involving the postulation of an equilibrium between two "electromers" ("isomers" differing in electron distribution only), one exhibiting primary and the other secondary acid-base properties. After Lewis' death in 1946 the problem of secondary acids and bases faded into the background and was eventually forgotten.

### C. Quantum Mechanical Developments

Though not published in a standard chemical journal, Lewis' second presentation of his definitions did not meet the same fate as his first attempt had. Within a year they were brought to the attention of the chemical community via a symposium on Theories and Teaching of Acids and Bases conducted by the Division of Physical and Chemical Education at the 37th National Meeting of the American Chemical Society. The resulting symposium papers were printed in the *Journal of Chemical Education* and were issued in book form.<sup>27</sup> They, in turn, stimulated such interest that yet a second set of journal articles dealing with the pros and cons of the new definitions was also issued in book form.<sup>28</sup> Interest was aroused in research circles as well, largely through a review written by Luder in 1940.<sup>29</sup> In this paper Luder explicitly outlined the relationship of the electronic definitions to the older definitions and supplemented Lewis' paper with additional examples of how they could be used to systematize chemical reactions. In 1946 Luder, in conjunction with Zuffanti, expanded the results of this review and several other papers into a book entitled "The Electronic Theory of Acids and Bases".<sup>30</sup> This volume has remained a standard reference on Lewis acid-base theory and is still in print.

As pointed out earlier, the usefulness of the Lewis definitions is intimately bound up with contemporary views on the nature of the chemical bond itself. Although Lewis' original formulation of his definitions still remains quite useful, a growing need was

felt from the late 1940's onward for their translation into the idiom of quantum mechanics. Such a translation was initiated by Mulliken in a series of papers beginning in 1951.<sup>31</sup> He was originally attracted to the subject via his attempt to quantum mechanically treat the spectra of a class of weak Lewis adducts known as charge-transfer complexes.

The wave function for a one-to-one adduct can be approximated as:

$$\Psi_{AB} = a\Psi_0(AB) + b\Psi_1(A^-B^+) \quad (8)$$

where  $\Psi_0(AB)$  represents the system in the absence of any charge transfer, but subsumes any electrostatic interactions between A and B, be they due to dipoles, polarization effects, or net ionic charges on the original acid and base (remembering A and B can be ions or neutral molecules).  $\Psi_1(A^-B^+)$ , on the other hand, represents the system after the net transfer of one electron from the base B to the acid A. The actual state of any AB complex involving an intermediate stage of electron transfer or "degree of electron donation" can be approximated by varying the ratio of the weighting coefficients ( $a^2:b^2$ ) for these two extreme structures.

From this point of view weak intermolecular forces (or idealized ion associations when A and B are ions) and redox reactions are merely the extremes of a continuum with approximately zero donation at one end and complete transfer of one or more electrons at the other. The interactions of odd electron species or free radicals can also be represented in this manner. Hence, Mulliken's treatment is in some ways closer in spirit to Ingold's original electrophilic-nucleophilic definitions or the cationoid-anionoid categories of Lapworth and Robinson than to Lewis' more restricted acid-base definitions.

However, despite the fact that we can view all of these interactions as part of a continuum, we do encounter discontinuities in our description of them owing to the use of approximate models for limiting cases. For those interactions involving extensive orbital perturbation and electron redistribution we must use quantum mechanics to calculate the new distributions and the accompanying energy changes. As the degree of donation decreases the orbital perturbation and degree of electron redistribution also decrease, and the quantum mechanical model can be approximated with classical electrostatic models which use point charges, permanent or induced dipoles, etc. The only forces operating at all levels of interaction are electrostatic forces. However, in keeping with common practice we will restrict the term electrostatic to those limiting case interactions which can be adequately approximated with the classical models and use the term covalent or orbital perturbation for those interactions requiring full use of the quantum mechanical model.

Application of second-order perturbation theory to wave function 8 yields the following expression for the energy,  $E_{AB}$ , of a weak AB complex:

$$E_{AB} = E_0 - \frac{(\beta_{01} - E_0 S_{01})^2}{(E_1 - E_0)} \quad (9)$$

Here  $E_0$  represents the energy of the state  $\Psi_0(AB)$ ,  $E_1$  represents the energy of the excited state  $\Psi_1(A^-B^+)$ ,  $\beta_{01}$  is the resonance integral between  $\Psi_0(AB)$  and  $\Psi_1(A^-B^+)$ , and  $S_{01}$  the overlap integral.

Both Lewis and Ingold had recognized that there was no simple relationship between acid-base strength and net ionic charge. The neutral NH<sub>3</sub> ligand, for example, displays a greater affinity for the acid Ag<sup>+</sup> than does the charged OH<sup>-</sup> ion, whereas for the acid H<sup>+</sup> the converse is true. For this reason both Lewis and Ingold had objected to the cationoid-anionoid terminology introduced by Lapworth. However, aside from the suggestion that electron-pair donation was involved, neither of them was able, on the basis of the electronic theory of bonding then extant, to

provide a theoretical treatment of the factors contributing to acid-base strength. By analysis of eq 9, Mulliken was able to at least qualitatively remedy this defect. Roughly speaking, the energy of a complex can be approximated as an additive sum of an electrostatic energy term (I) and a charge transfer or covalent energy term (II). The first of these is obviously dependent on the net charge densities at the donor and acceptor sites. The second is a function of the valence-state ionization potential of the donor orbital and the electron affinity of the acceptor orbital, the extent of their overlap, and their inherent symmetry properties (hence the geometry of the interaction). Thus, both net electrical charges and specific orbital or covalent interactions are involved.

Again, in separating the interaction energy into an electrostatic term and a covalent term, we are not implying that two separate kinds of forces are operative in bond formation. The separation arises, rather, out of the mathematical approximations used and can be physically interpreted as those energy effects which are understandable in terms of the original (or slightly polarized) electron distributions of A and B (i.e., the so-called electrostatic terms) and those energy effects understandable in terms of the redistribution of the valence electrons in the composite AB system (i.e., the so-called covalent terms). Both of these ultimately lead, via the virial theorem, to a lowering of the electrostatic potential energy of the AB system over that of the isolated acid and base.

In 1967 Hudson and Klopman<sup>32-36</sup> used perturbational MO theory (PMO) to derive a version of eq 9 which makes explicit the role which certain ground-state properties of the acid and base play in determining the course of adduct formation. The wave function  $\Psi_{AB}$  of a given complex can be approximated as:

$$\Psi_{AB} = a\Psi_A + b\Psi_B \quad (10)$$

where again varying degrees of donation can be indicated by the  $a^2:b^2$  ratio. For that case of the general PMO expression applying to electron-pair donors and acceptors, the initial change in the energy of the system, upon incipient adduct formation, is approximated by:

$$\Delta E = \frac{-q_s q_t}{R_{st}\epsilon} + 2 \sum_{\substack{\text{occupied} \\ \text{orbitals} \\ m \\ \text{of} \\ \text{species} \\ B}} \sum_{\substack{\text{unoccupied} \\ \text{orbitals} \\ n \\ \text{of species} \\ A}} \frac{(c_s^m c_t^n \beta_{st})^2}{(E_m^* - E_n^*)} \quad (11)$$

Here again the first term is electrostatic, depending on the net charge densities and radii of the donor and acceptor atoms (s and t). The second term is covalent in nature and is a function of the overlap, symmetry, and energies of the donor and acceptor orbitals (m and n) as modified by the solvent in which the reaction is occurring. It is usually assumed that the highest occupied MO (HOMO) of the base and the lowest unoccupied MO (LUMO) of the acid dominate the summation in the second term of eq 11 and that these two "frontier" orbitals correspond to the traditional donor and acceptor orbitals of the Lewis definitions.

For multisite interactions eq 11 may be summed over all interacting atoms as well as interacting orbitals. Solvent effects are included not only in the  $E_m^*$ ,  $E_n^*$  terms, but also in term I via the presence of the solvent's dielectric constant  $\epsilon$ . The terms in eq 11 are defined in detail in Table I.

Acids having large net positive charge densities at their acceptor sites and bases having large net negative charge densities at their donor sites should form strong adducts by maximizing the first term of either eq 9 or eq 11. Likewise, donor and acceptor orbitals should have the proper symmetries so that the resonance integrals in the second terms of eq 9 and 11 will have

**TABLE I. The Terms in the Klopman Reactivity Equation (Eq 11)**

s	Donor atom on base B
t	Acceptor atom on acid A
m	Donor orbital on base B
n	Acceptor orbital on acid A
$q_s$	Total net charge density at donor atom s
$q_t$	Total net charge density at acceptor atom t
$R_{st}$	Distance between s and t
$\epsilon$	Dielectric constant of the solvent
$c_s^m$	Coefficient of the donor orbital m at donor atom s
$c_t^n$	Coefficient of acceptor orbital n at acceptor atom t
$\beta_{st}$	Resonance integral between s and t at distance $R_{st}$
$E_m^*$	Energy of the donor orbital m in the field of acid A corrected for any solvation or desolvation accompanying the removal of an electron from the orbital
$E_n^*$	Energy of the acceptor orbital n in the field of base B corrected for any solvation or desolvation accompanying the addition of an electron to the orbital

nonzero values and good overlap so that the magnitudes of  $\beta$  are maximized. Lastly, the energies of the donor and acceptor orbitals should be similar in order to minimize the denominators of the second terms.

The relationship between eq 9 and eq 11 is made clearer if one realizes that, in addition to the change of sign, the following approximate identities hold:

$$E_0 - (E_A + E_B) \approx q_s q_t / R_{st} \epsilon$$

(where  $E_A$  and  $E_B$  are the energies of the isolated acid and base and only permanent dipoles or net charges are assumed)

$$E_1 - E_0 \approx \Delta E(\Psi_0 \rightarrow \Psi_1) \approx E_m^* - E_n^* \approx |IP_m| - |EA_n|$$

(within the limits of Koopman's theorem)

$$(\beta_{01} - E_0 S_{01})^2 \approx 2(c_s^m c_t^n \beta_{st})^2$$

(and the summation in eq 11 is dominated by the HOMO and LUMO).

Frequently those molecular properties which maximize the first terms are mutually exclusive of those which maximize the second terms. Klopman has suggested that on the basis of eq 11 donor-acceptor reactions can be divided into the categories of "charge controlled" (those dominated by term I) and "orbital controlled" (those dominated by term II).

Reactivity equations similar to eq 11 have also been derived by, among others, Salem,<sup>37,38</sup> Devaquet,<sup>37,39</sup> Fukui,<sup>40,41</sup> and Fujimoto.<sup>40</sup>

## D. Summary and Conclusions

In summary, then, we see that between 1923 and 1934 several independent investigators arrived at some type of electronic classification of reactants and/or reaction types based on a consideration of the interactions between electron-rich and electron-poor species in a variety of chemical systems. Lewis first proposed such a classification in 1923 by generalizing the traditional categories of acid and base. Sidgwick arrived at a classification by considering the valence requirements of the transition elements and the reactions of classical coordination complexes. However, Sidgwick's use of his classification was restricted by his views on chemical bonding. Similar categories were suggested by early attempts to develop an electronic theory of organic reactivity. Lapworth proposed a classification modeled on the experimental behavior of cations and anions, whereas Ingold arrived at his classification by generalizing earlier electronic interpretations of oxidation-reduction reactions.

Indeed, in reading the reviews written by Robinson and Ingold one is struck by the fact that the organic chemist had succeeded by 1934 in developing, under the guise of cationoid-anionoid or electrophilic-nucleophilic reagents, almost all of the qualitative principles of Lewis acid-base chemistry. The close

relation of these reagents to the Brønsted definitions, on the one hand, and to oxidizing and reducing agents on the other was clearly recognized. Detailed qualitative rationales for the way in which substituents could increase or decrease electron density at a reaction site, for ordering reagents in terms of increasing electrophilicity or nucleophilicity using trends in periodic properties, as well as a clear recognition of the purely relative nature of such orders, were all developed during this period and in retrospect make the 1938 and 1939 papers of Lewis and Usanovich<sup>42</sup> seem somewhat anachronistic.

For a variety of reasons there was little convergence of these different classifications until after 1940. This was largely due to parochialism enforced by the traditional boundaries between organic and inorganic chemistry, between transition metal chemistry and main group element chemistry, and to a period of confusion over the nature of the chemical bond accompanying the transition from the era of the Lewis-Bohr atoms to that of modern quantum mechanics.

In the 1950's yet another stream of research was added by Mulliken's quantum mechanical treatment of molecular or charge-transfer complexes and his generalization of this treatment to donor-acceptor reactions as a whole. Finally, contributions have again come from the field of organic reactivity, this time from the Klopman-Hudson PMO treatment of electrophilic and nucleophilic reactions.

Since the 1940's explicit use of the Lewis definitions as a systematizing tool in both teaching and research has steadily grown. Yet the definitions have not been without their critics.<sup>23-25,43,44</sup> Of the many weaknesses pointed out, the most commonly mentioned are: (1) the semantic problem of secondary acids and bases and of acid-base terminology in general; (2) the belief that the definitions are so general as to subsume most, if not all, of chemistry, making the terms acid-base synonymous with the word reactant; and (3) the belief that, unlike the Brønsted definitions, the Lewis definitions cannot be quantified.

We have already discussed criticism 1 above. In section III of this article we will look at the use of the definitions as a systematizing tool in light of the MO approach developed by Mulliken and Klopman and consider criticism 2. Finally, in section IV, we will look at some recent attempts to quantify the Lewis concepts.

## III. Lewis Definitions as a Systematizing Tool

### A. Generalized Lewis Definitions

As pointed out in section II, the usefulness of the Lewis concepts is in large part a function of contemporary views on the nature of the chemical bond itself. As the theory of bonding becomes more unified and more flexible, so do the Lewis definitions. Consequently, in this section we will emphasize a qualitative MO approach as this not only eliminates many of the difficulties inherent in older formulations based on dot formulas, but substantially broadens the scope of the definitions. Whenever possible we will point out the relationship between this approach and the octet rule and electron dot formulas still used in most textbooks.

When translated into the idiom of MO theory<sup>31</sup> the Lewis definitions read as follows: A *base* is a species which employs a doubly occupied orbital in initiating a reaction. An *acid* is a species which employs an empty orbital in initiating a reaction. The term *species* may mean a discrete molecule such as  $BF_3$  or  $NH_3$ , a simple or complex ion such as  $Cu^{2+}$ ,  $Ag(NH_3)_2^+$ ,  $Cl^-$  or  $NO_3^-$ , or even a solid material exhibiting nonmolecularity in one or more dimensions.  $TaS_2$ , for example, crystallizes in a layer-type structure (lack of discrete molecules in two dimensions). Each of the resulting layers or sheets can function as a multisite Lewis acid, and it is possible to carry out topochemical reactions in which a variety of Lewis bases are inserted between

the  $\text{TaS}_2$  layers.<sup>45</sup> Graphite, on the other hand, is a good example of a layer type solid which can function as a Lewis base.<sup>46</sup> Free atoms seldom act as Lewis acids and bases. They usually have one or more unpaired electrons and their reactions are more accurately classified as free radical (see below).

The term orbital refers to a discrete molecular orbital or to a band on any of the above species or, in the case of monoatomic species, to an atomic orbital. The donor orbital on the base is usually the highest occupied MO or HOMO. The acceptor orbital on the acid is usually the lowest unoccupied MO or LUMO.<sup>47</sup>

The qualifying phrase ". . . in initiating a reaction" is used on purpose. It is assumed that the general characteristics of a reaction are determined primarily by the initial HOMO-LUMO interaction. However, as the system proceeds along the reaction coordinate it is conceivable, particularly in strong interactions, that other orbitals will be perturbed as well.

Because the Pauli principle limits each spatial orbital to only two electrons, the definitions retain the most salient feature of the Lewis concepts: the donation or sharing of electron pairs. Moreover, they may, in many cases, be directly related to traditional Lewis dot representations of Lewis acid-base reactions by means of MO localization procedures like those developed by Edmiston and Reudenberg.<sup>48</sup> Such translations can also be made at a more elementary level by means of the simple qualitative spin-charge correlation models developed by Linnett<sup>49</sup> and Bent<sup>50</sup> for approximating localized MO domains. Such models are quite attractive at the introductory level as they do not require the use of complex mathematics.

The MO definitions have a number of important consequences which were absent or, at best, only implicit in older formulations:

1. Though often the case, it is *not necessary* that the donor and acceptor orbitals be localizable on a single atom or between two atoms, as implied by Lewis dot structures. That is, the orbitals may still be multi-centered even in a relatively localized representation. Thus donor-acceptor interactions involving delocalized electron systems like that between the benzene  $\pi$  ring and iodine or between carborane cluster anions and transition metal cations<sup>51</sup> are naturally subsumed by the definitions.

2. There is no requirement that the donor and acceptor orbitals always be nonbonding in nature as is often assumed from the identification of bases with lone pairs and acids with incomplete octets in their Lewis dot structures. A long-lived species will usually adopt a structure in which the number of bonding MO's generated is equal to the number of valence electron pairs in the system. If the structure also gives rise to nonbonding MO's these may be partially or completely populated as well. Thus the HOMO or donor orbital on a base is likely to be *either bonding or nonbonding*<sup>52</sup> in character, the latter always being the case for monoatomic species. Similarly the LUMO or acceptor orbital on an acid is likely to be *either antibonding or nonbonding* in character, the latter again always being the case for monoatomic species.

3. All degrees of electron donation are possible, ranging from essentially zero in the case of weak intermolecular forces and idealized ion associations (if the reactants are ionic) to the complete transfer of one or more electrons from the donor to the acceptor. This continuity can be represented by wave functions like those discussed in section II, where the degree of donation increases as the ratio  $a^2/b^2$ :

$$\Psi_{AB} = a\Psi_1(A^-B^+) + b\Psi_0(AB) \quad (12)$$

charge transfer      electrostatic

$$\Psi_{AB} = [a\Psi_A + b\Psi_B]^2 \quad (13)$$

Points 2 and 3 have interesting implications for the mechanisms of acid-base reactions. Table II summarizes the various

TABLE II. Possible Adducts Classified In Terms of the Bonding Properties of the Donor and Acceptor Orbitals of the Constituent Acid and Base.<sup>a</sup>

		Acceptor orbital	
		n	a
Donor orbital	n	n · n	a · n
	b	n · b	a · b

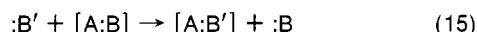
<sup>a</sup> n = nonbonding, a = antibonding, b = bonding.

conceivable donor-acceptor interactions on the basis of MO bonding type. Of these possible combinations, n-n interactions should always lead to association reactions of the form:

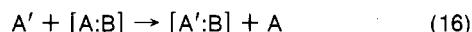


The other combinations may also lead to this type of reaction if the degree of donation does not populate an antibonding MO or depopulate a bonding MO sufficiently to cause bond cleavage. However, in such cases partial population or depopulation should lead to bond weakening (i.e., lengthening) effects within the acid or base fragment upon neutralization. Such effects are in fact observed, even in cases where the interaction is weak enough to be classed as a strong intermolecular attraction.<sup>53</sup> If the Walsh diagram of an acid or base indicates that the energy of the donor or acceptor orbital is strongly dependent on bond angles, the acid or base may attempt to minimize such bond weakening effects by undergoing a geometric distortion upon neutralization such that the acceptor orbital becomes less antibonding by lowering its energy or the donor orbital more antibonding by increasing its energy.  $\text{BF}_3$ , for example, goes from a  $D_{3h}$  to a local  $C_{3v}$  symmetry upon reacting with  $\text{NH}_3$ . If the donor and acceptor orbitals are fairly localized these distortions can be predicted by VSEPR theory,<sup>54</sup> the number of electron pairs about the central atom of the acid gradually increasing, and that about the central atom of the base gradually decreasing as the degree of donation increases. For delocalized cluster species the corresponding distortions can be predicted by means of Wade's rules.<sup>55</sup>

If an antibonding MO is sufficiently populated, bond rupture within the acceptor species will occur, the net result being a base displacement reaction:

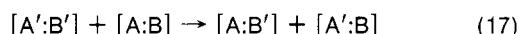


If, on the other hand, a bonding orbital is completely depopulated, bond rupture will occur within the donor species leading to an acid displacement:



In these cases the donor or acceptor species is arbitrarily considered to be an acid-base adduct undergoing a displacement of either its constituent acid or base moiety. The division of the donor or acceptor species into the proper A and B subregions is determined by the bond correlating with the donor or anti-bonding acceptor orbital involved.

Lastly, the b-a combination in Table II can lead to a double acid-base displacement reaction:



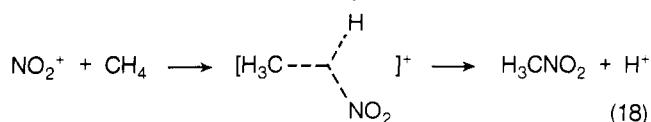
Most reactions occurring in solutions in which the solvent is coordinated to one or more of the reactants fall into this category. Various combinations of reactions 14-16 may also give a double displacement reaction as the net result.

Thus, MO theory provides a simple solution to the problem of displacement reactions discussed in section II. Species do not necessarily require incomplete octets in order to function as acids. All that is needed is a favorable HOMO-LUMO perturbation with a donor species. However, in the case of full octets, the acceptor orbital is generally antibonding in nature and interactions with bases of increasing strength lead to a pro-

gressive weakening of one or more bonds within the acceptor and finally to displacement. A large number of acceptors fall into this category, and their association reactions, whether they lead to strong intermolecular attractions or weak molecular adducts, can be viewed as incipient or frozen displacement reactions.<sup>53</sup> Indeed, it has long been known that the octet rule is strictly valid only for period 2 elements, where it is a consequence of there being only four readily available valence orbitals per atom. But even here it does not restrict the maximum coordination number per atom to four as MO theory allows a species to expand its coordination number via delocalized bonding without making use of high-lying d orbitals.<sup>56,57</sup> Many acid-base adducts and displacement reaction transition states appear to involve such delocalization. The electron-deficient transition states of acid displacement reactions can be described in terms of a MO bonding scheme like that used for  $\text{H}_3^+$  (that is, by means of three-center, two-electron bonds), whereas the electron-rich transition states of base displacement reactions can be described in terms of a MO bonding scheme like that used for  $\text{I}_3^-$  (that is, by means of three-center, four-electron bonds). Linnett double quartet theory provides an alternative means of qualitatively describing base displacement transition states and has been applied to  $\text{S}_{\text{N}}2$  reactions in organic chemistry by Firestone.<sup>58</sup>

Both Lewis' categories of primary and secondary acids and Ingold's associative and dissociative electrophiles, discussed in section II, represent an imperfect anticipation of acids with nonbonding vs. antibonding acceptor orbitals.

The identification of Lewis basicity with lone pairs or nonbonding electrons is much more firmly ingrained than any corresponding electronic criterion for acidity, and the idea that electrons in bonding orbitals may also give rise to base-like properties may seem foreign. A moment's reflection, however, will show that electrophilic attack at a double bond is a familiar example of this phenomenon.  $\pi$ -Type bonding electrons are often sufficiently exposed so as to be easily accessible to electrophilic reagents, although the underlying  $\sigma$ -bonding system prevents a complete acid displacement from occurring. Olah<sup>59</sup> has recently shown that  $\sigma$ -type bonding electrons may also act as donors, particularly in superacid solvents, which allow the generation of very strong attacking electrophiles. An example is the nitration of methane in anhydrous HF:



Here the octet rule is preserved by invoking a three-center, two-electron bond in the transition state to explain the existence of "pentavalent" carbon. Such reactions result in complete acid displacements.

As can be seen, it is often useful to distinguish between  $\sigma$ - and  $\pi$ -type acids and bases. Such symmetry properties are important in determining both the geometries of the adducts formed and which reaction mechanisms are feasible.<sup>41</sup> However, one should remember that such an orbital symmetry classification is one of convenience rather than necessity and that the same donor-acceptor principles underlie both  $\sigma$  and  $\pi$  acid-base reactions.

## B. The Relative Nature of Reactivity

One of the more important consequences of the Lewis definitions, emphasized by Luder<sup>30</sup> and by Lewis<sup>22</sup> himself, is the relative nature of Lewis acidity and basicity. Again this conclusion falls directly out of the MO approach and can be illustrated with simple perturbational MO treatments of acid-base reactions like those of Mulliken and Klopman discussed in section II. Although the resulting equations are approximate and it is fre-

quently impossible to obtain the necessary data to quantitatively evaluate them for specific cases, they, nonetheless, provide a concrete model which allows us to make important qualitative conclusions about the reactivity of acid-base systems. This can be seen by applying Klopman's equation to some generalized examples; see eq 11.

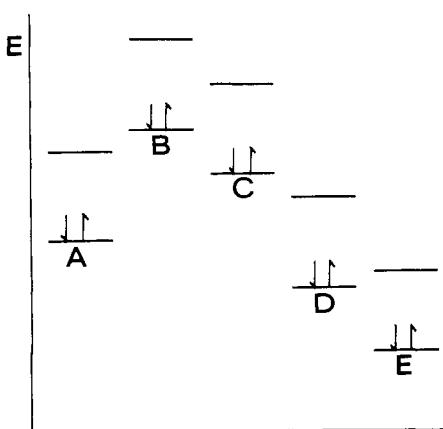
We can imagine two acids,  $A'$  and  $A''$ , such that  $A'$  has a high net positive charge density at its acceptor atom and high-lying LUMO energy and  $A''$  has the opposite properties. Let us consider the interactions of  $A'$  and  $A''$  with a series of bases,  $B'$ ,  $B''$ , and  $B'''$ , such that the net negative charge density at the donor atoms follows the order  $B' > B'' > B'''$  and the energy of the HOMO increases in the opposite order. Because of its high-lying LUMO and high net positive charge density, the reactivity of  $A'$  with respect to the three bases will be dominated by term I; i.e., its reactions will be charge controlled. Thus,  $A'$  will give the apparent base strengths  $B' > B'' > B'''$ . On the other hand, because of its low positive charge density and low-lying LUMO, the reactivity of  $A''$  will be determined by term II and, in particular, by the size of the  $\text{HOMO}(E_m^*)-\text{LUMO}(E_n^*)$  gap in the denominator. That is, the higher the energy of the base HOMO, the closer it approaches the energy of the acid LUMO, the smaller will be the denominator and the larger the favorable perturbation energy. Thus  $A''$  will give the apparent base strengths  $B''' > B'' > B'$ . Inversions of this type are common among simple cationic and anionic species in aqueous solutions and are the basis for dividing ions into the categories of (a) and (b) class donors and acceptors or hard-soft acids and bases.<sup>34</sup>

If  $A''$  happens to be a complex species with an antibonding acceptor orbital, a fourth base,  $B''''$ , giving an even smaller HOMO-LUMO gap, may populate the orbital sufficiently to cause  $A''$  to undergo a displacement reaction instead of an association reaction as discussed in the previous section. We can envision a number of other extremes as well. Consider a complex acid  $A'''$  having two possible acceptor sites, one having a high net positive charge density and a small orbital coefficient for the LUMO and the second the opposite properties. Attack at the first site would be largely charge controlled, giving preference to  $B'$ , whereas attack at the second site would be orbital controlled, giving preference to  $B'''$ . This type of behavior is termed ambident and is found in many systems for both acids and bases. For example, the ability of the thiocyanate anion  $[\text{:NCS:}]^-$  to form N vs. S coordinated adducts with a variety of cations is determined by factors of this type.<sup>34</sup>

Finally, we can imagine the situation in Figure 1, which shows the relative HOMO and LUMO energies (as perturbed by the field of the other reactant) for a hypothetical species A and several possible reaction partners: B, C, D, and E. With respect to B, complete electron transfer from B to A will be favorable and A will act as an oxidizing agent. With respect to C, the  $\text{A(LUMO)}-\text{C(HOMO)}$  perturbation will be favorable and A will act as an acid. With respect to D, the  $\text{A(HOMO)}-\text{D(LUMO)}$  perturbation will be favorable and A will act as a base. Lastly, with respect to E, complete electron transfer from A to E will be favorable and A will act as a reducing agent. Examples of this extreme amphoteric behavior are the reactions of water given in Table III.

Figure 1 is intended to represent possible variations of donor-acceptor properties in the broadest possible context: i.e., not only those species encountered in aqueous solution under normal conditions of temperature and pressure but also high-temperature species and those stabilized by nonaqueous environments, ranging, on the one hand, from the polycations and carbocations isolated by Gillespie<sup>60</sup> and Olah<sup>59</sup> in superacid solvents to the recently isolated  $\text{Na}^-$  anion<sup>61</sup> on the other.

In addition to the above cases we might consider the case where the frontier orbitals of A are approximately degenerate with those of some species, F (i.e.,  $\text{A(HOMO)} \approx \text{F(HOMO)}$ ,  $\text{A(LUMO)} \approx \text{F(LUMO)}$ ). Here neither species is clearly the donor or acceptor and species may display both functions simulta-



**Figure 1.** The relative energies (as perturbed by the field of the other reactant) of the frontier orbitals of a hypothetical species A and of the frontier orbitals of several hypothetical reaction partners: B, C, D, and E. With respect to B, complete electron transfer from B to A will be favorable and A will act as an oxidizing agent. With respect to C, the A(LUMO)–C(HOMO) perturbation will be favorable and A will act as an acid. With respect to D, the A(HOMO)–D(LUMO) perturbation will be favorable and A will act as a base. Lastly, with respect to E, complete electron transfer from A to E will be favorable and A will act as a reducing agent.

neously. Examples of this situation appear to be the multisite interactions encountered in concerted organic cycloaddition reactions and, to a lesser degree, in the phenomenon of back-donation in transition metal complexes.

Though we have simplified our examples by neglecting the overlap and symmetry effects, which are also contained in eq 11, we can still see that the MO treatment rationalizes the relative nature of Lewis acidity and basicity quite well.

Most species are, so to speak, electronically amphoteric. *The inherent strength of an acid or base, the point of attack, the question of whether an association or displacement reaction will occur, of whether the species is hard or soft, or even of whether it will act as an acid, base, oxidant, or reductant—all of these are purely relative, depending not only on the electronic structure of the species itself but on the unique matching of that structure with the electronic structures of the other species composing the system.*

### C. Limitations and Qualifications

Under ambient conditions most long-lived species have closed-shell configurations, a fact which might lead one to conclude that all chemical reactions are acid–base and that the terms are merely synonyms for the word reactant. Such is not the case. Although anticipated in some ways by earlier work in the electronic theory of organic chemistry,<sup>62</sup> Luder and Zuffanti<sup>30</sup> appear to have been the first to explicitly suggest that all elementary reactions could be electronically classified in one of three ways:

- I. Acid–Base                     $A + :B \rightleftharpoons A:B$
- II. Free Radical (Odd Molecule)  $X\cdot + \cdot Y \rightleftharpoons X:Y$
- III. Oxidation–Reduction (Redox)  $R_1\cdot + Ox_1 \rightleftharpoons Ox_2 + \cdot R_2$

The categories of acid–base and free radical differentiate between the processes of heterolytic and homolytic bond formation and cleavage, whereas the redox category subsumes complete electron transfers. The reactions of each category can, in turn, be further classified at a purely stoichiometric level as neutralization (addition), decomposition (dissociation), single, or double displacement reactions.

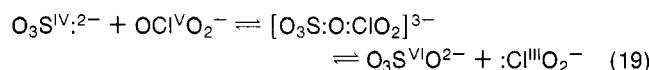
Clear-cut examples of each category are easy to find: Brønsted reactions and ligand substitution belong to the class of acid–base reactions, photochemical phenomena and gas-phase thermolytic reactions are generally free radical in nature,

**TABLE III. Reactions Illustrating the Amphoteric Nature of Water**

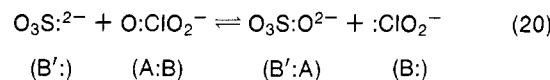
$xH_2O + :Cl^- \rightleftharpoons Cl:(H_2O)_x^-$ (acid)
$yH_2O + Mg^{2+} \rightleftharpoons Mg(H_2O)_y^{2+}$ (base)
$2H_2O + 2Na \rightleftharpoons 2Na^+ + 2OH^- + H_2\uparrow$ (oxidant)
$2H_2O + 2F_2 \rightleftharpoons 4H^+ + 4F^- + O_2\uparrow$ (reductant)

and electrode processes and outer-sphere electron transfers are cases of redox reactions. Thus, large areas of chemical phenomena belong to each category,<sup>63,64</sup> and it is just as reasonable to object that the electronic concepts of free radical and redox reactions are too broad as it is to level such criticism at the Lewis definitions.

While every elementary reaction can in principle be related to one of the three idealized processes listed above, actual macroscopic reaction systems may be a composite of several elementary steps. Such systems may involve elementary steps which are concerted and which, therefore, cannot be uniquely distinguished, or they may involve the coupling of several kinds of elementary processes. Examples of the latter case are those redox systems in which acid–base as well as electron-transfer steps play a key role. In addition, the wide variation in electronic structure possible for the reactants generates a corresponding variation in the characteristic experimental behavior of the reaction systems. The result is that, while there are certain classical systems whose characteristic experimental behavior has become closely identified with each reaction category (e.g., proton transfers, photohalogenation of alkanes, electrolysis, etc.), there are many other systems whose experimental behavior makes their unique assignment to one of the above categories more difficult. The term redox, for example, has traditionally been applied to a large number of reactions which do not actually involve complete electron transfers. Thus, the reaction:

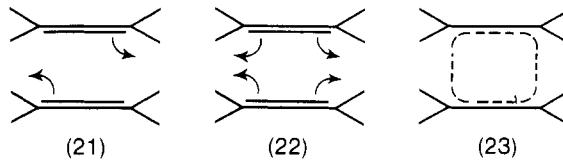


is usually thought of as an inner-sphere redox reaction, involving the transfer of an oxygen atom from the oxidant ( $ClO_3^-$ ) to the reductant ( $SO_3^{2-}$ ). However, it can also be classified as a base displacement at one of the oxygen atoms (singlet state) of  $ClO_3^-$ :



Likewise, one-equivalent redox reactions involving atom transfers can be alternatively classified as free radical displacement reactions.

Cycloadditions represent another gray area. In the absence of detectable intermediates one cannot distinguish between an acid–base mechanism (21) and a free radical mechanism (22), the best representation being a concerted process symbolized by (23). Problems of this nature also arise in classifying oxidative



additions, reductive eliminations, and reactions involving large amounts of back-donation.

In light of these ambiguities it is probably best to think of acid–base, free radical, and redox reactions not as absolutely

TABLE IV. Relation between Reactant Type, Reaction Type, and Degree of Donation<sup>a</sup>

REACTANT TYPE	REACTION TYPE
I    Closed Shell - Closed Shell Interactions a) Ions (simple or complex)  b) Neutral molecules or lattices	Increasing donation $(B:)^{-m}$ to $(A)^{+n}$  ACID-BASE → REDOX (ionic salt formation) (coordinate bond formation)  Increasing donation $(B:)^{-m}$ to $(A)^{+n}$  ACID-BASE → REDOX (weak intermolecular forces) (molecular ionization) or charge- transfer complexes (bond formation)
II    Open Shell - Open Shell Interactions a) Neutral free radicals (free atoms, odd molecules)  b) Radical cations and anions	Increasing donation $X^{\cdot}$ to $Y^{\cdot}$  FREE RADICAL → REDOX (covalent bond formation)
III    Open Shell - Closed Shell Interactions Any combination from category I and category II.	Just as the above diagrams indicate a gradual merging of both acid-base and free radical reactions with redox reactions, so this category represents a gradual merging of acid-base and free radical reactions, depending on the extent to which the odd electron(s) is considered to be a core versus a valence electron. This ambiguity occurs in transition metal species having unpaired d electrons. Depending on the nature of the closed shell ligands, the d electrons can be considered as core electrons whose energy levels are split by the ligand field (e.g. $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ) or as valence electrons participating in the bonding via back donation (e.g. $\text{V}(\text{CO})_6^-$ ). The latter are typically free radical in behavior and the former acid-base.

<sup>a</sup> For the closed-shell category a separate diagram has been given for both ions and neutral molecules in order to facilitate comparison with traditional names (which are given in parentheses). In reality they may, like free-radical reactions, be combined into a single diagram containing only acid-base and redox reactions.

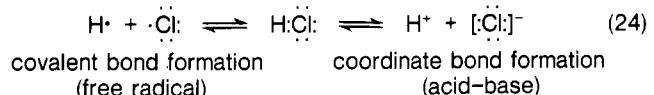
distinct processes but as sections of a continuum, their boundaries gradually merging into one another. This picture is implied by the MO treatment. A close parallel would be the use of the ionic, covalent, and metallic bonding models to classify chemical bonds. Although a large number of substances contain bonds corresponding to one of these extremes, many more substances contain bonds of an intermediate type. Nevertheless, it is often useful to classify these intermediate cases in terms of one of the limiting models (Table IV).

This parallelism also raises a semantic problem. The terms acid-base, free radical, and redox are used to classify possible electronic mechanisms for bond formation, whereas the terms ionic, covalent, and metallic are used to describe the electron distribution within bonds as they already exist in a molecule. Historically, however, the terms ionic and covalent bond, in conjunction with the term coordinate bond, have also been used to describe mechanisms for bond formation.<sup>6</sup> More recent examples of this usage are the terms dative bond and  $\pi$  back-bonding.

The use of the term bond in this context is unfortunate as there is no necessary relationship between the properties of a bond as it exists in a molecule and the mechanism by which it was formed. That is, ionic reactants do not automatically result in ionic bonds or neutral molecules and atoms in covalent bonds. In each case the degree of donation may vary from zero upwards, as indicated by eq 12 and 13, and the resulting bonds may lie anywhere on a continuum from idealized ionic to idealized covalent bonding.

Similarly, the same bond may be formed by several alternative

routes. HCl, for example, can be made via the photochemical reaction of  $H_2$  and  $Cl_2$  or by boiling a hydrochloric acid solution (eq 24). One route would appear to give a covalent bond, the



other a coordinate bond. Of course, the actual bond is the same in both cases. Thus, terms such as acid-base reaction and back-donation do not contain the potentially misleading implications of such terms as coordinate bond and  $\pi$  back-bonding, and one avoids confusing the concepts of reaction type and bond type.

#### D. Applications

Table V lists the major classes of chemical phenomena which are subsumed under the general category of Lewis acid-base reactions. The relevance of the Lewis concepts to each of these areas is for the most part self-evident so that it is only necessary to comment briefly on each and to indicate where the reader can find a more detailed treatment.

Discussions of the relationship between the Lewis definitions and the more restricted Arrhenius, Lux-Flood, solvent-system, and proton definitions have been given by several authors, the most thorough being that of Day and Selbin.<sup>65</sup> Figure 2 summarizes these relationships by means of a Venn diagram.

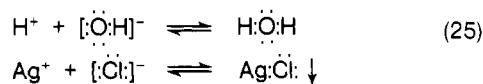
The isomorphism of the Lewis concepts and the donor-acceptor relationships by means of a Venn diagram.

**TABLE V. Chemical Phenomena Subsumed by the Category of Lewis Acid–Base (Donor–Acceptor) Reactions**

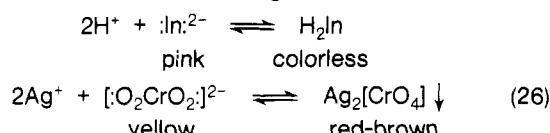
- (A) Systems covered by the Arrhenius, solvent system, Lux–Flood, and proton acid–base definitions
- (B) Traditional coordination chemistry and “nonclassical” complexes
- (C) Solvation, solvolysis, and ionic dissociation phenomena in both aqueous and nonaqueous solutions
- (D) Electrophilic and nucleophilic reactions in organic and organometallic chemistry
- (E) Charge-transfer complexes, so-called molecular addition compounds, weak intermolecular forces, H-bonding, etc.
- (F) Molten salt phenomena
- (G) Various miscellaneous areas such as chemiadsorption of closed-shell species, intercalation reactions in solids, so-called ionic metathesis reactions, salt formation, etc.

ceptor terminology of traditional coordination chemistry is obvious. The MO approach also allows one to apply these concepts to so-called nonclassical complexes (e.g., the metallocenes). However, it is less often appreciated that coordination systems frequently exhibit experimental behavior similar to aqueous protonic acids and bases. An example of this analogy are the reactions involved in the classical Mohr determination of  $\text{Cl}^-$  and those involved in a standard proton determination using  $\text{OH}^-$  and phenolphthalein ( $:\text{In}^-$ ) as an indicator. These may be represented in simplistic terms as shown in eq 25 and 26. The color changes

#### Neutralization



#### Indicator Change

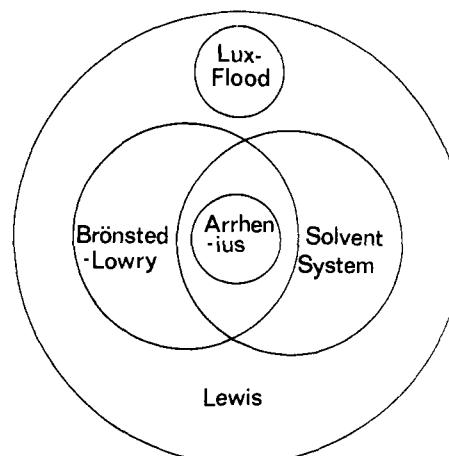


occurring upon neutralization of the weakly basic indicator species can be rationalized in principle by the theory of charge-transfer complexes developed by Mulliken.

Historically, of course, it would have been just as reasonable to reverse this analogy and view Brønsted acids as coordination complexes of the  $\text{H}^+$  ion in which  $\text{H}^+$  exhibits a coordination number of one (with an incipient coordination number of two in the case of hydrogen bonding):  $K_a$  values would then be nothing more than the corresponding aqueous instability constants for these complexes.

Solvation, solvolysis, and ionic dissociation phenomena in both aqueous and nonaqueous solutions are subsumed by the Lewis definitions via the coordination model of solvent behavior. Although Sidgwick<sup>6</sup> made early use of this model, its elaboration is largely the work of Drago and Purcell<sup>66</sup> and Gutmann.<sup>67</sup> Solvation is simply an acid–base neutralization between the solute and solvent; ionic dissociation is a solvent-induced displacement reaction within the solute species and solvolysis a solute-induced displacement reaction within the solvent molecule itself. Likewise, such aqueous equilibrium constants as  $K_{\text{instability}}$ ,  $K_{\text{ionization}}$ ,  $K_{\text{hydrolysis}}$ ,  $K_{\text{solubility}}$ ,  $K_b$ , and  $K_a$  all deal with special cases of Lewis reactions in which excess water functions as a reference acid or base.

The concept of electrophilic and nucleophilic reagents has long been used to systematize both organic and organometallic reactions. Nevertheless, many inorganic chemists feel uncomfortable with the apparently arbitrary way in which organic species are divided, depending on the reaction, into acid and base fragments, and question whether such fragments have an objective existence. This discomfort is largely due to the fact that most of our concepts of acid–base behavior are based on the reactions of simple salt-like species in water. Chemical



**Figure 2.** Venn diagram showing the relationship between the various chemical systems classified as acid–base by the five major acid–base definitions.

experience in this area is extensive and is summarized by both our convention for oxidation numbers and our chemical nomenclature. Consequently, one can almost always predict which portion of these salt-like species will act as an acid and which as a base in water by glancing at its formula. However, if one were to consider the reactions of more complex inorganic species which, like organic species, do not exhibit large electronegativity differences between their components, or even salt-like species in a variety of nonaqueous solvents, one would find the same type of apparently arbitrary behavior. It is a reflection of the relative nature of Lewis acidity and basicity discussed above and is a part of the experimental facts, however we interpret them. As for the objective existence of organic acid–base fragments, carbanions have long been well characterized<sup>68–71</sup> and many postulated carbenium and carbonium ion intermediates have actually been detected in superacid solvents.<sup>59,72–74</sup>

It should be noted in passing that the meaning of electrophile and nucleophile has changed somewhat since the time of Ingold. It is currently the vogue to use the terms nucleophilicity and electrophilicity when referring to the kinetic efficiency of a donor–acceptor reaction and the term acid–base strength when referring to its thermodynamic efficiency. Lastly, mention should be made of an interesting article by Sunderwirth giving localized MO representations of some typical organic donor–acceptor reactions.<sup>75</sup>

A number of books have appeared since the early 1960's dealing with both the theoretical<sup>31,76</sup> and descriptive aspects<sup>77–83</sup> of charge-transfer complexes. Of particular interest is a review by Bent<sup>53</sup> which emphasizes both a general donor–acceptor approach to these complexes and the close relationship of this topic to the more traditional area of weak intermolecular forces. Finally, an elementary, but somewhat outdated, discussion of the application of the Lewis concepts to molten salts can be found in an article by Audrieth and Moeller.<sup>84</sup>

## E. Summary and Conclusions

The Lewis definitions are in the final analysis an example of the advantages to be gained by employing generalized electronic reaction types to classify chemical reactions, much as bonds are electronically classified in terms of the ionic, covalent, and metallic bonding models. Within this context it is reasonable to expect a wide variation in the reactivity, degree of donation, types of bonds formed, etc., as the electronic structures of the donor and acceptor are varied. One would also expect that some donors and acceptors will tend to clump into groups having closely related properties which distinguish them from other donors and acceptors, particularly when the periodic chart in-

dicates that they have similar electronic structures. The proton, for example, is unique in being derived from a period having only one active element and in experiencing no Pauli restrictions on its reactions due to an inner kernel of electrons.<sup>50</sup> Likewise, the alkali metal ions and transition metal ions both form groups having their own characteristic properties. These clumpings are reflected in the traditional categories of acid-base, salt formation, and coordination chemistry covered by the Lewis definitions. However, it is almost always possible to find examples of donors and acceptors whose properties represent a gradual transition between the characteristic properties of one group and another, and just as it cannot be denied that these groups have certain unique properties, so it cannot be denied that this uniqueness represents a predictable variation within the larger context of electron-pair donor-acceptor reactions. In short, the systematic use of electronic reaction types can provide an organizational framework for discussing the relation between periodic properties and reactivity.

Whether one prefers the terms generalized acid-base, central atom-ligand, electrophile-nucleophile, cationoid-anionoid, electrophile-electrodote,<sup>30</sup> EPA-EPD agents,<sup>67</sup> donor-acceptor, or the quantum mechanical terminology of closed-shell-closed-shell interactions, the fact remains that the Lewis definitions represent a unique convergence of concepts from such diverse areas as traditional acid-base definitions, coordination chemistry, organic chemistry, organometallic chemistry, solubility, solvolysis, and ionic dissociation phenomena, nonaqueous solvents, molten salt chemistry, weak intermolecular forces, and chemical bonding and reactivity theory. This body of material can, in turn, be related to such areas as photochemistry and electrochemistry via the complementary concepts of free-radical and redox reactions. As such the Lewis definitions offer an outstanding opportunity for presenting the facts and theories of chemistry from a unified viewpoint.

#### IV. Empirical Reactivity Approximations

##### A. General Considerations

From what has been said in section III, it is obvious that any principle which allows the prediction of Lewis acid-base reactivity, even if it be of the rule-of-thumb variety, will be of great importance to the chemist. In this section we will discuss three empirical approaches to the problem of predicting donor-acceptor reactions: the donor number (DN) approach of V. Gutmann, the *E & C* equation of R. S. Drago, and the hard-soft acid-base principle (HSAB) of R. Pearson.

The origins of these approaches reflect, in turn, the variety of phenomena subsumed by the Lewis concepts: donor numbers having evolved from the study of nonaqueous solvents and ionization phenomena, the *E & C* equation from Mulliken's quantum mechanical treatment of weak charge-transfer complexes, and the HSAB principle from a combination of linear free energy treatments of nucleophilic displacement reactions and the study of aqueous stability constants for coordination complexes.

In addition, we will again refer to the theoretical treatments of acid-base reactions derived by Klopman and Mulliken which we discussed in sections II and III:

$$E_{AB} = E_0 - \frac{(\beta_{01} - E_0 S_{01})^2}{(E_1 - E_0)} \quad (9)$$

$$\Delta E = -\frac{q_s q_t}{R_{st}\epsilon} + 2 \sum_{\substack{\text{occupied} \\ \text{orbitals } m \\ \text{of species} \\ B}} \sum_{\substack{\text{unoccupied} \\ \text{orbitals } n \\ \text{of species} \\ A}} \frac{(c_s m c_t n \beta_{st})^2}{(E_m^* - E_n^*)} \quad (11)$$

Equations 9 and 11 are but two examples of the enormous number of procedures for predicting reactivity which have evolved out of organic chemistry within the last two decades. Indeed, the problem of predicting organic reactivity is a subject with a complex and fascinating history of its own.<sup>85</sup> However, eq 9 and 11 have been singled out for two reasons. First, they are the only cases in which the authors have attempted to explicitly connect their approach with the Lewis concepts (which evolved largely within the confines of inorganic chemistry). Second, many of the reactivity treatments used by the organic chemist are of limited scope only. Most correspond to the orbital controlled limit of Klopman's equation and often make use of properties belonging only to a limited number of chemical species (such as conjugated  $\pi$  systems, aromatic-antiaromatic or Hückel-Möbius transition states, etc.).

##### B. Donor and Acceptor Numbers (DN-AN)<sup>21,67,86-98</sup>

As was pointed out in section III, solvation, solvolysis, and ionic dissociation phenomena, in both aqueous and nonaqueous solutions, are subsumed by the Lewis definitions. Donor numbers were developed in order to correlate the behavior of a solute (such as its solubility, redox potential, or degree of ionization) in a variety of donor solvents with a given solvent's coordinating ability, that is, with its basicity or donicity. A relative measure of the basicity of a solvent D is given by the enthalpy of its reaction with an arbitrarily chosen reference acid. For Gutmann's scale the reference acid is  $SbCl_5$ , and the negative of the heat of reaction of a dilute solution of the solvent, D, and of  $SbCl_5$  in 1,2-dichloroethane is called the donor number (DN) or donicity of solvent D.<sup>86</sup> It is assumed (and graphically tested by plotting  $\log K$  of the D- $SbCl_5$  reaction vs. DN) that entropy effects are constant and that one-to-one adducts are formed so that the DN is a reflection of the inherent D- $SbCl_5$  bond strength.

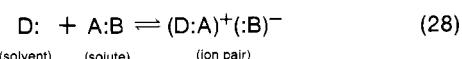
The most important assumption of the DN approach, however, is that the order of base strengths established by the  $SbCl_5$  scale remains constant for all other acids (solute), the value of the  $\Delta H$  formation of a given adduct being linearly related to the DN of the base (solvent) via the equation:

$$-\Delta H_{D \cdot A} = a \cdot DN_D \cdot SbCl_5 + b \quad (27)$$

(where *a* and *b* are constants characteristic of the acid).

Graphically this means that a plot of the DN for a series of donor solvents vs. the  $-\Delta H$  formation of their adducts with a given acid will give a straight line. Example plots are shown in Figure 3. By experimentally measuring the  $\Delta H$  formation of only two adducts for a given acid, one can predict, via the resulting characteristic line of the acid, the  $\Delta H$  formation of its adducts with any other donor solvent for which the DN is known.

An example of the use of DN values is the rationalization of the degree of ionic dissociation of a given solute in a series of donor solvents. The ionization process can be broken conceptually into two steps. The first involves a base displacement whereby the solvent displaces the basic or anionic portion of the solute, giving a solvated ion pair:



The second step involves the separation of the ion pair to give a free solvated cation and an anion. The first step is a function of the DN of the solvent, the second is a function of its local dielectric constant, and the resulting degree of ionization, as measured by the solution's conductivity, is a function of both. Likewise, the shift in  $E^\circ_{red}$  for a species in a variety of solvents can be correlated with the DN of the solvent. The greater the DN, the more electron density is shifted from the solvent to the solute species and the easier it is to remove an electron from the solute

**TABLE VI.** Donicities (DN) and the Dielectric Constants of Various Donor Solvents<sup>a</sup>

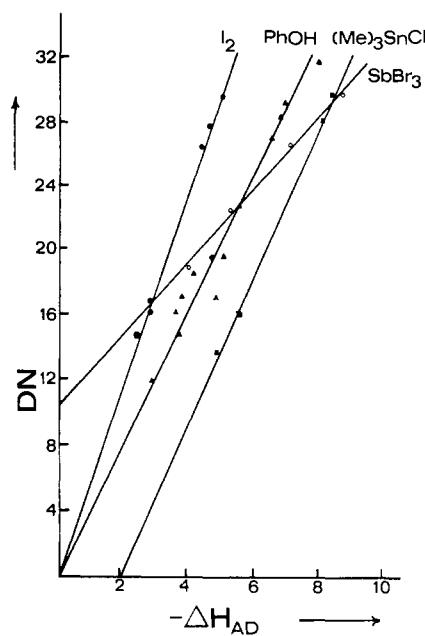
Solvent	DN, kcal mol <sup>-1</sup>	$\epsilon$
1,2-Dichloroethane	10.1	
Benzene	0.1	2.3
Sulfuryl chloride	0.1	10.0
Thionyl chloride	0.4	9.2
Acetyl chloride	0.7	15.8
Tetrachloroethylene carbonate (TCEC)	0.8	9.2
Benzoyl fluoride (BF)	2.3	23.0
Benzoyl chloride	2.3	23.0
Nitromethane (NM)	2.7	35.9
Dichloroethylene carbonate (DEC)	3.2	31.6
Nitrobenzene (NB)	4.4	34.8
Acetic anhydride	10.5	20.7
Phosphorus oxychloride	11.7	14.0
Benzonitrile (BN)	11.9	25.2
Selenium oxychloride	12.2	46.0
Acetonitrile (AN)	14.1	38.0
Sulfolane (tetramethylene sulfone, TMS)	14.8	42.0
Dioxane	14.8	2.2
Propanediol 1,2-carbonate (PDC)	15.1	69.0
Benzyl cyanide	15.1	18.4
Ethylene sulfite (ES)	15.3	41.0
Isobutyronitrile	15.4	20.4
Propionitrile	16.1	27.7
Ethylene carbonate (EC)	16.4	89.1
Phenylphosphonic difluoride	16.4	27.9
Methyl acetate	16.5	6.7
n-Butyronitrile	16.6	20.3
Acetone (AC)	17.0	20.7
Ethyl acetate	17.1	6.0
Water	18.0 (33.0 <sup>b</sup> )	81.0
Phenylphosphonic dichloride	18.5	26.0
Diethyl ether	19.2	4.3
Tetrahydrofuran (THF)	20.0	7.6
Diphenylphosphonic chloride	22.4	
Trimethyl phosphate (TMP)	23.0	20.6
Tributyl phosphate (TBP)	23.7	6.8
Dimethoxyethane (DME)	≈24	7.2
Dimethylformamide (DMF)	26.6	36.1
N-Methyl-ε-caprolactam (NMC)	27.1	
N-Methyl-2-pyrrolidinone (NMP)	27.3	
N,N-Dimethylacetamide (DMA)	27.8	37.8
Dimethyl sulfoxide (DMSO)	29.8	45.0
N,N-Diethylformamide (DEF)	30.9	
N,N-Diethylacetamide (DEA)	32.2	
Pyridine (py)	33.1	12.3
Hexamethylphosphoramide (HMPA)	38.8	30.0
Hydrazine	44.0 <sup>b</sup>	51.7
Ethylenediamine	55.0 <sup>b</sup>	14.2
Ethylamine	55.5 <sup>b</sup>	6.9
Isopropylamine	57.5 <sup>b</sup>	6.0
tert-Butylamine	57.5 <sup>b</sup>	6.0
Ammonia	59.0 <sup>b</sup>	17.0
Triethylamine	61.0	

<sup>a</sup> Values are taken from ref 97. <sup>b</sup> Bulk donicity, e.g., the donicity of the solvent in the associated liquid.

(i.e., the more negative  $E_{\text{red}}^{\circ}$  becomes). DN values have been measured for about 53 donor solvents. A selection of typical DN values is shown in Table VI.

An approach similar to Gutmann's has been used by Satchell and Satchell<sup>99,100</sup> to measure the relative strength of a series of bases toward a large variety of acidic metal halides. They measure  $-\log K$  of the reaction between the acid and base in a dilute solution and use the hydronium ion as their reference acid. Again  $-\log K$  of a given metal halide-base reaction is linearly related to the  $-\log K$  of the corresponding  $\text{H}_3\text{O}^+$ -base reaction (i.e.,  $pK_a$  of the base in the Brønsted sense) via the equation:

$$pK_{AB} = apK_a + b \quad (29)$$



**Figure 3.** Typical donor number plots showing that the heats of formation of the adducts between a given acid and a series of bases are linearly proportional to the donor numbers of the bases involved. Data points have not been labeled with the corresponding bases to simplify the graph.

**TABLE VII. Acceptor Numbers (AN) and Corresponding  $^{31}\text{P}$  NMR Shifts Induced in  $\text{Et}_3\text{PO}$  for a Variety of Acceptor Solvents<sup>a</sup>**

Solvents	$\delta^{31}\text{P}$ , ppm	AN
Hexane (reference solvent)	0	0
Diethyl ether	-1.64	3.9
Tetrahydrofuran (THF)	-3.39	8.0
Benzene	-3.49	8.2
Carbon tetrachloride	-3.64	8.6
Diglyme	-4.20	9.9
Glyme	-4.35	10.2
HMPA	-4.50	10.6
Dioxane	-4.59	10.8
Acetone	-5.33	12.5
N-Methyl-2-pyrrolidinone (NMP)	-5.65	13.3
DMA	-5.80	13.6
Pyridine	-6.04	14.2
Nitrobenzene (NB)	-6.32	14.8
Benzonitrile (BN)	-6.61	15.5
DMF	-6.82	16.0
Dichloroethane carbonate (DEC)	-7.11	16.7
PDC	-7.77	18.3
$\text{CH}_3\text{CN}$	-8.04	18.9
DMSO	-8.22	19.3
$\text{CH}_2\text{Cl}_2$	-8.67	20.4
Nitromethane (NM)	-8.74	20.5
$\text{CHCl}_3$	-9.83	23.1
Isopropyl alcohol	-14.26	33.5
Ethyl alcohol	-15.80	37.1
Formamide	-16.95	39.8
Methyl alcohol	-17.60	41.3
Acetic acid	-22.51	52.9
Water	-23.35	54.8
$\text{CF}_3\text{COOH}$	-44.83	105.3
$\text{CH}_3\text{SO}_3\text{H}$	-53.77	126.3
$\text{SbCl}_5$ as ref in DCE	-42.58	100

<sup>a</sup> Values are taken from ref 97.

where again  $a$  and  $b$  are constants characteristic of the acid. Both eq 27 and 29 contain three parameters: one for each base (DN and  $pK_a$ , respectively) and two for each acid (the  $a$ 's and  $b$ 's, or characteristic slopes and intercepts).

Mayer and Gutmann<sup>101</sup> have recently introduced an analogous acceptor number (AN) scale for the correlation of solute-solvent

TABLE VIII. Acid and Base Parameters<sup>a</sup>

Acid	A. Acid Parameters			C <sub>A</sub>	E <sub>A</sub>
	C <sub>A</sub>	E <sub>A</sub>	Acid		
Iodine	1.00	1.00	Perfluoro- <i>tert</i> -butyl alcohol	0.731	7.34
Iodine monochloride	0.830	5.10	Boron trifluoride (gas)	1.62	9.88
Iodine monobromide	1.56	2.41	Trimethylboron	1.70	6.14
Thiophenol	0.198	0.987	Trimethylaluminum	1.43	16.9
<i>p</i> - <i>tert</i> -Butylphenol	0.387	4.06	Triethylaluminum	2.04	12.5
<i>p</i> -Methylphenol	0.404	4.18	Trimethylgallium	0.881	13.3
Phenol	0.442	4.33	Triethylgallium	0.593	12.6
<i>p</i> -Fluorophenol	0.446	4.17	Trimethylindium	0.654	15.3
<i>p</i> -Chlorophenol	0.478	4.34	Trimethyltin chloride	0.0296	5.76
<i>m</i> -Trifluoromethylphenol	0.530	4.48	Sulfur dioxide	0.808	0.920
<i>tert</i> -Butyl alcohol	0.300	2.04	Bis(hexafluoroacetylacetone)copper(II)	1.40	3.39
Trifluoroethanol	0.451	3.88	Antimony pentachloride	5.13	7.38
Hexafluoroisopropyl alcohol	0.623	5.93	Chloroform	0.159	3.02
Pyrrole	0.295	2.54	1-Hydroperfluoroheptane	0.226	2.45
Isocyanic acid	0.258	3.22	Methylcobaloxime	1.53	9.14
Isothiocyanic acid	0.227	5.30	Bis(hexamethyldisilylamo)zinc(II)	1.09	4.94
Base	B. Base Parameters <sup>a</sup>			C <sub>B</sub>	E <sub>B</sub>
	C <sub>B</sub>	E <sub>B</sub>	Base		
Pyridine	6.40	1.17	Chloroacetonitrile	0.530	0.940
Ammonia	3.46	1.36	Dimethylcyanamide	1.81	1.10
Methylamine	5.88	1.30	Dimethylformamide	2.48	1.23
Dimethylamine	8.73	1.09	Dimethylacetamide	2.58	1.32
Trimethylamine	11.54	0.808	Ethyl acetate	1.74	0.975
Ethylamine	6.02	1.37	Methyl acetate	1.61	0.903
Diethylamine	8.83	0.866	Acetone	2.33	0.987
Triethylamine	11.09	0.991	Diethyl ether	3.25	0.963
Acetonitrile	1.34	0.886	Isopropyl ether	3.19	1.11
<i>n</i> -Butyl ether	3.30	1.06	Benzene	0.681	0.525
<i>p</i> -Dioxane	2.38	1.09	<i>p</i> -Xylene	1.78	0.416
Tetrahydrofuran	4.27	0.978	Mesitylene	2.19	0.574
Tetrahydropyran	3.91	0.949	2,2,6,6-Tetramethylpyridine N-oxyl	6.21	0.915
Dimethyl sulfoxide	2.85	1.34	1-Azabicyclo[2.2.1]octane	13.2	0.704
Tetramethylene sulfoxide	3.16	1.38	7-Oxabicyclo[2.2.1]heptane	3.76	1.08
Dimethyl sulfide	7.46	0.343	Dimethyl selenide	8.33	0.217
Diethyl sulfide	7.40	0.339	1-Phospho-4-ethyl-1,5,7-trioxabicyclo[2.2.1]octane	6.41	0.548
Trimethylene sulfide	6.84	0.352	Hexamethylphosphoramide	3.55	1.52
Tetramethylene sulfide	7.90	0.341	1-Methylimidazole (imine nitrogen)	8.96	0.934
Pentamethylene sulfide	7.40	0.375	Trimethyl phosphite	5.99	1.03
Pyridine N-oxide	4.52	1.34	4-Picoline	7.71	1.12
4-Methylpyridine N-oxide	4.99	1.36	Piperidine	9.32	1.01
4-Methoxypyridine N-oxide	5.77	1.37	Trimethylphosphine oxide	5.99	1.03
Tetramethylurea	3.10	1.20			
Trimethylphosphine	6.55	0.838			

<sup>a</sup> Values taken from ref 107.

interactions in acidic solvents. They use Et<sub>3</sub>PO as the reference base and correlate the AN of a given solvent with the relative <sup>31</sup>P NMR shift produced by dissolving the reference base in the solvent. AN values are scaled to an arbitrarily chosen value of 100 for the shift produced by the 1:1 Et<sub>3</sub>PO-SbCl<sub>5</sub> adduct in 1,2-dichloroethane. AN values have been measured for 34 solvents. Again, it is assumed that the relative solvent acceptor order established by the Et<sub>3</sub>PO scale remains constant for all other basic solutes. A selection of typical AN values is shown in Table VII. For strongly amphoteric solvents one must, of course, consider the relative importance of both the donor number and acceptor number simultaneously.

### C. The E & C Equation<sup>102-109</sup>

In 1965 Drago and Wayland<sup>102</sup> proposed a four-parameter equation for predicting acid-base reaction enthalpies in the gas phase or in poorly solvating solvents:

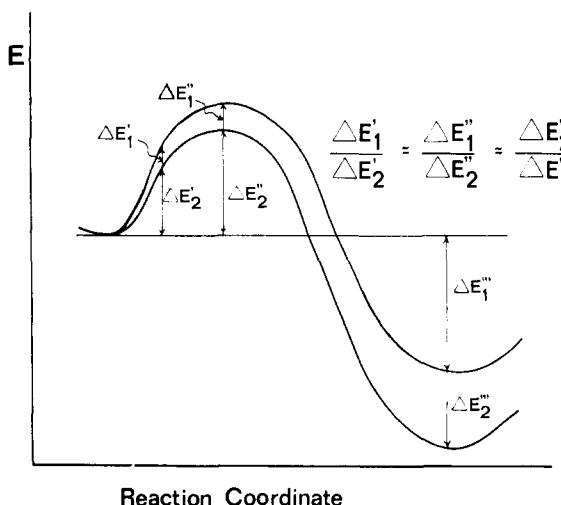
$$-\Delta H_{AB} = E_A E_B + C_A C_B \quad (30)$$

The acid, A, and base, B, are each characterized by two independent parameters: an E value which measures their ability to participate in electrostatic bonding, and a C value which mea-

sures their ability to participate in covalent bonding. Both E and C are derived empirically to give the best curve fit of calculated to experimental heats of formation for the largest possible number of adducts. A self-consistent set of E & C values is now available for about 33 acids and 48 bases, allowing the prediction of  $\Delta H$  for over 1584 adducts.<sup>107</sup> Again, it is assumed that the conditions under which measurements are made (i.e., gas phase or solutions in poorly coordinating solvents) give approximately constant entropy contributions and that most of the adducts are of a one-to-one stoichiometry, making  $\Delta H$  a measure of the inherent A-B bond strength. A selection of typical E and C values is given in Table VIII.

Equation 30 was originally justified by qualitatively appealing to Mulliken's equation (9) for charge-transfer complexes which also divides the energy into electrostatic and covalent contributions. Strictly speaking, however, Mulliken's equation refers to the energy of the final adduct, and it is Klopman's equation (11), which refers to the change in energy upon adduct formation, which parallels Drago's equation.

It is important to note that both eq 9 and 11 can be used in two widely different contexts. Both are second-order perturbations and can be derived from the secular determinant for a one-to-one AB adduct only by assuming that  $E_m^* \gg E_n^*$  and that  $|E_m^* -$



Reaction Coordinate

**Figure 4.** The noncrossing rule. The sign convention in eq 11 is such that favorable initial perturbations give large positive  $\Delta E$ 's. Therefore, the ratio of the perturbation energies, calculated by eq 11, for two alternative reactions is inversely proportional to the ratio of their energies at  $E'$  and  $E''$  and directly proportional to their ratio at  $E'''$ .

$E_n^*|^2 \gg 4\beta_{st}^2$ . That is, the donor and acceptor orbitals differ greatly in energy and the degree of covalent interaction,  $\beta_{st}$ , is small relative to this difference. Hence,  $\Delta E$  of eq 11 approximates the net  $\Delta E$  of reaction only for weakly interacting adducts, many of which have  $\Delta H$  values of the same order of magnitude as strong intermolecular attractions or hydrogen bonds. It is to this class that Drago has applied his equation. Most of the acids and bases for which  $E$  and  $C$  values are known are discrete neutral molecules and most of the resulting adducts have  $\Delta H$  values much less than 50 kcal/mol. Predictably the  $E$  &  $C$  equation fails for many strongly interacting systems, for example, cation-anion reactions.

The second context in which Klopman's equation can be applied assumes that  $\Delta E$  represents not the net  $\Delta E$  of reaction but rather the initial perturbation or change in the energy of the system as it begins to move along the reaction coordinate. If one assumes that the noncrossing rule applies to the energy-reaction coordinate profiles for two alternative reactions (Figure 4), then a qualitative comparison of their initial  $\Delta E$  values, as calculated by eq 11, will also give the order of their  $\Delta E^\ddagger$  values and  $\Delta E$  total values, allowing one to qualitatively predict which reaction will be favored. Thus the equation is used to calculate the relative, rather than the absolute, values of the reaction rates or equilibrium constants of closely related reactions. As long as the noncrossing rule is approximately true, the resulting predictions are independent of the actual shapes of the energy-reaction coordinate profiles and hence of the details of the reaction mechanisms involved. In that eq 11 calculates changes in  $\Delta E$  and not  $\Delta G$ , one must also assume that differences in  $\Delta H$  dominate the differences in  $\Delta G$  and, therefore, that either the changes in  $T\Delta S$  are similar for both reactions or that  $T\Delta S$  is some monotonic function (preferably linear) of  $\Delta H$ . Solvation effects, on the other hand, may be incorporated in eq 11 via the  $\epsilon$  and  $E^*$  orbital parameters.

The assumptions of dominant enthalpy changes and the noncrossing rule, of course, are not true in general. However, for closely related reactions, occurring under the same conditions, for example, two bases competing for the same acid, or an acid choosing between alternative donor sites on an ambient base, the assumptions are sufficiently justified to make the equation a valuable tool for predicting reactivity. It is in this context that eq 11 was used in section III to discuss the relative nature of Lewis acidity and basicity and it is in this sense that it is applied to the HSAB principle, as will be seen in the next section.

TABLE IX. Acid and Base Parameters<sup>a</sup>

A. Acid Parameters		B. Base Parameters			
Acid	D	O	Acid	D	O
H <sup>+</sup>	311.6	81.95	Mg <sup>2+</sup>	253.7	17.75
Li <sup>+</sup>	132.6	9.14	Ca <sup>2+</sup>	213.2	12.45
Na <sup>+</sup>	112.6	5.86	Sr <sup>2+</sup>	199.9	9.13
K <sup>+</sup>	100.0	3.46	Ba <sup>2+</sup>	190.6	7.50
Rb <sup>+</sup>	95.6	2.65	Sc <sup>2+</sup>	234.5	16.85
Cs <sup>+</sup>	90.7	2.90	Ti <sup>2+</sup>	253.8	17.34
Cu <sup>+</sup>	160.1	27.65	Zr <sup>2+</sup>	252.2	74.68
Ag <sup>+</sup>	158.0	18.87	V <sup>2+</sup>	262.5	17.53
Al <sup>+</sup>	155.1	17.54	Cr <sup>2+</sup>	257.4	21.41
In <sup>+</sup>	132.6	8.68	Mn <sup>2+</sup>	255.7	17.11
Tl <sup>+</sup>	129.3	5.74	Fe <sup>2+</sup>	270.8	22.49
CH <sub>3</sub> <sup>+</sup>	204.8	50.00	Co <sup>2+</sup>	273.1	20.47
C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	173.4	40.01	Ni <sup>2+</sup>	283.0	19.73
n-C <sub>3</sub> H <sub>7</sub> <sup>+</sup>	164.0	41.33	Cu <sup>2+</sup>	293.0	21.63
C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	196.1	55.44	Zn <sup>2+</sup>	281.4	22.44
NO <sup>+</sup>	140.0	35.41	Cd <sup>2+</sup>	260.4	17.34
Cl <sup>+</sup>	251.8	52.73	Hg <sup>2+</sup>	294.5	6.87
Br <sup>+</sup>	224.5	38.48	Si <sup>2+</sup>	295.9	24.03
I <sup>-</sup>	196.5	25.73	Ge <sup>2+</sup>	270.3	20.65
Te <sup>2-</sup>	329.6	25.84	Sn <sup>2+</sup>	241.8	18.97
Be <sup>2+</sup>			Pb <sup>2+</sup>	232.5	10.58

<sup>a</sup> Values are taken from ref 109.

Drago's equation relates to eq 9 or eq 11 in the first context, that is, where  $\Delta E$  represents the total change in energy. Hence, in addition to the approximations inherent in eq 11 itself, the  $E$  &  $C$  equation contains the following additional assumptions:

$$\begin{aligned} H_{AB} &\approx E_{AB} \\ R_{st} &\approx R_s \\ E_m - E_n &\approx E_m \end{aligned} \quad (31)$$

Thus:

$$\begin{aligned} E_A &= q_t \\ E_B &= -q_s/R_s \\ C_A &= (c_t^n)^2 \beta_t \\ C_B &= (c_s^m)^2 \beta_s/E_m \end{aligned}$$

Marks and Drago<sup>108,109</sup> have recently derived an alternative empirical equation from the secular determinant for a simple one-to-one AB adduct using approximations suitable for strongly interacting ionic systems:

$$-\Delta H_{AB} = [(D_A - D_B)^2 + (O_A O_B)]^{1/2} \quad (32)$$

Here again the acid and base are each characterized by two independent parameters: a  $D$  value related to the diagonal elements and an  $O$  value related to the off-diagonal elements of the secular determinant. Some example  $D$  and  $O$  values are given in Table IX.

## D. The HSAB Principle

Of the three empirical approaches discussed in this article, the HSAB principle is perhaps the best known.<sup>110</sup> It has been

**TABLE X. Historical Development of Linear Free Energy Relations for Nucleophilic Displacement Reactions**

Brønsted (1924)

$$\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = \alpha \log \left( \frac{K_a \text{ of } B_n}{K_a \text{ of } B_{ref}} \right)$$

for bases where donor atom is oxygen

Swain-Scott (1953)

$$\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = sn$$

s and n both empirical—for bases where donor atom is S, I, etc.

Edwards (1954, 1956)

$$\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = \alpha E_n + \beta H_n$$

$$\log \left( \frac{K_n}{K_{ref}} \right) \text{ or } \log \left( \frac{k_n}{k_{ref}} \right) = a P_n + b H_n$$

 $(\alpha, \beta)$  or  $(a, b)$  are empirical constants characteristic of the substrate at given temperature and solvent

$H_n = pK_a + 1.74$  for base  $B_n$

$E_n = E^\ominus_{ox} + 2.6$  for base  $B_n$

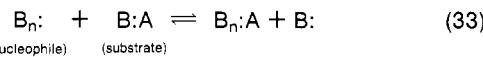
$P_n = \log(R_{B_n}/R_{H_2O})$ , R is refractive index

used to rationalize such diverse phenomena as solubility rules, rules for selection of ligands to stabilize different oxidation states,<sup>111</sup> geometry trends,<sup>112</sup> catalyst poisoning,<sup>113,114</sup> electrode absorption phenomena,<sup>115,116</sup> organic nucleophilic-electrophilic reactivity,<sup>117,118,135</sup> selection of organic catalysts,<sup>119</sup> and most of aqueous inorganic coordination chemistry.<sup>120-123</sup> However, unlike the DN approach and the E & C equation, both of which can be quantitatively tested by their ability to predict the  $\Delta H$  formation of a given adduct, the HSAB principle is, at best, only semiquantitative and predicts only which of two competing reactions will have the most favorable equilibrium constant. It tells us nothing about the absolute values of the constants. Because of this essentially qualitative nature, it is more difficult to pin down the approximations inherent in the HSAB principle. For this reason we will outline its historical evolution as this reveals many of its assumptions and limitations. As noted earlier, this evolution may be succinctly viewed as a fusion of data from the use of linear free energy relations for the correlation of nucleophilic displacement reactions with the study of aqueous stability constants for coordination complexes.

### 1. Linear Free Energy Relations (LFER)

Linear free energy relations<sup>124,125</sup> assume that the relative order of the rate constants or equilibrium constants for a series of closely related reactions, occurring at the same temperature and in the same solvent environment, may be correlated with some ground-state property of the reactants such as their ionization potentials, redox potentials, proton basicities, variations in their substituent groups, etc. This assumption can be shown to be identical with the requirement that the reactions obey the noncrossing rule (Figure 4).

An early application of LFER was in correlating the rates of nucleophilic displacement reactions toward a common substrate with some ground-state property of the attacking nucleophile:



For nucleophiles having oxygen as the donor atom, it was found that the nucleophilicity of the donor could be correlated with its proton basicity or Brønsted  $K_a$  value (eq 1, Table X). This is known as the Brønsted relation, and the resulting equation contains two independent parameters; one for the nucleophile ( $K_a$ ) and one characteristic of the substrate and the reaction conditions ( $\alpha$ ). However, in the 1950's Swain and Scott found that nucleophilic attack at saturated carbon centers by nucleo-

**TABLE XI. Historical Development of Correlations for Aqueous Stability Constants**

Goldschmidt (1922)

Lithophiles

Chalcophiles

Siderophiles

Bjerrum (1950)

 $H^+$ -like cations: correlation of stability of complexes with  $Z/r$  of cation $Hg^{2+}$ -like cations: correlation of stability of complexes with  $E^\ominus_{ox}$  or electronegativity of cation.

Schwarzenbach (1956, 1961)

A class ions  $F^- > I^-$ B class ions  $I^- > F^-$ 

A ions use electrostatic forces. B ions also have sizable covalent contributions which correlate with IP of cation.

Ahrland, Chatt, Davies (1958)<sup>a</sup>

Class (a) ions

$N \gg P > As > Sb > Bi$

$O \gg S > Se > Te$

$F \gg Cl > Br > I$

Class (b) ions

$N \ll P > As > Sb > Bi$

$O \ll S \sim Se \sim Te$

$F < Cl < Br \ll I$

<sup>a</sup> Most data at 25 °C in aqueous solution. Based on  $\log K_{equil}$  or  $\Delta G$  values.

philes having iodine or sulfur as the donor atom did not follow the Brønsted relation. They proposed instead an equation (eq 2, Table X) in which both parameters were empirical.

In 1954 and 1956 Edwards<sup>126,127</sup> partially resolved this conflict by proposing two alternative versions of a four-parameter equation (eq 3 and 4, Table X). Each equation contains two independent parameters characteristic of the substrate and conditions of reaction ( $\alpha$  and  $\beta$  or  $a$  and  $b$ ) and two independent parameters characteristic of the attacking nucleophile (terms proportional to its Brønsted  $pK_a$ ,  $H_n$ , and to either its oxidation potential,  $E_n$ , or its polarizability,  $P_n$ ; see Table X for exact definitions). The Brønsted and Swain-Scott relations may be qualitatively viewed as limiting cases of the Edwards equation. In 1961 Pearson and Edwards<sup>128</sup> summarized the available experimental data on the Edwards equation and concluded that nucleophiles and substrates tended to sort into two large categories: those whose displacement reactions correlated well with the  $pK_a$  of the nucleophile and the  $\beta$  or  $b$  of the substrate, and those correlating well with the  $E_n$  or  $P_n$  of the nucleophile and with  $\alpha$  or  $a$  of the substrate.

### 2. Aqueous Stability Constants

In 1950 Bjerrum<sup>129</sup> wrote an important review "On the Tendency of Metal Ions Toward Complex Formation". He concluded that in aqueous solution metal ions tended to sort into two categories: those which were  $H^+$ -like in behavior and whose complexing ability paralleled their charge-to-size ratio, and those which were  $Hg^{2+}$ -like in behavior and whose complexing ability paralleled their  $E^\ominus_{ox}$  values or electronegativities. The latter class of ions tended to have a large number of d electrons in their valence shells, to favor large polarizable ligands like  $I^-$ , and to bind primarily by means of covalent interactions, whereas the former tended to have inert gas configurations, to favor small unpolarizable bases like the  $F^-$  ion, and to bond primarily by means of electrostatic forces.

In a paper in 1956, and again in 1961, Schwarzenbach<sup>130,131</sup> extended these observations and labeled the  $H^+$ -like group of ions class A acceptors and the  $Hg^{2+}$ -like group class B acceptors. Again, the division was largely based on the relative stabilities in water of the halide complexes. The seminal paper in this area was a 1958 review by Ahrland, Chatt, and Davies.<sup>132</sup> They again divided the species they studied (most of which were

TABLE XII. Correlations Subsumed by the HSAB Principle

Pearson (1963)	
Substrates correlating with $pK_a$ of base (high $\beta$ or $b$ ); class A or (a) acceptors, $H^+$ -like ions or lithophiles	hard acids
Substrates correlating with $E_n$ or $P_n$ of base (high $\alpha$ or $a$ ); class B or (b) acceptors, $Hg^{2+}$ -like ions or chalcophiles	soft acids
Bases with large $pK_a$ values; donors high on the class (a) affinity series	hard bases
Bases with large $E_n$ or $P_n$ values; donors high on class (b) affinity series	soft bases

aquated ions) into class (a) and class (b) acceptors, paralleling Schwarzenbach's class A and class B categories. They, however, extended the data used to characterize each class to include bases having group V and group VI, as well as group VII, donor atoms. Their stability series are shown in Table XI.

Although not directly related to the topic of aqueous stability constants, an interesting precursor of these conclusions is to be found in the studies which Goldschmidt<sup>133</sup> made in the 1920's on the geological distribution of the elements. He found that the elements (in ionic form) tended to preferentially sort into either an oxide environment (lithophilic elements) or a sulfide environment (chalcophilic elements), an observation which goes back at least as far as Berzelius in the first half of the 19th century. The ions of lithophilic elements tend to be identical with class A or (a) acceptors and those of chalcophilic elements with class B or (b) acceptors.

### 3. HSAB Rules

In 1963 Pearson<sup>134</sup> unified the conclusions from his earlier study of the Edwards equation with those deduced from the study of aqueous stability constants and made the identifications in Table XII. He also proposed the following rules to summarize the experimental data:<sup>117,135–139</sup>

*Rule 1.* Equilibrium: Hard acids prefer to associate with hard bases and soft acids with soft bases.

*Rule 2.* Kinetics: Hard acids react readily with hard bases and soft acids with soft bases.

The idea that the kinetics and thermodynamics of a series of reactions follow the same correlation is valid only to the extent that the reactions obey the noncrossing rule. A selection of typical hard and soft acids and bases is given in Table XIII.

## E. Problems of Interpretation

### 1. Gas-Phase-Noncoordinating Solvents

The terms hard and soft reveal the debt which the HSAB principle owes to the Edwards equation. In his early papers Pearson pointed out that the experimental inversions in the affinity series, corresponding to the class (a) and (b) categories, required that the reactivity of a Lewis acid or base depend on something more than a single monotonic scale of relative strengths like those determined by competitive equilibria with an arbitrarily chosen reference acid or base. It is this additional factor which Pearson called the hard–soft parameter (after a suggestion made by D. H. Busch), soft corresponding to a large value of the parameter and hard to a small value. In later papers Pearson further clarified this definition by suggesting that a possible quantitative statement of the HSAB principle would be an equation of the form:

$$\log K = S_A S_B + \sigma_A \sigma_B \quad (34)$$

where  $K$  is the equilibrium constant for the formation of  $AB$ , the  $S$ 's represent the strength factors for the acid and base, and the  $\sigma$ 's represent the hard–soft factors. The analogy of these terms to the  $\beta_{H_n}$  and  $\alpha_{E_n}$  or  $a_{P_n}$  terms of the Edwards equation is obvious and has been qualitatively confirmed by Yingst and McDaniel.<sup>140</sup>

TABLE XIII. Classification of Hard and Soft Acids and Bases

A. Acids	
Hard Acids	
$H^+, Li^+, Na^+, K^+ (Rb^+, Cs^+)$	
$Be^{2+}, Be(CH_3)_2, Mg^{2+}, Ca^{2+}, Sr^{2+} (Ba^{2+})$	
$Sc^{3+}, La^{3+} = Ce^{4+}, Gd^{3+}, Lu^{3+}, Th^{4+}, U^{4+}, UO_2^{2+}, Pu^{4+}$	
$Ti^{4+}, Zr^{4+}, Hf^{4+}, VO^{2+}, Cr^{3+}, Cr^{6+}, MoO_3^{2+}, WO_4^{2+}, Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+}$	
$BF_3, BC_2, B(OR)_3, Al^{3+}, Al(CH_3)_3, AlCl_3, AlH_3, Ga^{3+}, In^{3+}$	
$CO_2, RCO^+, NC^+, Si^{4+}, Sn^{4+}, CH_2Sn^{3+}, (CH_3)_2Sn^{2+}$	
$N^{3+}, RPO_2^+, ROPO_2^+, As^{3+}$	
$SO_3, RSO_2^+, ROSO_2^+$	
$Cl^{3+}, Cl^{7+}, I^{3+}, I^{7+}$	
$HX$ (hydrogen-bonding molecules)	
Borderline Acids	
$Fe^{2+}, CO_2^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$	
$Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}$	
$(CH_3)_3, GaH_3$	
$R_3C^+, C_6H_5^+, Sn^{2+}, Pb^{2+}$	
$NO^+, Sb^{3+}, Bi^{3+}$	
$SO_2$	
Soft Acids	
$Co(CN)_5^{3-}, Pd^{2+}, Pt^{2+}, Pt^{4+}$	
$Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+, Hg^{2+}, CH_3Hg^+$	
$BH_3, Ga(CH_3)_3, GaCl_3, GaBr_3, GaI_3, Ti^+, Ti(CH_3)_3$	
$CH_2$ , carbenes	
$\pi$ acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, etc.	
$HO^+, RO^+, RS^+, RSe^+, Te^{4+}, RTe^+$	
$Br_2, Br^+, I_2, I^+, ICN$ , etc.	
bulk metals	
B. Bases	
Hard Bases	
$NH_3, RNH_2, N_2H_4$	
$H_2O, OH^-, O^{2-}, ROH, RO^-, R_2O$	
$CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-$	
$F^-(Cl^-)$	
Borderline Bases	
$C_6H_5NH_2, C_5H_5N, N_3^-, N_2$	
$NO_2^-, SO_3^{2-}$	
$Br^-$	
Soft Bases	
$H^-$	
$R^-, C_2H_4, C_6H_6, CN^-, RNC, CO$	
$SCN^-, R_3P, (RO)_3P, R_3As$	
$R_2S, RSH, RS^-, S_2O_3^{2-}$	
$I^-$	

Equation 34 is not intended for actual application. However, it clearly indicates that strength and hardness–softness are to represent two independent factors and that the HSAB rules, which are based solely on a consideration of the hard–soft parameters of the acid and base, are two-parameter correlations which correspond to the limiting cases of some more general four-parameter equation. Even then, the rules are true only if, in general, hard species are always strong and soft species always weak. This is not always the case, and Pearson himself has noted many examples for which the predictions of the HSAB rules are incorrect owing to the intervention of strength factors.

There are a number of ways to empirically determine the strength and softness of a given species. One can establish scales based on competitive equilibria with an arbitrarily chosen reference acid or base by using a typically hard but strong standard for the strength scale (such as  $H^+$  or  $OH^-$ ) and a typically weak but soft standard for the softness scale (such as  $HgCH_3^+$  or  $I^-$ ). Thus, for example, Brønsted  $pK_a$  values are often used to characterize the strength of a given Lewis base as in the Edwards equation. One might also attempt to correlate strength and softness with the electronic structures of the species or with

**TABLE XIV. Properties Used to Categorize Species as Hard or Soft**

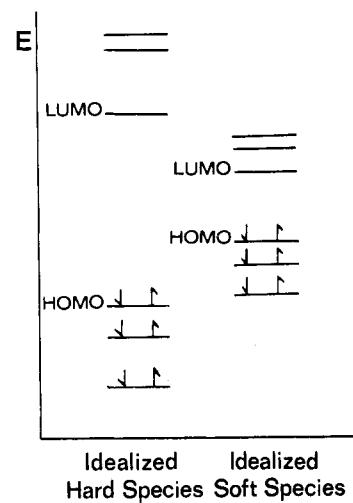
Soft
High polarizability
Low $pK_a$ (bases)
Low oxidation state (acids)
Easy to oxidize, low $E^\circ_{\text{red}}$ , low IP (bases)
Easy to reduce, high $E^\circ_{\text{red}}$ (acids), low on electromotive series
Large size
Low electronegativity differences between donor and acceptor atoms <sup>a</sup>
Low positive charge density at acceptor site (acids)
Low negative charge density at donor site (bases)
Often have low-lying empty orbitals suitable for $\pi$ back-bonding (bases)
Often have large number of d electrons (acidic cations)
Hard
Low polarizability
High $pK_a$ (bases)
High oxidation state (acids)
Hard to oxidize, high $E^\circ_{\text{red}}$ , large IP (bases)
Hard to reduce, low $E^\circ_{\text{red}}$ (acids), high on electromotive series
Small size
High electronegativity difference between donor and acceptor atoms <sup>a</sup>
High positive charge density at acceptor site (acids)
High negative charge density at donor site (bases)

<sup>a</sup> This refers to the electronegativity of the donor and acceptor sites as atoms as it is for this state that most electronegativity scales are calculated. If one uses electronegativity in the Hinze-Jaffe sense then one can define the electronegativities of full and empty orbitals, ions, etc., in which case the reverse statements are true. Thus Na and F have a large electronegativity difference whereas  $\text{Na}^+$  and  $\text{F}^-$  have a small difference.

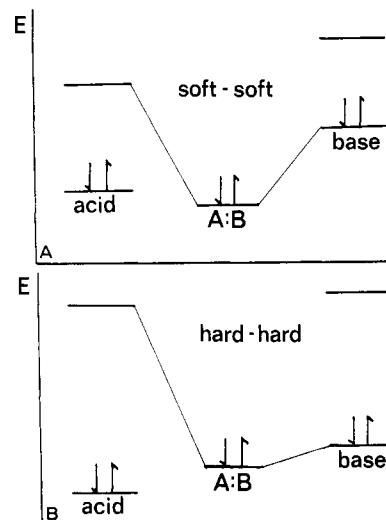
periodic trends in properties which, in turn, reflect periodic trends in the electronic structures. Although both of these approaches have been used to sort species, like those in Table XIII, into the categories of hard, soft, and borderline, in general emphasis is placed on the second method.

Table XIV lists many of the properties used to categorize a given species as hard or soft. Jorgensen<sup>141</sup> has pointed out that the properties in the first list point to species having a high density of low-lying states or empty orbitals, whereas the properties in the second list point to species having isolated ground states (Figure 5). If, for the moment, we restrict ourselves to reactions in the gas phase or in poorly coordinating solvents, then these properties imply that soft species have a high probability of initially interacting via favorable short-range orbital perturbations, that is, via covalent interactions (Figure 6A). On the other hand, the initial orbital perturbations experienced by hard species will not be as favorable, owing to the large energy separation between their frontier orbitals, and they will have to interact primarily by means of long-range electrostatic forces due to the presence of any permanent dipoles or net charges they might possess (Figure 6B). It is interesting to note that favorable orbital perturbations for closed-shell species can only occur between complements, that is between the LUMO on an acid and the HOMO on a base. The interaction of two empty acceptor orbitals, of course, does not generate a bonding situation and that between two donor orbitals requires that both the resulting bonding and antibonding "inter" molecular orbitals be populated, leading to a net repulsive interaction. Open-shell species or free radicals are not specific in the same way. The interaction of a singly occupied molecular orbital or SOMO with a LUMO, HOMO, or another SOMO will give a favorable perturbation. Hence, free radicals are generally highly reactive, particularly with soft species which are likely to have a large variety of energetically available orbitals.

Thus, under these conditions, it is not unreasonable to equate softness with susceptibility to covalent bonding or with the orbital control term of Klopman's equation (and hardness with its absence), and strength with susceptibility to electrostatic bonding or with the charge control term of Klopman's equation.<sup>142</sup> In short, soft acids are characterized by low-lying acceptor orbitals and soft bases by high-lying donor orbitals. Hard acids and bases



**Figure 5.** Idealized hard and soft species. Soft species are characterized by a high density of low-lying empty orbitals and/or by a high-lying HOMO. Hard species are characterized by isolated ground states, i.e., by relatively few high-lying empty orbitals and/or by a low-lying HOMO.



**Figure 6.** Initial orbital perturbations for soft-soft vs. hard-hard interactions. The former are characterized by a large initial orbital perturbation due to a small acid(LUMO)-base(HOMO) energy gap. The latter are characterized by a small initial orbital perturbation due to a large acid(LUMO)-base(HOMO) energy gap and must react by means of any net charges or permanent dipoles they happen to possess.

have the opposite properties. Strong acids are characterized by large net positive charge densities at the acceptor atom and strong bases by large net negative charge densities at the donor atom. Weak acids and bases have small net charge densities. Klopman's equation is both the most sophisticated and the most successful theoretical rationale of the HSAB principle given to date.

Again, if we restrict ourselves to reactions in the gas phase or in poorly solvating solvents in which the number of bonds broken equals the number made (so that the making or breaking of a single strong bond will not be overshadowed by the making or breaking of several weak bonds) and the total number of independent particles remains constant (so that entropy effects are approximately constant), then it is reasonable that a qualitative estimate of the relative strengths of the bonds made and broken for two alternative reactions will allow one to predict which reaction will have the most favorable equilibrium constant. This, in turn, can be done by using the properties in Table XIV to make an educated, but qualitative, guess about the relative strength and softness of each species in the system and hence

about its relative ability to participate in short-range covalent interactions vs. long-range electrostatic interactions. These conditions are most generally met in the case of homogeneous double displacement reactions for which HSAB predictions are usually correct.

It is important to note the repeated use of the word relative. In a system containing  $\text{Cs}^+(\text{g})$ ,  $\text{F}^-(\text{g})$ , and  $\text{I}^-(\text{g})$ , for example, the  $\text{Cs}^+$  ion is a strong hard acid, and theoretical cycle calculations indicate that it will prefer the hard but strong  $\text{F}^-$  ion over the softer  $\text{I}^-$  ion.<sup>143</sup> In the  $\text{Li}^+(\text{g})$ ,  $\text{Cs}^+(\text{g})$ ,  $\text{F}^-(\text{g})$ ,  $\text{I}^-(\text{g})$  system, on the other hand, the  $\text{Cs}^+$  ion is both soft and weak relative to  $\text{Li}^+$  and will end up with the  $\text{I}^-$  ion instead.

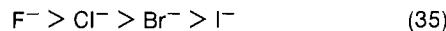
As can be seen from Table XIV, most of the properties used to characterize hard species are, in fact, properties characterizing strength. Hardness itself is, strictly speaking, a negative property, corresponding only to a lack of softness (electron polarizability, covalent bonding capacity, etc.). For many monoatomic ionic species it so happens that those properties which make a species strong also make it hard, and this appears to be both a source of confusion and the reason the HSAB rules work as often as they do. However, in general, hardness need not imply strength nor softness lack of strength, and one must estimate both factors.  $\text{CO}_2$ , for example, is a hard but weak acid, whereas  $\text{S}^{2-}$  is a soft but strong base.

## 2. Coordinating Solvents

When we consider reactions in strongly solvating solvents, two alternative courses of action are available. We can retain the relative values of strength and softness assigned to species in the gas phase, assign similar parameters to the solvent, and explicitly treat any solvation-desolvation effects as additional competing acid-base reactions, or we can absorb any solvation-desolvation effects in the strength and softness parameters themselves thereby making them a function of the solvent environment in which the species finds itself.

It is the latter course which has been taken in the HSAB principle. In the Edwards equation, for example,  $\text{pK}_a$  and  $E^\circ_{\text{ox}}$  do not measure the proton affinity and ionization potential of an isolated gas-phase species, but rather those of a solvated species. Likewise, most of the theoretical scales proposed for strength and softness include solvation effects.<sup>34,144-146</sup> In Klopman's equation, for example, the charge control term is modified by the dielectric constant of the solvent and in the orbital control term the energies of the donor and acceptor orbitals,  $E_m^*$  and  $E_n^*$ , are corrected for the energy of any solvation or desolvation which might accompany changes in the net charges of the species due to the addition or removal of electrons from the orbitals.

We would expect, then, that any solvent which preferentially interacts with either strong hard species or weak soft species will tend to strongly differentiate their experimental behavior and will lead to inversions in affinity series like those observed in water. Theoretical cycle<sup>143</sup> calculations, for example, for simple gas-phase neutralization reactions between monoatomic metal cations and halide anions indicate that almost all metal ions exhibit the same affinity series in the gas phase:



The same reactions for aquated ions, however, result in those inversions which characterize class (a) vs. class (b) acceptors. Thermodynamic studies<sup>147-150</sup> on aqueous ions show that strong hard-hard interactions are often endothermic, the driving force being due to the entropy increase resulting from the destruction, upon complex formation, of the highly organized solvation spheres about each ion. Soft, but weak, ions, on the other hand, are poorly solvated in water and indeed may actually break up the hydrogen-bonding structure of the pure solvent. Their reactions are usually exothermic and may be accompanied by a

slight decrease in entropy due to the restoration of solvent structure. The same type of differentiation should occur with a typically soft solvent although soft-soft interactions tend to be short range and highly directional so that solvation numbers should be smaller and entropy effects less significant than for strong, hard solvents like water. The data for soft solvents are not as extensive as those for water but tend to qualitatively support these conclusions.<sup>151-153</sup>

## F. Comparisons and Conclusions

It is difficult to untangle the manner in which the DN approach, the  $E$  &  $C$  equation, and the HSAB principle are interrelated. If one accepts Klopman's equation as the best rationale, then the HSAB principle appears to rely heavily on the validity of the noncrossing rule, and strength and softness appear to be related to the relative initial susceptibility of a species to long-range electrostatic vs. short-range orbital perturbations in a given solvent environment and reaction system. These initial susceptibilities, when used to estimate the initial perturbation energies of alternative reactions, give, in turn, an estimation of the relative stabilities of the products within the limits of the noncrossing hypothesis. However, as they represent the situation in the early stages of the reaction, they will not, in general, represent the final distribution of covalent vs. ionic bonding contributions in the products. If they did, we would expect soft-soft adducts to be completely covalent and strong hard-hard adducts to be completely ionic (as has been frequently assumed). Bonding studies<sup>154</sup> indicate that sizable covalent contributions exist even in such strong hard-hard adducts as  $\text{HF}$  and  $\text{LiF}$ .

Again, it is worth emphasizing that not only is one assuming the noncrossing hypothesis but that enthalpy rather than entropy changes are the dominant factor in differentiating between the reactions being compared. This assumption is less severe than the assumption that  $T\Delta S = 0$  and does not necessarily require that the  $T\Delta S$  changes be the same for both reactions or that the reactions be exothermic. All that is necessary is that  $T\Delta S$  be some roughly monotonic function of  $\Delta H$ . These assumptions are perhaps not unreasonable for closely related organic reactions in which the components do not exhibit extremely large variations in electronegativity and hence in net charge densities. For the reactions of highly charged ions in a polar solvent like water they are more open to question. Indeed, the significant role which entropy effects play in stabilizing strong hard-strong hard interactions in these systems suggests that the qualitative agreement between predictions based on  $\Delta E$  and experimental data based on  $\Delta G$  may often be due to a fortuitous compensation of effects. In light of these problems it is remarkable just how successful Klopman's equation is in predicting chemical reactivity.

As pointed out, the HSAB rules, which are based solely on a consideration of the softness parameters, are not strictly valid. In general one must estimate both the strength and softness of the species involved. The terminology of the HSAB principle is in many ways unfortunate. Most chemists would consider  $K_{\text{equil}}$ , or perhaps  $\Delta H$ , as a measure of the strength of a Lewis acid-base reaction, and the idea that strength (in the thermodynamic sense) is itself a function of strength (in a more limited sense?), plus an additional factor called softness, can easily lead to confusion. It appears to semantically imply that one has succeeded in separating magnitude from quality. That such confusion exists is borne out by the fact that most popular accounts of the HSAB principle fail to mention strength at all or, if they do, they fail to operationally define it (as strength in the Brønsted sense, for example). Use of the term hard in its popular, but incorrect, sense as synonymous with strength would require that some species be simultaneously both hard and soft in contrast to the accepted dictionary definition of these words as representing mutually exclusive properties. The best choice appears

TABLE XV. Comparison of "Two" Term Reactivity Equations for Lewis Acid-Base Systems

Author	First term	Second term(s)
Mulliken (1951)	Electrostatic or "no bond" term $[E_0]$	Charge-transfer or resonance term $\frac{(\beta_{01} - S_{01}E_0)^2}{(E_1 - E_0)}$
Hudson and Klopman (1967)	Charge control term $\left[ \frac{-q_s q_t}{R_{st}^{\epsilon}} \right]$	Orbital control term $\left[ 2 \sum_{\text{occ.}} \sum_{\text{unocc.}} \frac{(c_s^m c_t^n \beta_{st})^2}{(E_m^* - E_n^*)} \right]$
Drago and Wayland (1965)	Electrostatic factors $[E_A \cdot E_B]$	Covalent factors $[C_A \cdot C_B]$
Pearson (1963)	Strength factors $[S_A \cdot S_B]$	Hardness-softness factors $[\sigma_A \cdot \sigma_B]$
Edwards (1954) (1956)	Basicity factors $\left[ b \cdot H_n \right]$ or $\beta H_n$	Nucleophilicity factors $\left[ a \cdot P_n \right]$ or $\alpha \cdot E_n$
Kossel and Fajans (1916-1928)	Ion-permanent dipole term $\left[ \frac{-eP}{r^2} \right]$	Polarization <sup>a</sup> terms $\left[ \frac{-ep'}{r^2} - \frac{2(P + p')P_A}{r^3} + \frac{(P')^2}{2\alpha} + \frac{P_A^2}{2\alpha_A} \right]$

<sup>a</sup> The terms in the Kossel-Fajans expression are as follows:  $P$  = permanent dipole of ligand,  $p'$  = additional induced dipole of ligand,  $\alpha$  = polarizability of ligand,  $P_A$  = dipole or quadrupole moment induced on central atom,  $\alpha_A$  = polarizability of central atom,  $e$  = electron charge,  $r$  = interaction distance.

to be the charge control-orbital control terminology introduced by Klopman.

Because in the  $E & C$  equation the magnitudes of  $E$  and  $C$  are scaled so as to actually reproduce the  $\Delta H$  of reaction, it is unclear whether they also represent initial susceptibilities or the actual distribution of covalent-ionic contributions in the final bonding. A plausible rationale for the  $E$  and  $C$  parameters was given earlier. However, whether  $E$  and  $C$  values quantitatively correspond to these identities is not known and, given their empirical nature, it is doubtful. Experience, in any case, has shown that  $E$  and  $C$  values do not parallel the qualitative concepts of strength and softness very well in their behavior, although there is an obvious kinship between the two approaches, at least in the gas phase.

The advantage of the  $E & C$  approach is that it is only applied to carefully defined systems and it is fully quantitative in its predictions. The disadvantages are that, in its present form, it cannot be applied to the strongly solvated systems generally of interest to the synthetic chemist and its use of purely empirical numbers disguises any relationship between Lewis acid-base reactivity and chemical periodicity.

Table XV summarizes the variety of "two"-term equations which have been proposed to correlate the reactivity of Lewis acid-base systems.<sup>155</sup> We do not mean to imply that the terms in each column are mathematically equivalent, but rather that all of the approaches converge to a model containing a term characteristic of long-range electrostatic perturbations (column 1) and a term (or terms) characteristic of short-range orbital perturbations (column 2). If each of these terms is, in turn, decomposed into a contribution characteristic of the acid and a contribution characteristic of the base, we arrive at a four-parameter reactivity equation. However, the model or molecular property used to approximate each term is different in each case.

For the sake of historical completeness, we have included the electrostatic model of coordination complex formation whose essential principles were outlined by Kossel and Fajans between 1916 and 1928.<sup>156</sup> The model assumed that the primary driving force of complex formation was the electrostatic attraction between the net ionic charges or permanent dipoles of the central atom and the ligands (term I). However, this interaction could be modified by the mutual polarization of both the central atom and ligands (term II), a factor which, in turn, depended on both their ability to polarize and to be polarized (i.e., their polarizability). This second term could actually lead to an inversion of the affinity orders dictated by the first term alone.

One important use of the Kossel-Fajans model was in rationalizing the differences in reactivity shown by the inert gas IA and IIA ions and that shown by the d electron containing IB and IIB ions. The latter were considered to be both inherently stronger polarizers and more polarizable (owing to the poor nuclear

shielding and penetration of the d electrons) than their IA and IIA counterparts. Their chemistry was therefore dictated by the polarization terms whereas that of the inert gas ions was dictated by the electrostatic terms. The parallel between this concept and the HSAB rules is obvious.

The polarization term may be viewed as an attempt to approximate the orbital perturbation term with a classical model. For strong perturbations, however, it fails. In fact, in the Mulliken equation, polarization effects are completely absorbed within the electrostatic term  $E$ .

As was shown in section II, Klopman's equation and Mulliken's equation are essentially equivalent. This is clearly seen if one derives Klopman's expression using configuration interaction.<sup>40,41</sup> However, the reactivity implications of Mulliken's expression were never fully exploited and its uses were largely restricted to the purposes for which it was originally derived, namely, rationalizing the heat of formation and the spectra of weak complexes between neutral molecules. This neglect is probably due in part to the fact that its use of a simple VB wave function tends to obscure the relationship between the value of  $\Delta E$  and the ground-state properties of the acid and base. Indeed, in some cases the wave function appears to have been incorrectly interpreted as a literal time-dependent resonance rather than as a mathematical approximation using a weighted superposition of limiting case configurations, and one can find references to mysterious "charge-transfer" forces which supposedly hold these complexes together and distinguish them from those complexes formed by normal covalent or electrostatic interactions.

The three parameter correlations of Gutmann and of Satchell and Satchell are definitely more limited in scope than either the  $E & C$  equation or the HSAB principle as they are based on the incorrect idea that a single universal order of relative strengths exists. Their success is due to the fact that in a given series of reactions the electronic structure of the donor atom is kept relatively constant (in this case hard). Satchell and Satchell use bases having mostly oxygen or nitrogen as the donor and the vast majority of solvents for which DN's have been measured also have oxygen or nitrogen as the donor atoms.

The relationship between the equations of Gutmann and of Satchell and Satchell, on the one hand, and the "two"-term equations in Table XV, on the other, is most easily illustrated by means of the Edwards equation:

$$\log K_n / K_{\text{ref}} = \alpha E_n + \beta H_n \quad (36)$$

By making the "softness" factors,  $\alpha E_n$ , constant we can make the following identities (for a given acid and set of reaction conditions):

$$-[\alpha E_n + 1.74\beta + \log K_{\text{ref}}] = \text{constant} = b \quad (37)$$

$$-\beta = a$$

By rearranging eq 36 and substituting we obtain the equation of Satchell and Satchell:

$$-\log K_n = apK_a + b \quad (38)$$

Gutmann's equation is similar to this, as was shown earlier, but uses the addition reactions with  $SbCl_5$  as its standard rather than the displacement reactions with  $H_3O^+$ . In addition, Gutmann assumes constant entropy contributions. Thus, Gutmann's DN scale, like the  $pK_a$  scale, can function as a measure of "strength" (in Pearson's sense) when applied to hard solvent systems where it can be used to rationalize a large amount of chemistry, as can be seen by consulting the many excellent reviews written by Gutmann and Mayer.<sup>21,67,86-98</sup>

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