An Overview of Lewis Basicity and Affinity Scales

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ABSTRACT: The impossibility of establishing a universal scale of Lewis basicity does not prevent the determination of the quantitative behavior of Lewis bases, thanks to scales constructed against particular Lewis acids: BF_3, 4-FC_6H_4OH, I_2, Li^+, Na^+, K^+, Al^+, Mn^+, $CpNi^+$, and $CH_3NH_3^+$. These scales encompass important types of bonds formed in a Lewis acid−base adduct: the dative bond, the conventional and ionic hydrogen bonds, the halogen bond and cation−molecule bonds for metal cations of groups 1, 7, 10, 11, and 13. Moreover, although these scales are generally not interrelated, there exist family-dependent relationships that permit ranking, in a rather general order, of bases belonging to a given chemical family, for example, the family of oxygen bases. Therefore, the skepticism about the quantitative usefulness of the Lewis concept of acids and bases is no longer founded.

KEYWORDS: Upper-Division Undergraduate, Organic Chemistry, Physical Chemistry, Misconceptions/Discrepant Events, Textbooks/Reference Books, Acids/Bases, Lewis Acids/Bases
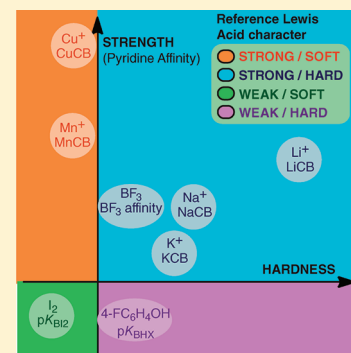
Two definitions of acids and bases are generally given to students: the Brønsted definition and the Lewis definition. In the Brønsted definition (1923),[1] an acid is a species capable of donating a proton, and a base is a species capable of accepting a proton. The Brønsted definition uses the proton as an intrinsic reference acid and is therefore easily translated into quantitative measurements: the quantitative study of proton exchange reactions enables the relative strength of Brønsted acids and bases to be measured unambiguously. These data on proton exchange in the gas phase and in water have been compiled in extensive tables and databases. In the Lewis definition (1923, 1938),[2a,3] acids are electron-pair acceptors and bases are electron-pair donors. In modern usage, the term "electron density" is preferred to "electron-pair". The proton is a Lewis acid because it can accept electron density into its empty 1s atomic orbital. It follows that a base in the Lewis sense is the same as in the Brønsted one. However, a much wider range of species can be classified as acids in the Lewis definition than in the Brønsted one.

The fundamental reaction between a Lewis acid A and a Lewis base B is the formation of a complex (or adduct) AB,

$$A + B \rightleftharpoons A \cdots B \tag{1}$$

where the three dots denote a bond.[a] Clearly, increasingly strong Lewis bases or Lewis acids will increasingly shift the equilibrium toward the formation of the Lewis adduct. It follows that Lewis basicity (acidity) can be defined as "the thermodynamic tendency of a substance to act as a Lewis base" (acid) and that "comparative measures of Lewis basicity (acidity) are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis bases (acids) with a common reference Lewis acid (base)".[4]

Compared to the protonic definition of Brønsted, the Lewis definition broadens considerably the chemistry of acids and bases. A major criticism, however, is often made of the Lewis concept: it is not possible to establish any universal order of Lewis acid and base strength, as it is done for the Brønsted acids and bases. In fact, because there is no single reference that is naturally operational, there is no obvious reason to choose one reference rather than another, and there are virtually as many possible Lewis acidity or basicity scales as possible references. Because the order of complexation constants is not invariant when the reference acid (base) is changed,[b] skepticism about the quantitative usefulness of the Lewis concept of acids and bases is frequently encountered in chemistry textbooks, and some instructors do not go beyond a mere qualitative presentation of the generalized concept of acids and bases.

The impossibility of establishing a universal scale of Lewis basicity (acidity) does not prevent the determination of the quantitative behavior of Lewis bases (acids), thanks to scales constructed with a particular reference Lewis acid (base). These particular scales have admittedly a limited domain of validity, but in most cases, the chemist does not need a general Lewis basicity (acidity) scale. For example, for a medicinal chemist studying the interaction of a drug with a protein and trying to optimize a network of hydrogen bonds, a hydrogen-bond donor (acceptor) scale is clearly the relevant one. In other cases, chemists focus on a basicity-dependent property of a series of related molecules. Then, any particular basicity scale can be useful,[c] because there are many relationships between basicity scales within families of

bases (called "family-dependent relationships"), as shown by Kamlet et al.[5] Many attempts of quantifying Lewis acid—base interactions have been proposed.[6] These empirical treatments have mainly historical merits today and progress in the quantitative understanding of the Lewis concept and in the knowledge of the strength of Lewis acids and bases will be mostly achieved in the future by (i) quantum chemical calculations[d] and (ii) the measurement of reliable, homogeneous, diversified, and extensive quantitative experimental data.

The first translation of Lewis' definition into quantum-mechanical terms is generally attributed to Mulliken (1952) who described complexes AB by a valence-bond model.[7] Then followed (non-exhaustively, references may be found in chapter 1 of ref 13):

- Klopman's perturbation molecular orbital calculation of the electronic energy change upon formation of the adduct AB (1968).[8]
- Morokuma's decomposition scheme (1971)[9] of the energy of complexation into electrostatic, polarization, exchange-repulsion, and charge-transfer terms. The dispersion term must be calculated separately.
- The definition of the absolute hardness of acids and bases by Parr and Pearson (1983).[10]
- The natural bond orbital (NBO) method of Weinhold (1980 and monograph in 2005),[11] which emphasizes the calculation of delocalization of electron density into unoccupied orbitals.
- The theory of "atoms in molecules" of Bader (monograph in 1990),[12] which enables the existence and the nature of bonds to be determined from the topological analysis of the electron density.

The strength of the interaction between a Lewis acid and a Lewis base can be computed as (i) the electronic interaction energy, (ii) the dissociation energy of the A···B bond, (iii) the binding enthalpy, or (iv) the Gibbs energy of complexation, both at a specified temperature, usually 298 K. Only the last quantity is relevant to basicity (acidity) when the IUPAC definition[4] based on equilibrium constants of complexation is followed. The corresponding enthalpy and entropy are the enthalpy and entropy of basicity (acidity). The term "affinity" is in common use in the field of gas-phase ion—base reactions. Thus, the negative enthalpy of the protonation reaction $B + H^+ \rightarrow BH^+$ is generally called "proton affinity". For homogeneity, the same terminology has been adopted for molecular complexes and the negative enthalpies of complexation of bases with the Lewis acids $SbCl_5$, BF_3, $4\text{-}FC_6H_4OH$, or I_2 will be named antimony pentachloride, boron trifluoride, 4-fluorophenol, or diiodine affinities, respectively. In the same vein, the Gibbs energy of complexation (or the related logarithm of complexation constants) of H^+, $4\text{-}FC_6H_4OH$, or I_2 with bases must be called proton basicity, 4-fluorophenol basicity, or diiodine basicity, respectively.

The development of many new computational methods and the exponential growth of computer power permit, in principle, routine calculations of the basicity and of the acidity of most chemical compounds by means of apparently user-friendly software packages. However, these calculations are fraught with difficulties, the most important being to account for solvent effects. In actual fact, the costly level of theory required to obtain good agreement with experimental data often limits the calculations to (i) complexes of small size, (ii) limited samples of acids and bases, and (iii) the gas-phase medium.

Therefore, the collection of reliable and diversified experimental data on Lewis basicity and acidity remains essential to computational chemists for the validation and calibration of their methods. Extensive scales of Lewis basicity and acidity will also enable experimental chemists to understand and better predict the numerous chemical and biological properties that depend upon Lewis basicity or acidity. Indeed, basicity or acidity parameters are important explanatory variables in many linear solvation energy relationships, quantitative structure—property relationships, and quantitative structure—biological activity relationships.

The search for these scales in the literature and their presentation and analysis is the subject of this article. Because there do not yet exist extensive Lewis acidity scales, this overview is limited to Lewis basicity (Gibbs energy) and affinity (enthalpy) scales. The results of this search were rather disappointing, not so because of the paucity of data but rather because of their lack of homogeneity. Although there are, in principle, a lot of possible reference Lewis acids, in practice there are not many systems in which the same Lewis reference acid reacts with a series of diversified bases for which a series of reliable equilibrium constants can be measured easily over a large range of values in the same conditions. For this reason, in spite of a very large amount of data, the stability constants of aqueous metal—ion complexes could not furnish any useful basicity or acidity scale. Because of a lack of homogeneous thermodynamic scales, chemists have turned to the determination of spectroscopic scales of Lewis basicity (affinity).

In the following, successively scales are presented constructed from four categories of reference Lewis acids:

- Affinity scales toward the covalent halides $SbCl_5$ and BF_3.
- Basicity, affinity, and spectroscopic scales toward hydrogen-bond donors.
- Basicity, affinity, and spectroscopic scales toward halogen-bond donors.
- Basicity and affinity scales toward cations in the gas phase.

In all, these scales contain more than 2400 complexation constants, about 1500 enthalpies of basicity, and, for spectroscopic scales, nearly 2000 infrared and ultraviolet—visible shifts upon complexation. These values and the corresponding literature references have been compiled in a recent book.[13]

■ THE DONOR NUMBER OR SbCl₅ AFFINITY SCALE

Gutmann proposed, in 1966, the concept of donor number (DN) to express quantitatively the Lewis basicity of solvents.[14] DN was defined as the negative enthalpy of the reaction of complexation (eq 2)

$$ (2) $$
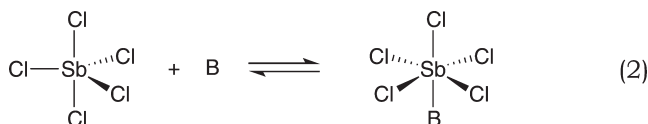
of Lewis bases B with the reference Lewis acid $SbCl_5$ in 1,2-dichloroethane. The structure of a representative $SbCl_5$ complex is shown in Figure 1. Although the DN scale has been proposed and used as a solvent parameter of Lewis basicity, it relies on measurements of enthalpies made on dilute solutions of bases. It is, therefore, a *solute* scale of Lewis *affinity* and not a *solvent* scale of Lewis *basicity*. There are differences between solute and
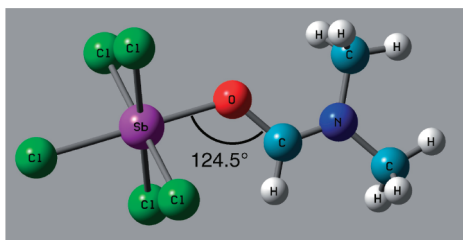
Figure 1. Structure of the HCONMe$_2$—SbCl$_5$ complex. The dative Sb—O bond points in the direction of a putative sp^2 oxygen lone pair (the less sterically hindered one).
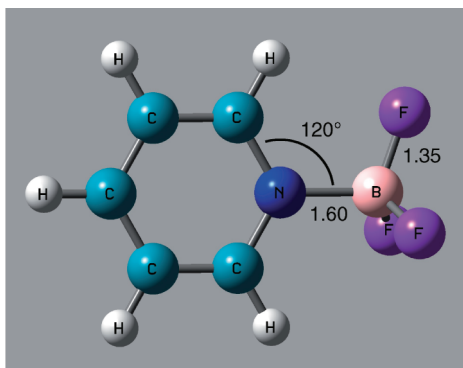

Figure 2. Structure of the pyridine—BF$_3$ complex. The dative B—N bond points in the direction of the putative sp^2 nitrogen lone pair (bond lengths in Å).

solvent scales, mainly for self-associated solvents, and between SbCl$_5$ affinity and SbCl$_5$ basicity.[13]

Convergent critical analyses have pointed out the limitations of DN. They concern:

(i) The choice of SbCl$_5$ as the reference Lewis acid. It appears unfortunate for theoretical reasons: the 136 electrons of SbCl$_5$ and the relativistic behavior of the inner shells electrons of Sb make accurate quantum mechanical calculations on SbCl$_5$ complexes difficult and costly.

(ii) The sample of bases. The chemical variety is very low because 90% of them are oxygen bases. There is a serious lack of nitrogen bases, and the carbon π bases, the halogen bases, and the sulfur bases are totally missing.

(iii) The quality of calorimetric measurements. A number of them appear to be unreliable, probably because of the high reactivity and catalytic effect of SbCl$_5$ and, for weak bases, because the complexation reaction (eq 2) was incorrectly assumed to be complete.

(iv) The domain of validity of the scale. Many correlations with the DN scale, established with a restricted sample of bases, have been unduly generalized.[ε]

For the above reasons, the use of the DN scale is discouraged; an alternative better scale, the BF$_3$ affinity scale, is now available.

■ THE BF$_3$ AFFINITY SCALE

BF$_3$ is an archetypical Lewis acid. The central boron is electron deficient because it has only six electrons in its outer shell and the highly electronegative fluorine atoms further decrease its electron density. The structure of a representative BF$_3$ complex is shown in Figure 2. The BF$_3$ affinity scale was constructed
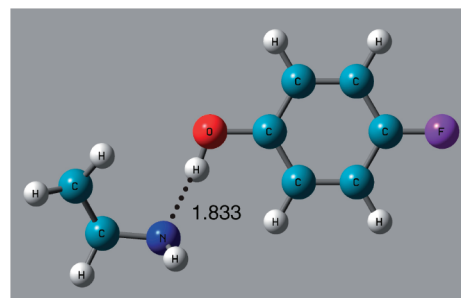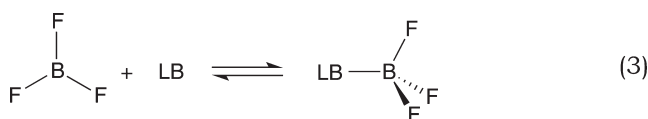

Figure 3. Structure of the cyclopropylamine—4-fluorophenol complex. The hydrogen bond points to the direction of the putative sp^3 nitrogen lone pair (bond length in Å).

(1971—1993) by Gal, Maria et al.[13,15] It was defined as the negative enthalpy of the reaction of complexation (eq 3) of gaseous BF$_3$ with a series of bases LB in a dilute solution of dichloromethane at 298 K:

$$\begin{array}{c} \text{F} \\ | \\ \text{B} \\ \diagup \quad \diagdown \\ \text{F} \qquad \text{F} \end{array} \;+\; \text{LB} \;\rightleftharpoons\; \text{LB} - \text{B} \begin{array}{c} \diagup \text{F} \\ \cdots \text{F} \\ \diagdown \text{F} \end{array} \qquad (3)$$

The concepts of the BF$_3$ and SbCl$_5$ affinity scales are the same, BF$_3$ and SbCl$_5$ have about the same strength, and both are classified as hard in the Pearson classification of Lewis acids.[13] However, the BF$_3$ affinity scale represents an improved version of the DN scale for the following reasons:

(i) BF$_3$ is a better reference than SbCl$_5$. Experimentally it gives cleaner complexation reactions and the much simpler electronic structure of BF$_3$ permits easier quantum chemical calculations of BF$_3$ affinities.

(ii) The sample of bases is more diversified and three times more numerous. It contains 72 nitrogen bases, 4 sulfur bases, and 1 phosphine. The other compounds are diversified oxygen bases: ethers and carbonyl, nitro, sulfinyl, sulfonyl, and phosphoryl compounds.

(iii) The calorimetric method, a discontinuous titration of the base by the acid BF$_3$ in a heat-flux microcalorimeter, allows the detection of incomplete complexation and of spurious secondary reactions. Its accuracy is estimated to be 1—2%.

However, whatever its reliability, the BF$_3$ affinity scale is a scale specific to dative-bond formation processes. The extension of its validity domain requires multiparameter treatments.

■ THERMODYNAMIC AND SPECTROSCOPIC SCALES OF HYDROGEN-BOND BASICITY AND AFFINITY

According to the IUPAC definition, the hydrogen bond X-H···B is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X—H in which X is more electronegative than H and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. A natural bond orbital (NBO) analysis of the hydrogen bond shows that a (small) electron density is transferred from nonbonding or π-bonding electron pairs of B to the antibonding orbital σ^* of the X—H bond. Hydrogen bonding and hydrogen-bonded complexes can thus be considered a class of Lewis acid—base interactions and Lewis adducts, respectively.

From the observation that the hydrogen bond is stronger when B is an oxygen base than when it is a sulfur base, hydrogen-bond donors are classified as hard Lewis acids. The structure of a representative hydrogen-bonded complex is shown in Figure 3.

The thermodynamic and spectroscopic properties of thousands of hydrogen-bonded systems have been measured. From these data, many thermodynamic and spectroscopic scales of hydrogen-bond basicity and affinity have been constructed.[13] In the following, four scales are presented that are reliable and that refer to numerous and diversified samples of nitrogen, oxygen, sulfur, halogen, and carbon bases.

The pK_{BHX} hydrogen-bond basicity scale[16] has been constructed from $\log K$ values measured in CCl_4 at 298 K for a series of bases B against 4-fluorophenol as the reference Lewis acid (eqs 4–6). The pK_{BHX} values can be converted to a Gibbs energy scale (eq 7).

$$4\text{-}FC_6H_4OH + B \rightleftharpoons 4\text{-}FC_6H_4OH \cdots B \qquad (4)$$
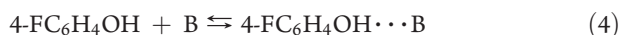
$$K_c/(\text{L mol}^{-1}) = C(\text{complex})/[C(\text{base}) \times C(4\text{-}FC_6H_4OH)] \qquad (5)$$

$$pK_{BHX} = \log_{10}[K_c/(1 \text{ L mol}^{-1})] \qquad (6)$$

$$\Delta G^{\circ}/(\text{kJ mol}^{-1}) = -5.708\, pK_{BHX} \text{ (at 298 K)} \qquad (7)$$

For Lewis bases bearing n possible hydrogen-bond acceptor sites (polybases), the method yields the total equilibrium constant. Methods have been developed to measure the n individual constants, so that the polybase can be described by n pK_{BHX} values, each corresponding to complexes of 1:1 stoichiometry.

The pK_{BHX} values have been scaled to 4-fluorophenol in CCl_4, but other hydrogen-bond donors and other media are chemically and biochemically relevant. The pK_{BHX} scale appears to be a reasonably general scale that applies to many OH, NH, and NH^+ donors in a satisfactory range of solvent polarity. The 4-fluorophenol affinity scale[17] corresponds to the enthalpy of reaction (eq 4). The correlation of 4-fluorophenol affinity and basicity scales exhibits a scatter. For unhindered bases, the scatter can be analyzed into a series of family dependent relationships.

The X–H stretching infrared frequency of hydrogen-bond donors is significantly lowered upon hydrogen bonding. This shift has been used as a spectroscopic measurement of the hydrogen-bond acceptor strength of Lewis bases. The scale based on the $\nu(OH)$ frequency shifts of methanol in CCl_4[13] is preferred:

$$\Delta\nu(OH) = \nu(OH \text{ of the "free" methanol})$$
$$- \nu(OH \text{ of hydrogen-bonded methanol}) \qquad (8)$$

The measurement of infrared shifts is easy for undergraduate students and is particularly attractive for difficult systems such as gaseous compounds, very weak bases, or ion pairs.

UV shifts have also been recognized as useful spectroscopic descriptors of the basicity of solvents. The shifts of a $\pi \rightarrow \pi^*$ transition of 4-nitrophenol in going from the gas phase to basic solvents are due to hydrogen bonding with the solvent and to other interactions. The latter contribution can be evaluated by using 4-nitroanisole, which resembles 4-nitrophenol in all ways except in the ability to hydrogen bond. The enhanced shifts of 4-nitrophenol compared to 4-nitroanisole, $\Delta\nu(OH-OMe)$, can be scaled in a range from 0 (non-hydrogen bonding solvents) to 1, by dividing by the 2030 cm^{-1} shift of hexamethylphosphoric
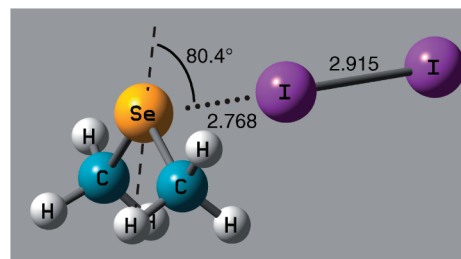

Figure 4. Structure of the dimethyl selenide–diiodine complex. The halogen bond points to the direction of a putative selenium lone pair (bond lengths in Å).

triamide, which yields the revised beta scale[13] of solvent basicity:

$$\beta(OH) = \Delta\nu(OH-OMe)/2030 \qquad (9)$$

The enhanced solvatochromic shifts of 4-nitrophenol are well correlated with the 4-fluorophenol affinities. This indicates that the most appropriate use of the $\beta(OH)$ solvent scale is for measuring the effect of basic solvents on enthalpy-dependent properties.

■ THERMODYNAMIC AND SPECTROSCOPIC SCALES OF HALOGEN-BOND BASICITY AND AFFINITY

The development of the theory of charge-transfer complexes by Mulliken[7] initiated a wealth of thermodynamic, spectroscopic, and structural measurements on complexes formed by halogen compounds YX

$$YX + B \rightleftharpoons B \cdots X-Y \qquad (10)$$

from which emerged in recent years the concept of a halogen bond $B \cdots X$. A halogen bond may be defined as the attractive interaction in which halogen atoms function as electropositive sites (a IUPAC definition is underway). Because of a small transfer of electron density from the nonbonding or π-bonding electron pairs of B to the antibonding orbital σ^* of the Y–X bond, YX is a Lewis acid, halogen bonding is a Lewis acid–base interaction, and halogen-bonded complexes $B \cdots X-Y$ are Lewis adducts between a halogen-bond acceptor B and a halogen-bond donor YX. The structure of a representative halogen-bonded complex is shown in Figure 4.

Halogen Lewis acids correspond to a large number of compounds because Y may be inorganic (e.g., F, Cl, Br, I, OH, NH_2, N_3) or organic (e.g., CR_3, $C \equiv N$, C_6R_5, $C(R) = CR_2$, $C \equiv CR$, where R is any electron-withdrawing substituent) and X is any halogen (although fluorine bonds are much weaker than iodine bonds). Moreover, halogen bonding has recently been recognized as a significant interaction in molecular recognition and self-assembly processes, and therefore employed for a wide range of applications in materials, synthetic, and medicinal chemistry.[18] There is therefore a need for scales measuring the strength of halogen-bond acceptors. Surprisingly, there has been no attempt to use the many thermodynamic and spectroscopic data on the reaction (eq 10) to set up halogen-bond basicity, affinity, or spectroscopic scales for a broad and varied sample of bases, until these values were compiled in a recent monograph.[13] In the following, the diiodine basicity scale pK_{BI2} and the $\Delta\nu(I-CN)$ scale are presented.

The pK_{BI2} scale has been constructed[13] toward diiodine (in alkanes as solvents) in the same manner as the pK_{BHX} scale
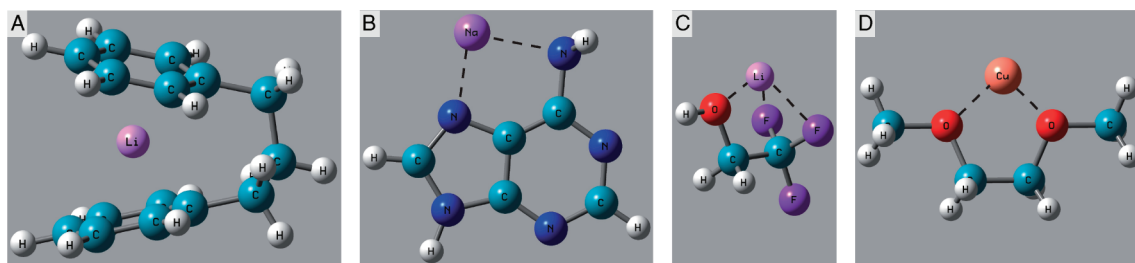
Figure 5. Most stable calculated structures of (A) $Li^+-1,3$-diphenylpropane, (B) Na^+-adenine, (C) $Li^+-1,1,1$-trifluoroethanol, and (D) Cu^+-1,2-dimethoxyethane.

toward 4-fluorophenol (in eqs 4–7 replaces 4-FC_6H_4OH by I_2). Diiodine has the lowest absolute hardness of common molecular acids. The pK_{BI2} scale is therefore a soft basicity scale. Indeed, the stability of the complexes formed with bases of groups 16 and 17 follows the orders I > Br > Cl and Se > S > O. Opposite orders are observed with the pK_{BHX} scale. It is thus not surprising that the relationship between the two scales yields a low correlation coefficient. However, good family dependent relationships are found. For example, $r = 0.965$ for 110 oxygen bases.

When iodine cyanide $IC\equiv N$ is complexed to Lewis base, the I–C stretching is shifted to lower frequencies. This shift has been used for measuring (in the solvent dichloromethane) the strength of halogen-bond acceptors. The resulting $\Delta\nu(I-CN)$ scale[13] is correlated to the diiodine affinity scale. This correlation supports the use of $\Delta\nu(I-CN)$ as a spectroscopic scale of halogen-bond affinity. Moreover, $\Delta\nu(I-CN)$ values obey the hard and soft acid and base (HSAB) principle because they increase with the absolute softness of the atomic site of the base, in a given period (I > Br > Cl for halogenoalkanes and Se > S > O for phosphine chalcogenides). In the HSAB language, $\Delta\nu(I-CN)$ can also be described as a spectroscopic scale of soft affinity.

The spectroscopic ICN probe enables the measurement of important Lewis bases for which the direct determination of halogen-bond affinity is difficult, for example, bases reacting with diiodine (alkynes), gaseous bases (NH_3), aniline (a polybase with carbon and nitrogen sites), and ion pairs.

■ GAS-PHASE CATION AFFINITY AND BASICITY SCALES

The study of the formation of complexes between cations and Lewis bases in the gas phase offers the unique possibility of measuring intrinsic (i.e., free of solvent and counterion influences) Lewis basicity scales. The positive charge of the naked cation M^+ allows strong binding with Lewis bases. The M^+-B bond is largely electrostatic but there occurs some electron density transfer from the base to the cation, as shown by the neutralization of a fraction of the positive charge of M^+ in the adduct.

Apart from the proton, experimental studies have focused on the binding of alkali metal cations (mainly Li^+, Na^+, and K^+) and transition metal monocations (for example, Mn^+, Co^+, Ni^+, and Ag^+). Among main group metal cations, only the aluminum monocation appears to have been studied against a variety of bases. In addition to these simple monocations, a few polyatomic cations, such as $CpNi^+$ (Cp is cyclopentadienyl) and $BrFe^+$, were used as reference Lewis acids. Cations such as $CH_3NH_3^+$ corresponding to protonated bases BH^+ and forming an ionic hydrogen bond

$BH^+\cdots B'$ were also considered. Other typical organic cations that have been used as Lewis acids are carbenium ions X_3C^+ (X = H, alkyl, halogen; note that CF_3^+ is isoelectronic of BF_3) and their organoelement analogues Me_3Si^+, Me_3Ge^+, and Me_3Sn^+.

The thermochemistry of multicharged cation–ligand adducts may also be studied. Nevertheless, such studies are severely limited by competitive electron transfer, because the second ionization energy of a metal is usually much greater than that of molecules, and the charge exchange reaction

$$M^{2+} + L \rightleftharpoons M^+ + L^+ \qquad (11)$$

where M is the metal and L the ligand, may occur instead of adduct formation. Adducts of multicharged metal cations can be observed only when M^{n+} is bonded to several ligands or to a polydentate ligand which stabilize the high charge state.

In principle, Lewis basicity scales are defined from the formation of complexes of 1:1 stoichiometry, that is, in the case of cation basicity scales, for the coordination of one cation M^+ with one ligand L. Gibbs energy and enthalpy changes have also been obtained for two-ligand complexations of $FeBr^+$, Cu^+, Co^+, Ni^+, and Ag^+, that is, for the reaction:

$$M^+ + 2L \rightleftharpoons L_2M^+ \qquad (12)$$

Not all the literature data on the thermochemistry of ion–molecule complexation in the gas phase can be usefully translated into absolute cation Lewis basicity and affinity scales suitable for broad purposes. In ref 13, the basicity and affinity scales relative to the cations Li^+, Na^+, K^+, Mn^+, $CpNi^+$, Cu^+ (two-ligand), Al^+, and $CH_3NH_3^+$ have been purposely selected, for the reason that the corresponding data (i) are absolute or have been translated into absolute values, (ii) refer to the same temperature or have been referred to the same temperature, (iii) are available for a sufficient number of bases, and (iv) correspond to a sufficient variety of bases in terms of the atomic center and its functionality. For example, the lithium cation basicity (LiCB) scale (i) is absolute: relative LiCB values obtained from ligand-exchange equilibrium constants measured by Fourier transform ion cyclotron resonance have been anchored to the absolute LiCB value of H_2O, (ii) refers to the same temperature, (iii) is available for 252 ligands, and (iv) contains 23 carbon π bases, 62 variously hybridized nitrogen bases, 137 variously functionalized oxygen bases, 17 sulfur bases, 8 halogen bases, and 2 phosphorus bases.

The covalent part of the interaction of the alkali and Al^+ cations corresponds mainly to sigma bonding, whereas Mn^+, Cu^+, and $CpNi^+$ are additionally capable of π back-donation from the occupied d orbitals of the metal toward antibonding

empty orbitals of the ligand. The cation $CH_3NH_3^+$ provides scales of ionic hydrogen-bond basicity and affinity.

Chelation is a frequent structural feature of cation—molecule adducts. Some examples of chelate structures are given in Figure 5. The chelate effect increases the stability of the adduct, hence, the cation basicity of ligands. Chelate formation contributes to the entropy of basicity and is the main factor (with symmetry number changes upon adduct formation) provoking a departure from the extrathermodynamic linear relationships often observed between gas-phase cation basicity and affinity scales.

There is no satisfactory general relationship between the different gas-phase cation basicity scales (except between Li^+, Na^+, and K^+ basicity scales). However, there are good family dependent relationships. For example, metal cation basicity (MCB) scales correlate fairly well each other for the family of oxygen ligands.

■ CONCLUSION

The ongoing difficulties in quantifying Lewis acid—base interactions have their main origin in the dimensionality of the problem, a consequence of the broadening of the concept of acids and bases. The ranking of Brønsted acids and bases is monodimensional, whereas the ranking of Lewis acids and bases is multidimensional. In mathematical language, the aqueous Brønsted acidity and basicity scale correspond to a one-column matrix, whereas the Lewis acidity and basicity scales correspond to a data matrix of m rows and n columns, each row being a Lewis acidity scale toward a reference base and each column a Lewis basicity scale toward a reference acid. In principle, it is possible to fill the $[m \times n]$ matrix with computed data. Of course, the size of the matrix should first be reduced by selecting a set of highly informative reference acids and bases. Then, the choice of a common level of theory should permit to build a matrix of homogeneous interaction energies in vacuo. A matrix of Gibbs energies of complexation in a solvent seems beyond reach today.

Experimentally, the chemist has at hand a matrix of low occupancy rate. Moreover data appear disjointed at first glance. However, this overview has presented a number of columns of the matrix (i.e., basicity or affinity scales) that are filled with numerous, diverse, and reliable homogeneous data. There are few basicity or affinity scales but they are especially informative because they refer, for molecular complexes in the bidimensional space of hardness and strength, to three of the four possible classes of Lewis acids: hard and strong (BF_3), hard and weak (4-fluorophenol), and soft and weak (I_2). In terms of chemical bonding, these scales cover the dative bond, the conventional hydrogen bond, and the halogen bond, respectively. Moreover, the ionic hydrogen bond is covered by the methylammonium cation affinity and basicity scales. Finally, a large body of data on ion complexation in the gas-phase has been recently[13] organized in metal cation affinity or basicity scales corresponding to elements of groups 1 (Li^+, Na^+, K^+), 7 (Mn^+), 10 ($CpNi^+$), 11 (Cu^+), and 13 (Al^+).

Admittedly, these scales yield different rankings of the strength of Lewis bases; that is, there is no general relationship between two given scales. But the scatter observed in these relationships is most often resolved into family dependent relationships. By this very fact, the rankings of, for example, nitriles or aromatic N-heterocycles or phosphoryl compounds remain approximately the same toward most Lewis acids.

In summary, the skepticism about the quantitative usefulness of the Lewis concept of acids and bases is no longer founded. Instructors and textbook authors are encouraged to go beyond the historical DN scale and to present to their students the dative-bond, hydrogen-bond, halogen-bond, and gas-phase cation basicity or affinity scales.

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■ ADDITIONAL NOTE

[a] The formation of Lewis acid—base adducts covers a wide variety of bond-forming processes, from the weak van der Waals bond in $Ar \cdots BF_3$ to the strong dative bond in $H_3N—BF_3$. The term "bond" can be objectionable for weak adducts. These weakly bonded species are generally produced in a supersonic beam or a cryogenic matrix. Here, we are mainly interested by complexes that can be observed in a room temperature mixture of the Lewis acid and of the Lewis base.

[b] In water, the order of complexation constants of halide ions with the acid Fe^{3+} is $F^- > Cl^- > Br^- > I^-$, whereas with Hg^{2+}, it is $I^- > Br^- > Cl^- > F^-$. This reversal is explained by the hard and soft acid and base principle of Pearson.

[c] For example, the coordination of a series of azines to metallocenes has been correlated to the hydrogen-bond basicity scale of the azines.[19]

[d] See for example the ab initio computation of the Lewis acid strength of covalent metal halides in vacuo using the fluoride anion as the reference Lewis base.[20]

[e] For example, a DN value of triethylamine was estimated from a correlation between DN and the NMR chemical shift of the ^{23}Na nucleus for solutions of sodium salts in basic solvents. Later on, the direct determination gave a value that was half the estimated value.

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