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Lewis Basicity and Affinity Measurement: Definitions and Context

Two definitions of acids and bases are used nowadays, the Brönsted definition and the Lewis definition. This book deals with the quantitative behaviour of Lewis bases. However, since Lewis bases are also Brönsted bases, this chapter begins with a short presentation of the Brönsted definition and of the quantitative behaviour of Brönsted bases [1]. The Lewis definition and the many ways for its quantification will then be studied. This introductory chapter is intended to help in the understanding and use of the tables in Chapters 2–6, which contain quantitative data on Lewis basicity and affinity, and not to discuss the Lewis acid/base concept in depth. This subject has been excellently treated in a book [2] and a review [3] by Jensen, and books and chapters by Mulliken and Person [4], Gur'yanova *et al.* [5], Drago [6], Finston and Rychtman [7] and Weinhold and Landis [8], to quote just a few.

As far as possible, we have followed the IUPAC recommendations for the names and symbols of physical and chemical quantities (http://goldbook.iupac.org/) and have used the international system of units (SI) and the recommended values of the fundamental physical constants (http://physics.nist.gov/cuu/). Units that are not part of the SI have been used in appropriate contexts. These are: litre ($1\ \mathrm{l} = 10^{-3}\ \mathrm{m}^3$), ångström ($1\ \text{Å} = 10^{-10}\ \mathrm{m}$), electronvolt ($1\ \mathrm{eV} \approx 1.602\ 18 \times 10^{-19}\ \mathrm{J}$), Debye ($1\ \mathrm{D} \approx 3.336 \times 10^{-30}\ \mathrm{C\ m}$) and bar ($1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$).

In tabulating thermodynamic and spectroscopic basicity scales, 1 : 1 complexation constants, Gibbs energies, enthalpies, entropies and ultraviolet (UV) and infrared (IR) spectral shifts are therefore given in $\mathrm{l\ mol^{-1}}$ (identical with $\mathrm{dm^3\ mol^{-1}}$), $\mathrm{kJ\ mol^{-1}}$, $\mathrm{J\ K^{-1}\ mol^{-1}}$ and $\mathrm{cm^{-1}}$, respectively. Logarithms of equilibrium constants ($\log K$) are to base 10 and without units since the calculated quantity is $\log (K/1\ \mathrm{l\ mol^{-1}})$.

In naming compounds, we have not always followed the nomenclature rules. We have sometimes preferred the common name found in most chemical catalogues. For clarity, the

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Lewis Basicity and Affinity Scales: Data and Measurement Christian Laurence and Jean-François Gal

Table 1.1 *Symbols for families of Lewis bases used in the graphs.*

Family	Symbol	Family	Symbol	Family	Symbol
Carbon π bases		*Nitrogen bases*		*Selenium bases*	
Aromatics, alkenes, alkynes	×	sp-Hybridized	▣	Single-bonded, seleno-carbonyls, seleno-phosphoryls	∗
Oxygen bases		sp^2-Hybridized	■		
Single-bonded	▲	sp^3-Hybridized	□	*Halogen bases*	
Carbonyls	●	*Phosphorus, arsenic bases*	−	Fluoroalkanes	+
Sulfinyls	◍	*Sulfur bases*		Chloroalkanes	×
Phosphoryls, arsine oxides	○	Single-bonded	◇	Bromoalkanes	∗
N-Oxides	△	Thiocarbonyls	◆	Iodoalkanes	+
Nitros, sulfonyls	△	Thiophosphoryls	◇	*Miscellaneous bases*	−

name is followed, in most tables in Chapters 2–6, by a formula that allows the drawing of the structure, or by the drawing itself.

In the graphs, in order to facilitate the identification of family-dependent trends, bases are labelled as summarized in Table 1.1, unless otherwise stated in the legend of the graph.

1.1 The Brönsted Definition of Acids and Bases

A powerful definition of acids and bases was proposed in 1923 by J.N. Brönsted [9], namely an acid is a species capable of donating a proton, and a base is a species capable of accepting a proton. This can be expressed by the scheme

$$\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{H}^+ \tag{1.1}$$

where the acid A and the base B are termed a conjugate acid/base pair. Equation 1.1 represents a hypothetical scheme used for defining an acid and a base rather than a reaction. Indeed, reaction 1.1 cannot actually occur in a solvent because the bare proton H^+ cannot exist in solution, and cannot be studied directly in the gas phase because of the extremely large endoergic values involved.

The only reactions between Brönsted acids and Brönsted bases that can be observed in solution and studied directly in the gas phase are reactions of proton exchange between two conjugate acid/base pairs A^1/B^1 and A^2/B^2

$$\mathrm{A}^1 + \mathrm{B}^2 \rightleftharpoons \mathrm{A}^2 + \mathrm{B}^1 \tag{1.2}$$

For example, in aqueous solutions, the acid CH_3COOH reacts with water acting as a base:

$$\mathrm{CH_3COOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{CH_3COO^-} \tag{1.3}$$

Table 1.2 *Some types of neutral Brönsted acids*[a].

O—H acids	
Inorganic oxyacids	HNO_3, H_2SO_4, H_3PO_4, $HClO_4$
Carboxylic acids	RCOOH
Phenols, alcohols, water	ArOH, ROH, H_2O
N—H acids	$ArNH_2$, RSO_2NH_2, $RCONH_2$, HNCS, HNCO, HN_3
C—H acids	HC≡N, RC≡CH, $HC(NO_2)_3$
S—H acids	ArSH, H_2S
X—H acids	HF, HCl, HBr, HI

[a] In the formulae, R is an alkyl group and Ar an aryl group.

and the base NH_3 reacts with water acting as an acid:

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^- \tag{1.4}$$

In the gas-phase reaction 1.5, the proton is exchanged between the ammonium ion/ammonia and the pyridinium ion/pyridine pairs:

$$NH_4^+ + C_5H_5N \rightleftharpoons C_5H_5NH^+ + NH_3 \tag{1.5}$$

Any compound containing hydrogen can, in principle, be regarded as a Brönsted acid, but in many of them (e.g. most hydrocarbons) the tendency to lose a proton is so small that they do not show acidic behaviour under ordinary conditions. Examples of neutral Brönsted acids are given in Table 1.2.

The same kind of practical restriction should be applied to Brönsted bases. Neutral molecules or atoms can attach a proton in the gas phase because of the tremendous acidity of the bare proton: even rare gases may be protonated in the gas phase. For the liquid phase, superacid systems (such as $HF/SbCl_5$ that are more acidic than 100% sulfuric acid) can also protonate many molecules [10]. For example, the protonated form of methane, $CH_5{}^+$, which was discovered in the gas phase by mass spectrometry in the 1950s, has also been reported in superacid solutions. However, the important bases in chemistry are (i) anions and (ii) molecules containing elements of groups 15 and 16 with unshared electron pair(s).

1.2 Scales of Brönsted Basicity and Affinity in Solution

Brönsted definitions are easily translated into quantitative measurements. The equilibrium constant of reaction 1.2, $K = (A^2)(B^1)/(A^1)(B^2)$, where parentheses denote activities, is equal to the ratio of the hypothetical constants $(B^1)(H^+)/(A^1)$ and $(B^2)(H^+)/(A^2)$. K will therefore measure the ratio of the acid strengths of A^1 and A^2, or the ratio of the base strengths of B^2 and B^1. Since these two ratios are equal, it is not necessary to give separate definitions of base strength and acid strength. The base strength of any base B is usually given by the acid strength of its conjugate acid A. Thus, for the pair $C_5H_5NH^+/C_5H_5N$, the base strength of pyridine is described in terms of the acid strength of the pyridinium ion.

It is not possible to measure the absolute strength of an acid or base in solution but strengths can be measured relative to some standard pair, A°/B°. The acid strength of the studied pair, A/B, is then given by the equilibrium constant of the reaction

$$\mathrm{A} + \mathrm{B}^\circ \rightleftharpoons \mathrm{A}^\circ + \mathrm{B} \tag{1.6}$$

The standard pair, A°/B°, is usually chosen to be the acid/base pair of the solvent. In aqueous solutions, the pair H_3O^+/H_2O is commonly preferred to the other possible pair, H_2O/OH^-. The strength of any acid A is then measured by the equilibrium constant of the reaction

$$\mathrm{A} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{B} \tag{1.7}$$

When measurements are made in dilute aqueous solution, the concentration of water remains essentially constant and its activity can be taken as unity. The strength of the acid A is then measured by the acid dissociation constant:

$$K_\mathrm{a} = (\mathrm{B})\,(\mathrm{H_3O^+})/(\mathrm{A}) \tag{1.8}$$

The strength of a neutral base B is described in terms of the K_a of its conjugate acid BH^+, usually denoted $K_{\mathrm{BH^+}}$:

$$K_{\mathrm{BH^+}} = (\mathrm{B})\,(\mathrm{H_3O^+})/(\mathrm{BH^+}) \tag{1.9}$$

Since the observed equilibrium constants vary over many powers of 10, the convention to use the operator $\mathrm{p} \equiv -\log_{10}$ was adopted, leading to the quantity $\mathrm{p}K_{\mathrm{BH^+}}$:

$$\mathrm{p}K_{\mathrm{BH^+}} = -\log_{10} K_{\mathrm{BH^+}} \tag{1.10}$$

Clearly, a large positive value of $\mathrm{p}K_{\mathrm{BH^+}}$ describes a strong and a small or negative value describes a weak Brönsted base.

Tables of $\mathrm{p}K_{\mathrm{BH^+}}$ in aqueous solution have been compiled by Perrin [11]. They cover the literature until 1972 and contain more than 7000 organic bases, mainly sp^2 and sp^3 nitrogen bases. Many of the carbon, oxygen, sulfur and sp nitrogen bases are not protonated in dilute acid solutions, so that solutions with variable concentrations of a strong acid have to be used. In such media, $K_{\mathrm{BH^+}}$ values cannot be calculated without formulating some extrathermodynamic assumption. The $\mathrm{p}K_{\mathrm{BH^+}}$ values of many weak bases have been carefully measured by Scorrano *et al.* [12–21]. Table 1.3 gives selected $\mathrm{p}K_{\mathrm{BH^+}}$ values. The $\mathrm{p}K_{\mathrm{BH^+}}$ is directly converted into the Gibbs energy change of the proton exchange as follows:

$$\Delta G^\circ = \ln(10) RT \mathrm{p}K_{\mathrm{BH^+}} \tag{1.11}$$

The literature is poorer in enthalpies of proton exchange reactions. However, Arnett *et al.* have established an enthalpic scale of Brönsted basicity [22–25] (i.e. a Brönsted affinity scale) from the heats of protonation of many bases in fluorosulfuric acid. The heats of protonation (ionization), ΔH_i, correspond simply to the heat of transfer of the base from infinite dilution in the inert solvent CCl_4 to infinite dilution in the (often) completely protonating solvent HSO_3F. A surprisingly good correlation ($r = 0.986$, $n = 55$, $s = 5.4\ \mathrm{kJ\ mol^{-1}}$) is obtained [23] between the enthalpies of protonation and the corresponding aqueous $\mathrm{p}K_{\mathrm{BH^+}}$ values. Selected values of ΔH_i are given in Table 1.3.

Table 1.3 *Thermodynamic parameters for protonation of organic bases: pK_{BH^+} in water, ΔH_i (kJ mol^{-1}) in fluorosulfuric acid and GB and PA (kJ mol^{-1}) in the gas phase.*

Base	pK_{BH^+}	$-\Delta H_i$	GB	PA
Hexamethylbenzene	−14.65		836.0	860.6
Methylamine	10.65	193.9	864.5	899.0
Ethylamine	10.68	195.9	878.0	912.0
Dimethylamine	10.78	197.4	896.5	929.5
Diethylamine	11.02	199.5	919.4	952.4
Di-*n*-butylamine	11.25	194.1	935.3	968.5
Trimethylamine	9.80	196.8	918.1	948.9
Triethylamine	10.72	205.7	951.0	981.8
Tri-*n*-butylamine	9.93	189.2	967.6	998.5
Quinuclidine	11.15	191.6	952.5	983.3
Triphenylamine		79.9	876.4	908.9
3,5-Dichloropyridine	0.67	128.4		
2-Bromopyridine	0.90	126.2	873.0	904.8
2-Chloropyridine	0.72	132.5	869.0	900.9
3-Bromopyridine	2.85	144.9	878.2	910.0
Quinoline	4.85	150.9	921.4	953.2
Pyridine	5.20	161.3	898.1	930.0
4-Methylpyridine	6.03	163.4	915.3	947.2
2,6-Dimethylpyridine	6.72	170.3	931.1	963.0
2,4,6-Trimethylpyridine	7.43	178.5		
Aniline	4.60	142.3	850.6	882.5
N,*N*-Dimethylaniline	5.15	157.7	909.2	941.1
Methanol	−2.05		724.5	754.3
Ethanol	−1.94	79.9	746.0	776.4
Water	−1.74	68.6	660.0	691.0
Dimethyl ether	−2.48		764.5	792.0
Diethyl ether	−2.39	79.8	801.0	828.4
Tetrahydrofuran		82.0	794.7	822.1
Benzaldehyde	−4.48	67.4	802.1	834.0
Acetophenone	−3.87	79.1	829.3	861.1
Benzophenone	−4.71	70.7	852.5	882.3
Acetone	−3.06	79.9	782.1	812.0
Diethyl ketone	−3.88		807.0	836.8
Dicyclopropyl ketone	−2.40	87.0	850.6	880.4
Methyl acetate	−3.90		790.7	821.6
Methyl propionate	−4.37		799.2	830.2
Methyl benzoate	−7.05		819.5	850.5
N,*N*-Dimethylacetamide	−0.21	133.9	877.0	908.0
N,*N*-Dimethylformamide	−1.13	123.4	856.6	887.5
N-Methylpyrrolidone	−0.71	131.0	891.6	923.5
Tetramethylurea	−0.14	157.3	899.6	930.6
Dimethyl sulfoxide	−1.54	119.7	853.7	884.4
Hexamethylphosphoric triamide	−0.97		928.7	958.6
Triphenylphosphine oxide		87.4	876.4	906.2
Pyridine *N*-oxide	0.8	139.7	892.9	923.6
Nitrobenzene		27.6	769.5	800.3
N,*N*-Dimethylthioacetamide	−2.25		894.4	925.3
Methyl sulfide	−6.99		801.2	830.9
Ethyl sulfide	−6.68	79.5	827.0	856.7
Triphenylphosphine		120.0	940.4	972.8

1.3 Scales of Brönsted Basicity and Affinity in the Gas Phase

Various mass spectrometric techniques permit the study of proton transfer reactions in the gas phase and the definition of Brönsted basicity scales free of solvent effects [26].

The gas-phase basicity GB and the proton affinity PA of a base B are defined as the standard Gibbs energy change and the standard enthalpy change, respectively, of the formal deprotonation reaction 1.12:

$$\begin{aligned}&\mathrm{BH^+} \rightarrow \mathrm{B} + \mathrm{H^+}\\ &\varDelta H^\circ = \text{proton affinity} = \mathrm{PA}\\ &\varDelta G^\circ = \text{gas-phase basicity} = \mathrm{GB}\end{aligned} \tag{1.12}$$

Unfortunately, this terminology, currently in use, is not completely correct since an affinity is a chemical potential (a $\varDelta G$ value) whereas the proton affinity is an enthalpy. An alternative terminology for $\varDelta H^\circ$ might be 'enthalpy of basicity', but it seems unrealistic to propose a change of terminology now considering the accepted practice.

The absolute basicity and affinity cannot be obtained directly because the gas-phase reaction 1.12 is extremely endoergic and endothermic. It is common practice to resort to thermodynamic cycles, involving enthalpies of formation and dissociation thresholds, to calculate absolute PAs. The transformation of absolute PAs into absolute GBs (Equation 1.13) requires the evaluation of the entropy of basicity (Equation 1.14) (mainly through quantum chemical calculations today):

$$\mathrm{GB} = \mathrm{PA} - T\varDelta S^\circ \tag{1.13}$$

$$\varDelta S^\circ = S^\circ(\mathrm{B}) + S^\circ(\mathrm{H^+}) - S^\circ(\mathrm{BH^+}) \tag{1.14}$$

The number of absolute PA and GB values that can be accurately evaluated is very limited. In fact, most parts of the scales are obtained by measuring the relative basicity of an unknown using a reference base B° of known GB. Relative basicities, designated $\varDelta$GB, are obtained from equilibrium constants K of the proton exchange reaction 1.15 between bases B and B°:

$$\mathrm{BH^+} + \mathrm{B^\circ} \rightleftharpoons \mathrm{B^\circ H^+} + \mathrm{B} \tag{1.15}$$

$$\varDelta\mathrm{GB} = -RT\ln K = \mathrm{GB(B)} - \mathrm{GB(B^\circ)} \tag{1.16}$$

The known basicities span a very wide range of about 1300 kJ $\mathrm{mol^{-1}}$ from He to $\mathrm{Cs_2O}$. However, the basicity of the majority of organic bases falls within 700–1000 kJ $\mathrm{mol^{-1}}$. A selection is presented in Table 1.3. Thousands of PA and GB values have been critically compiled by Hunter and Lias [27, 28].

1.4 The Lewis Definition of Acids and Bases

In the original Lewis definition (1923 [29], 1938 [30]), acids are electron-pair acceptors and bases are electron-pair donors. The fundamental reaction between a Lewis acid A and a Lewis base B is the formation of a complex (or adduct or coordination compound or addition compound) A–B (reaction 1.17):

$$\mathrm{A} + :\mathrm{B} \rightleftharpoons \mathrm{A{-}B} \tag{1.17}$$

In this reaction, the unshared electron pair of the base forms a coordinate covalent bond (or dative bond or dipolar bond) with an electron-deficient atom of the acid. The archetype of a Lewis acid/base reaction is

$$BF_3 + :NH_3 \rightleftharpoons F_3B\text{–}NH_3 \tag{1.18}$$

BF_3 is a Lewis acid because the boron atom has only six electrons in its valence shell and, having room for eight, can accept the lone pair of the nitrogen atom of ammonia.

The proton is a Lewis acid because it can accept an electron pair into its empty 1s atomic orbital. It follows that all Brönsted bases are Lewis bases. All Brönsted acids are also Lewis acids because they are hydrogen-bond donors, that is, electron acceptors (see below).

However, a much wider range of species can be classified as Lewis acids than can be classified in the Brönsted scheme. The translation of Lewis's definition into quantum-mechanical terms by Mulliken (1952) [31] further widened the definition, so as to include those reagents that donate or accept a fraction, possibly very small, of an electron. With this extension, the compounds in Tables 1.4 and 1.5 are considered as Lewis acids (electron

Table 1.4 *Examples of Lewis acids.*

Metals: M
Cations
Proton: H^+
Metallic: M^{n+}
Organometallic: CH_3Hg^+
Halogens: I^+
Carbocations: $CH_3{}^+$

Covalent metal halides, hydrides or alkyls: MX_n, MH_n, MR_n
Group 4: $TiCl_4$
Group 8: $FeCl_3$
Group 12: $ZnCl_2$, CdI_2, $HgCl_2$
Group 13: BF_3, BCl_3, BH_3, BMe_3
    $AlCl_3$, $AlMe_3$
    $GaCl_3$, GaH_3, $GaMe_3$
Group 14: $SnCl_4$
Group 15: $SbCl_3$, $SbCl_5$

Halogen-bond donors
Dihalogens: I_2, Br_2, Cl_2
Interhalogens: ICl, IBr, ClF, BrCl
Organic halogens: $IC{\equiv}N$, ICF_3, $IC{\equiv}CR$

Hydrogen-bond donors (Brönsted acids)
OH: RCOOH, ArOH, ROH, H_2O
NH: $RCONH_2$, $ArNH_2$, HNCS
CH: $CHCl_3$, $RC{\equiv}CH$
SH: ArSH
XH: HF, HCl

π Acceptors
SO_2, SO_3
Ethylenic, acetylenic, aromatic hydrocarbons substituted with electron-withdrawing groups
Quinones

Table 1.5 *Important neutral and anionic Lewis (Brönsted) bases classified by their donor atom(s).*

Hydrogen	Anion H^-
Carbon	Alkenes, alkynes, arenes, cyclopropanes
	Carbon monoxide CO
	Isonitriles $R{-}N{\equiv}C$
	Carbanions, CN^-, $RC{\equiv}C^-$
Nitrogen	sp^3 NH_3, primary amines RNH_2, secondary amines $RR'NH$, tertiary amines $RR'R''N$
	sp^2 Six-membered aromatic *N*-heterocycles (e.g. pyridines)
	Five-membered aromatic *N*-heterocycles (e.g. imidazoles)
	Imines $R_2C{=}NR'$, amidines $R_2NC{=}NR'$, oximes $R_2C{=}NOR'$
	sp Nitriles $RC{\equiv}N$
	Anions NH_2^-, N_3^-, SCN^-, OCN^-
Phosphorus	Phosphines $RR'R''P$
Arsenic	Arsines $RR'R''As$
Oxygen	Water H_2O, alcohols ROH, ethers ROR′, peroxides ROOR′
	Carbonyls RCOR′: aldehydes, ketones, lactones, esters, carbonates, amides, lactams
	Sulfonyls $RR'SO_2$
	Sulfinyls RR′SO
	Seleninyls RR′SeO
	Phosphoryls RR′R″PO
	Arsine oxides RR′R″AsO
	Amine oxides RR′R″NO
	Nitrosos $R{-}N{=}O$
	Nitros RNO_2
	Isocyanates $R{-}N{=}C{=}O$
	Anions OH^-, RO^-, $RCOO^-$, $CO_3{}^{2-}$, $ClO_4{}^-$, $PO_4{}^{3-}$, $HPO_4{}^{2-}$, $H_2PO_4{}^-$, $SO_4{}^{2-}$, $HSO_4{}^-$, $SO_3{}^{2-}$, $NO_3{}^-$, $NO_2{}^-$
Sulfur	H_2S, thiols RSH, thioethers RSR′, disulfides RSSR′
	Thiocarbonyls RCSR′: thioamides, thioureas
	Isothiocyanates $RN{=}C{=}S$
	Thiophosphoryls RR′R″PS
	Anions SH^-, RS^-, SCN^-
Selenium	Selenoethers RSeR′
	Selenocarbonyls RCSeR′: selenoamides, selenoureas
	Selenophosphoryls RR′R″PSe
Tellurium	Telluroethers RTeR′
Halogens	Haloalkanes RF, RCl, RBr, RI
	Anions F^-, Cl^-, Br^-, I^-

acceptors) and Lewis bases (electron donors), respectively, and the following reactions (1.19)–(1.27) are considered today as Lewis acid/base reactions:

$$Co^{2+} + 6\,H_2O \rightleftharpoons [Co(OH_2)_6]^{2+} \tag{1.19}$$

$$Ag^+ + C_6H_6 \rightleftharpoons Ag^+ \cdots C_6H_6 \tag{1.20}$$

$$Ni + 4\,CO \rightleftharpoons Ni(CO)_4 \tag{1.21}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{1.22}$$

$$SiF_4 + 2\,F^- \rightleftharpoons SiF_6^{2-} \tag{1.23}$$

$$I_2 + Et_2O \rightleftharpoons I{-}I \cdots OEt_2 \quad (1.24)$$

$$(NC)_2C = C(CN)_2 + C_6H_6 \rightleftharpoons (NC)_2C = C(CN)_2, C_6H_6 \quad (1.25)$$

$$CH_3OH + CH_3C{\equiv}N \rightleftharpoons CH_3OH \cdots N{\equiv}CCH_3 \quad (1.26)$$

$$SO_3 + C_5H_5N \rightleftharpoons O_3S \cdots NC_5H_5 \quad (1.27)$$

In addition to the elementary reaction A + B → AB, other Lewis acid/base reactions are as follows:

(i) **Displacement reactions of one Lewis base by another:**

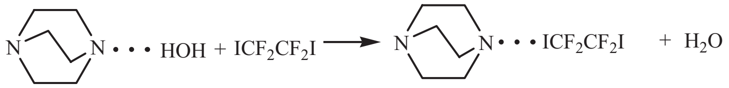
$$A{-}B^1 + B_2 \rightleftharpoons A{-}B^2 + B^1 \quad (1.28)$$

All Brönsted proton transfer reactions fit into this type.

(ii) **Displacement reactions of one Lewis acid by another:**

$$A^1{-}B + A^2 \rightleftharpoons A^2{-}B + A^1 \quad (1.29)$$

An interesting example [32] is the displacement of water hydrogen bonded to polyamines (or their *N*-oxides) by a halogen-bond donor:



(1.30)

This displacement reaction can be used to obtain hygroscopic bases in anhydrous form.

(iii) **Double displacement reactions:**

$$A^1{-}B^1 + A^2 - B^2 \rightleftharpoons A^1{-}B^2 + A^2{-}B^1 \quad (1.31)$$

Many heterolytic reactions can be classified within this group, insofar as reactants and products are formally dissected into Lewis acids and bases. For example, in reaction 1.32 the reactants methanol and hydrogen iodide are both formally the products of the acids $CH_3{}^+$ and H^+ and the bases OH^- and I^-:

$$CH_3{-}OH + H{-}I \rightleftharpoons CH_3{-}I + H{-}OH \quad (1.32)$$

Most reactions occurring in an amphoteric solvent $\alpha\beta$, with acid site α and basic site β coordinated to the two reactants, fall into this category:

$$A \cdots \beta\alpha + \beta\alpha \cdots B \rightleftharpoons A{-}B + \beta\alpha \cdots \beta\alpha \quad (1.33)$$

With the extension of the original Lewis definition, and its application to many fields of chemistry, many terms specific to those fields have been substituted for the very general ‘Lewis acid’ and ‘Lewis base’ terms. These synonyms are collected in Table 1.6.

Table 1.6 *Synonyms of 'Lewis acid' and 'Lewis base' used in various fields of chemistry.*

Field	Lewis acid synonym	Lewis base synonym
Brönsted acid/base chemistry	Proton donor	Proton acceptor
General chemistry	Electron acceptor	Electron donor
Organic chemistry (kinetics)	Electrophile	Nucleophile
Coordination chemistry	Central metallic atom (ion)	Ligand
Ionic bond	Cation	Anion
Cation solvation	Cation	Basic solvent
Anion solvation	Acidic solvent	Anion
Hydrogen bonding	Hydrogen-bond donor	Hydrogen-bond acceptor
Halogen bonding	Halogen-bond donor	Halogen-bond acceptor

1.5 Quantum Chemical Descriptions of Lewis Acid/Base Complexes

1.5.1 Valence-Bond Model

According to the Mulliken valence-bond model [4, 31], the complex AB between a Lewis acid A and a Lewis base B may be described by the wavefunction

$$\Psi_{\mathrm{AB}} = a\,\Psi_0(\mathrm{A, B}) + b\,\Psi_1(\mathrm{A^-\!-\,B^+}) \tag{1.34}$$

The no-bond wavefunction Ψ_0 describes a structure in which the binding of A and B is effected by electrostatic forces such as those between permanent dipoles of A and B, the permanent dipole of A(B) and the induced dipole of B(A), and fluctuating dipoles of A and B (London dispersion forces). The dative-bond wavefunction Ψ_1 corresponds to a structure, sometimes called a charge-transfer structure, in which an electron has been transferred from the base B (the donor) to the acid A (the acceptor). Equation 1.34 shows that, by varying the ratio of weighting coefficients a and b, all degrees of electron donation are possible.

The energy E_{AB} of a simple 1 : 1 adduct associated with the wavefunction Ψ_{AB} is given by the second-order perturbation theory

$$E_{\mathrm{AB}} = E_0 - \frac{(\beta_{01} - E_0\mathrm{S}_{01})^2}{E_1 - E_0} \tag{1.35}$$

where $E_0 = \langle\Psi_0|H|\Psi_0\rangle$, $E_1 = \langle\Psi_1|H|\Psi_1\rangle$, $\beta_{01} = \langle\Psi_0|H|\Psi_1\rangle$, $\mathrm{S}_{01} = \langle\Psi_0|\Psi_1\rangle$ and H represent the energy of the no-bond structure, the energy of the dative-bond structure, the resonance integral, the overlap integral and the total exact Hamiltonian respectively. It can be seen from Equation 1.35 that the energy of the acid/base complex is the sum of an electrostatic energy term (E_0) and a second term that is due to covalency (in the case where A and B are neutral, Ψ_1 corresponds to a covalent binding involving the odd electrons in $\mathrm{A^-}$ and $\mathrm{B^+}$).

1.5.2 Perturbation Molecular Orbital Theory

A general description of chemical reactivity has been given by Klopman [33]. It can be applied [2] to a simple Lewis acid–base reaction $\mathrm{A + B \rightarrow AB}$. Klopman [33] and Jensen

[2] used a perturbation molecular orbital (MO) theory and wavefunction $\Psi_{mn}(\mathrm{AB})$:

$$\Psi_{mn}(\mathrm{AB}) = a\,\Psi_n(\mathrm{A}) + b\,\Psi_m\,(\mathrm{B}) \tag{1.36}$$

where a and b are weighting coefficients and Ψ_m and Ψ_n are expressed as linear combinations of atomic orbitals (AOs), ϕ:

$$\Psi_m = \sum_r c_r^m \phi_r \qquad \Psi_n = \sum_s c_s^n \phi_s \tag{1.37}$$

where $c_r^m(c_s^n)$ is the AO coefficient of the mth (nth) MO at atom r (s). If the interaction occurs primarily between a single donor atom r on B and a single acceptor atom s on A, the energy change, ΔE, upon formation of the adduct AB in the gas phase can be approximated by the sum of three terms:

$$\Delta E \approx \frac{Q_r Q_s}{R_{rs}} + 2 \sum_{\substack{m \\ \text{base}}}^{\text{occ}} \sum_{\substack{n \\ \text{acid}}}^{\text{unocc}} \frac{\left(c_r^m c_s^n \beta_{rs}\right)^2}{E_m - E_n} + \Delta E(\text{repulsion}) \tag{1.38}$$

The first term is the coulombic attraction between the total net opposite charges Q_r and Q_s of the interacting atoms r and s of B and A at a distance R_{rs}. The second term is a second-order orbital perturbation due to the attractive interactions between the occupied orbitals on B (A) and the unoccupied orbitals on A(B). β_{rs} is the resonance integral between the AOs of r and s, and E_m (E_n) is the energy of orbital m (n) of B (A) in the field of A (B). The last term is a first-order orbital perturbation due to the repulsive interactions between the filled orbitals of A and B.

The largest contribution to the double summation over orbital pairs in the second term will arise when the denominator is smallest. This occurs when the energies of the highest occupied MO (HOMO) of the base and the lowest unoccupied MO (LUMO) of the acid become closer. By considering only this contribution in the double summation (the so-called frontier orbitals approximation), Equation 1.38 simplifies to

$$\Delta E \approx \frac{Q_r Q_s}{R_{rs}} + \frac{2\left(c_r^{\text{HOMO}} c_s^{\text{LUMO}} \beta_{rs}\right)^2}{E\,(\text{HOMO})_{\text{B}} - E\,(\text{LUMO})_{\text{A}}} + \Delta E(\text{repulsion}) \tag{1.39}$$

On the basis of Equation 1.39, the Lewis acid/base reactions can be divided into the categories of 'charge-controlled', those dominated by the first term, and 'orbital-controlled', those dominated by the second term. The factors determining the category are the following:

Category	Charge control	Orbital control
E(HOMO) − E(LUMO)	Large	Small
HOMO and LUMO overlap	Poor	Good
Polarity of A and B	High	Weak

Recent examples of the application of Klopman's approach to molecular complexes are the partitioning of the binding energies of SO_3 complexes with nitrogen bases [34] and of halogen-bonded complexes with diversified bases [35]. The results show that, for the Cl—I· · ·B complexes, the electrostatic (charge-controlled) bonding is predominant relative to covalent (orbital-controlled) bonding, whereas for $B \cdots SO_3$ complexes the electrostatic contribution to the bonding is comparable to the covalent contribution.

Despite evident shortcomings, Klopman's theory was popular in acid/base chemistry books and reviews in the 1970s because it reproduces the qualitative features of the concept of hard and soft Lewis acids and bases (see below). More satisfactory treatments of the perturbative calculation and partition of intermolecular energies are employed nowadays. An excellent summary of these approaches is available in the textbook by Stone [36]. The contributions collectively known as symmetry-adapted perturbation theory (SAPT) have been reviewed by Szalewicz and Jeziorski [37]. An intermolecular perturbation theory (IMPT) for the region of moderate overlap [38] is of particular interest in Lewis acid/base chemistry since it emphasizes the computation of charge-transfer energies [39] and is implemented in a freely available quantum chemistry package [40]. As an example [41], the electronic interaction energy components of the hydrogen-bonded complex $MeOH \cdots NEt_3$, calculated at the IMPT/6–31G(d)//B3LYP/6–31+G(d,p) level, are (in kJ mol^{-1}) -53.6 (electrostatic), $+54.5$ (exchange-repulsion), –6.4 (polarization), -7.6 (charge transfer), -19.6 (dispersion) and -32.7 (total).

The perturbation calculations of intermolecular energies are tedious, even for small molecules. On the other hand, the perturbation approach is advantageous (over the variational supermolecule approach, see below) because (i) the small interaction energy is calculated directly rather than as a difference between two large, almost identical, numbers (E_{AB} and $E_A + E_B$), (ii) the individual contributions to the intermolecular energy have a clear physical meaning, (iii) SAPT terms are free of the basis set superposition error (BSSE, see below) and (iv) each term can be evaluated using a different basis set, the most appropriate and economic for that particular component.

1.5.3 Variational Supermolecular Method and Energy Decomposition Schemes

In this method, the system of the two interacting molecules, A and B, is treated as a supermolecule and their interaction energy, ΔE, is the energy of the supermolecule minus the energies of the isolated molecules:

$$\Delta E = E_{AB} - (E_A + E_B) \tag{1.40}$$

The energy of the supermolecule AB is calculated by solving approximately the Schrödinger equation:

$$H\,\Psi_{AB} = E_{AB}\Psi_{AB} \tag{1.41}$$

by the variational method, in the same way as for the isolated molecules A and B. These calculations can be routinely performed using quantum chemistry program packages such as CAPDAC, GAMESS, GAUSSIAN, JAGUAR or SPARTAN, to cite the most popular in the chemistry community. However, they are fraught with difficulties [36, 42–45], as discussed below.

Method

The applicability of the self-consistent field (SCF) or Hartree–Fock (HF) method is evidently limited because electron correlation, and consequently the dispersion interaction which is wholly a correlation effect, are absent from any SCF calculation. A popular method in recent years has been the use of density functional theory (DFT) based on the theorem 'the energy is a functional of the electron density'. The literature contains many proposed functionals (for example, B3LYP). However, no functional for the correlation energy that yields values within so-called chemical accuracy (1 kcal $\text{mol}^{-1} = 4.184$ kJ mol^{-1}) seems yet to exist. Hence density functional approaches must be used cautiously to study molecular interactions where the contribution of dispersion energy is significant. A satisfactory approach to the correlation problem is the Møller–Plesset perturbation theory (MPn for perturbation theory to order n). MP2 calculations are significantly more expensive than SCF calculations but the MP2 method based on the 'resolution of identity' (RI) is about one order of magnitude faster than the exact MP2 method (with almost identical interaction energies for both methods). Therefore, the RI-MP2 method (implemented in the TURBOMOLE package) is well suited for the study of large complexes [46].

Atomic Orbital Basis Sets

These are the atomic orbitals used in the LCAO-MO process (ϕ in Equation 1.37). When choosing an atomic orbital basis set among the basis set libraries available in the quantum chemistry packages, one must specify (i) the size and nature of the primary core and valence basis, (ii) the so-called polarization functions added to the basis and (iii) the so-called diffuse functions that still augment the basis set. For example, 6–311++G** is a split-valence (represented by 6–311G) basis set plus polarization (represented by **) and diffuse functions (represented by ++). Large basis sets require a long computer time (roughly proportional to the fourth power of the number of basis functions), but the energy comes closer to the HF limit and the BSSE is less serious. BSSE arises from the fact that the supermolecule is described by a set that is formed by superposition of the basis sets of the two molecules A and B, that is, by a larger basis set than those of molecules A and B. A larger basis set of the supermolecule inevitably yields a larger E_{AB} value and, consequently, a larger ΔE value. This artificial increase in E_{AB} must be corrected by the counterpoise method [47, 48], in which the energies of the molecules A and B are calculated in the basis set of the supermolecule. The BSSE follows from the equation

$$\text{BSSE} = E_{\text{c}}^{\beta}(\text{B}) - E_{\text{c}}^{\alpha\cup\beta}(\text{B}) + E_{\text{c}}^{\alpha}(\text{A}) - E_{\text{c}}^{\alpha\cup\beta}(\text{A}) \tag{1.42}$$

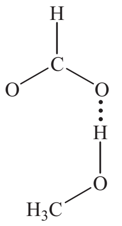
where $\alpha(\beta)$ means the A (B) basis set, $\alpha\cup\beta$ is the basis set of the supermolecule and the subscript c denotes that the energy of the molecule A (B) has been calculated using its geometry within the complex (supermolecule).

Geometry Optimization

Calculating the geometry of a supermolecule with N nuclei is an extraordinarily complex problem, since it is necessary to explore a correlated free energy hypersurface (FES) with $3N - 6$ degrees of freedom (paying special attention to the up to six coordinates describing the relative configuration of molecules A and B) by a counterpoise-corrected gradient optimization procedure. The aim is not only to locate the global minimum but also to identify other significant free energy minima for subsequent comparison of theoretical basicity with experimental results. When N is large and the FES contains many saddle points and energy minima separated by low-energy barriers, this issue requires the use of methods of molecular dynamics and statistical mechanical simulations.

In order to save computing time, several approximations are often used in the geometry optimization procedure:

(i) It is assumed that entropy does not play an important role and the potential energy surface (PES) is considered instead of the FES.
(ii) It is common to optimize the geometry at a DFT level and then to apply a higher (better correlated) level to compute the energy. Such calculations are indicated by a double slash (for example, MP2/6–311++G**//B3LYP/6–31+G**).
(iii) The BSSE is not *a priori* included in the geometry optimization cycles but a *a posteriori* in the correction of the interaction energy.
(iv) Libraries of molecular and supermolecular structures (such as the MOGADOC database [49] for the gas phase and the CSD [50] for the solid state) are searched to find starting geometries. Then the gradient optimization procedure localizes the nearest energy minimum and stops the calculation. Since there is no guarantee that the minimum so located is the global minimum, it is necessary to restart the optimization from a different geometry. After several trials, it is hoped that the main portions of PES have been properly sampled. For example, a CSD search furnishes three conformations for the hydrogen-bonded complexes of carboxylate anions: *syn* **1**, *anti* **2** and bifurcated **3**. Three starting geometries for the hydrogen-bonded complex of methanol with the formate anion might thus be



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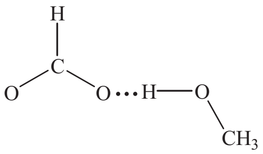

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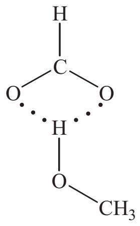


3

A B3LYP/6–31+G** optimization indicates (*in vacuo*) that **1** is the deepest minimum, **2** is a local minimum and **3** is a saddle point [41].

Anharmonicity

After an optimized structure has been obtained, the vibrational frequencies are calculated to characterize the structure as a local minimum (with no imaginary frequencies) and provide the data needed to evaluate (i) the zero-point energy, (ii) the thermal vibrational contribution to enthalpy and (iii) the vibrational entropy. *Ab initio* harmonic vibrational frequencies are typically larger than the values measured spectroscopically. A major source of this disagreement is the neglect of anharmonicity effects in the calculations (errors also arise because of the incomplete incorporation of electron correlation and the use of finite basis sets). It is customary to scale *ab initio* values for the imperfect calculations. A set of scale factors has been recommended [51]. A better approach is to compute the anharmonic corrections, but the methods recently implemented within quantum chemistry program packages are demanding of computer resources.

Relativity

The properties of molecules and supermolecules containing light atoms ($Z < 36$) are described accurately within the non-relativistic approximation. The relativistic character of inner shell electrons in heavier elements is successfully hidden inside effective core potentials (ECPs). The ECP basis set LANL2DZ* is a set with double-zeta functions for each of the two outermost shells augmented by polarization functions, which was shown to yield reasonably good results for the complexes of diiodine (see Chapter 5).

Comparison with Experimental Data

The comparison of calculated interaction energies with the experimental enthalpies is essential since it identifies the method and basis set that yield reliable energies at minimal computational expense, and assesses the validity of approximations. The interaction (binding) enthalpy at 298 K and 10^5 Pa and the interaction energy at 0 K are related as follows:

$$\Delta H^\circ_{298} = \Delta E_{\text{el}} + \Delta ZPVE + \Delta E_{\text{vib,therm}} + \Delta E_{\text{rot}} + \Delta E_{\text{trans}} + \Delta nRT \tag{1.43}$$

The operator Δ corresponds to the change upon the reaction $\text{A} + \text{B} \rightarrow \text{AB}$. The term ΔE_{el} is the BSSE-corrected electronic interaction energy. The second term is the zero-point vibrational energy contribution. The vibrational term, $\Delta E_{\text{vib,therm}}$, is the change in the vibrational energies in going from 0 to 298 K. The last terms are thermal terms, which account for the loss of rotational and translational degrees of freedom and the change in the number of moles of perfect gas ($\Delta n = -1$ for a 1 : 1 complexation). ΔE_{rot} and ΔE_{trans} are classically equal to $\pm\frac{1}{2}RT$ for each degree of freedom gained or lost in the reaction.

The dissociation energy of the A—B bond is given by

$$D_0 = -\Delta E_{\text{el}} - \Delta ZPVE \tag{1.44}$$

and the Gibbs energy of complexation, ΔG°_{298}, is

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298} \tag{1.45}$$

where the entropy of complexation, ΔS°_{298}, is the sum of the translational, rotational and vibrational entropy changes:

$$\Delta S^\circ_{298} = \Delta S_{\text{tr}} + \Delta S_{\text{rot}} + \Delta S_{\text{vib}} \tag{1.46}$$

Taking the hydrogen-bonded complex of methanol with methylamine, $CH_3OH\cdots NH_2CH_3$, as an example, the various contributions to ΔH° and ΔS°, calculated at the MP2/aug-cc-pVTZ//B3LYP/6–31+G** level, are listed in Table 1.7. There is a very good agreement between the calculated [41] and experimental [52] enthalpies since the difference lies within the experimental error. The agreement is far less good for entropies. The largest source of error arises in the vibrational term, calculated in the harmonic approximation and sensitive to the level of theory (frequencies calculated at the B3LYP/6–31+G** level).

Table 1.7 *Thermodynamic parameters of the reaction $CH_3OH + CH_3NH_2 \rightarrow CH_3OH\cdots NH_2CH_3$ at 298 K and 10^5 Pa. Energies in kJ mol^{-1}, entropies in J K^{-1} mol^{-1}.*

ΔE_{el}	−36.68		
BSSE	6.09		
$\Delta ZPVE$	6.58		
$D_o =$	24.0		
$\Delta E_{vib,therm}$	10.38	ΔS_{vib}	92.57
ΔE_{trans}	−3.72	ΔS_{trans}	−143.25
ΔE_{rot}	−3.72	ΔS_{rot}	−52.81
$-RT$	−2.48		
$\Delta H^{\circ}_{298} =$	−23.54	$\Delta S^{\circ}_{298} =$	−103.5
exp.	−23.4 ± 1.0	exp.	−73 ± 4

Energy Decomposition Schemes

The supermolecule method is capable of assessing the binding strength of species A and B through the dissociation energy, D_0. It shows that there is a continuum of binding energies from very weak van der Waals bonds (for example, between two rare gas atoms in a molecular beam) to strong dative bonds. However, in contrast to perturbation methods, it cannot determine the origin of the binding forces that hold the species A and B together. Physical intuition suggests that there are five different types of electric interactions between the species A and B as they approach one another [53].

At a large separation between the two species, the most important interaction arises from the direct *electrostatic* (ES) (coulombic) interaction between the unperturbed charge distributions of A and B. It is customary to express the charge distribution in terms of a multipole expansion: charge, dipole, quadrupole and so on. Then the direct electrostatic interaction between A and B is the sum of the interactions of their respective multipole moments.

When the separation decreases, an attractive term related to the mutual *polarization* (POL) of the two charge distributions will become significant. It arises from the deformation of the electron cloud of A induced by the electrical field produced by B (and vice versa).

Within the same range of mutual distance, an attractive interaction originates from an intermolecular correlation between the instantaneous fluctuations in the charge distributions of A and B. London called this inherently quantum mechanical phenomenon *dispersion* (DISP).

When the species A and B approach so closely that their electron clouds overlap, the Pauli exclusion principle keeps electrons of the same spin away from each other. Therefore, electron density is removed from the overlap region. The positively charged nuclei are thus incompletely shielded from each other and mutually repel. This interaction is described as exchange-repulsion or just *exchange* (EX).

Another short-range interaction has been described by Mulliken in interpreting the bonding that can occur between a species that has a low ionization energy (an electron donor) and one that has a high electron affinity (an electron acceptor). When the electron clouds of the approaching species overlap, a portion of the electrons may shift from one of the two species to the other (essentially from B to A). This attractive *charge transfer* (CT) interaction should occur for a complex to be designated as a Lewis acid/base complex. The question of how much charge is transferred in adducts is, however, very complex and will not be addressed here.

According to this description of the interaction effects, the whole interaction energy ΔE could be divided into separate and additive terms:

$$\Delta E = \Delta E_{\mathrm{ES}} + \Delta E_{\mathrm{POL}} + \Delta E_{\mathrm{DISP}} + \Delta E_{\mathrm{EX}} + \Delta E_{\mathrm{CT}} \tag{1.47}$$

There is no unequivocal operative definition of these terms allowing numerical computations. Consequently, many energy partition schemes have been proposed. Most are based on ideas presented first in 1971 by Morokuma [54, 55], who decomposed the variational Hartree–Fock interaction energy into ΔE_{ES}, ΔE_{POL}, ΔE_{EX} and ΔE_{CT} (note that this list does not include ΔE_{DISP}, which must be calculated separately). DFT-calculated interaction energies have also been partitioned (see a review [56] on various classes of donor/acceptor complexes of transition metals and main group elements).

1.5.4 Natural Bond Orbital Theory

The natural bond orbital (NBO) method of Weinhold *et al.* [8, 57] provides a scheme appropriate to the analysis of Lewis acid/base interactions [8, 58] as it emphasizes the calculation of delocalization of electron density into unoccupied orbitals.

The atomic orbital basis set is transformed into two sets of orbitals. The first set, consisting of core, lone pair and bond orbitals, is mathematically chosen to include the highest possible percentage of the electron density, and thus provides the most accurate possible 'natural Lewis structure' picture of the wavefunction. Since each valence bonding NBO must be paired with a corresponding valence antibonding NBO, the Lewis-type (donor) NBOs are complemented by a set of non-Lewis-type (acceptor) NBOs that are formally empty in an idealized Lewis structure picture. Weak occupancies of the valence antibonds correspond to irreducible departures from the idealized Lewis picture. These occupancies are a direct consequence of delocalizing interactions with the occupied donor orbitals. The energetic stabilization due to such donor/acceptor interactions can be estimated by second-order perturbation theory.

An interesting example is provided by the NBO analysis of the water dimer $H_2O\cdots HOH$, where the left and right molecules behave as the Lewis base and the Lewis acid, respectively. The interaction energy is decomposed into charge transfer (CT) and no charge transfer (NCT) as follows:

$$\Delta E = \Delta E_{\mathrm{NCT}} + \Delta E_{\mathrm{CT}} \tag{1.48}$$

ΔE_{CT} is defined as the loss in interaction energy that results when the energy is calculated after deleting the Fock matrix elements between the occupied orbitals of one molecule and the unfilled orbitals of the other. A large basis set HF calculation gives values of -17.2, $+10.0$ and -27.2 kJ mol^{-1} for ΔE, ΔE_{NCT} and ΔE_{CT}, respectively. The main origin of the charge transfer component ΔE_{CT} is identified by a second-order perturbative analysis of the Fock matrix as an $n \rightarrow \sigma^*$ charge transfer from one of the oxygen lone pairs, n, of the electron donor molecule (hydrogen-bond acceptor) to the proximate OH antibond, σ^*, of the electron acceptor molecule (hydrogen-bond donor), yielding a stabilization energy of -27.6 kJ mol^{-1}, in good agreement with the value of ΔE_{CT}. Accordingly, the NBO occupancies indicate that the proximate σ^* orbital has increased in occupancy by 0.0083 *e* from its monomer value of 0.0000 and that the proximate lone pair has decreased in occupancy by 0.0081 e from its monomer value of 1.9988. A correlated wavefunction confirms the $n \rightarrow \sigma^*$ picture of the water dimer and shows that dispersion is not important in this complex (~20% of the total interaction energy).

The values of the CT term calculated by the NBO scheme are very much larger than those found by most other methods. It should not be concluded that the NBO energy decomposition analysis is wrong in principle. The divergence should rather be attributed to a different operational definition of the charge transfer energy.

A unified NBO donor/acceptor perspective is given to the complexes of various Lewis acids (BF_3, transition metals and ions, hydrogen-bond donors, Br_2, NO^+, tricarbonylchromium, tetracyanoethylene, etc.) in a book by Weinhold and Landis [8]. This analysis emphasizes the importance of orbital interactions in the formation and properties of complexes. A nice example is the description of rare gases as unusual Lewis bases towards BeO because suitable matching orbitals can be found on this strong Lewis acid. In the linear complex He···BeO, the filled n_{He} orbital interacts strongly with the backside of the σ^*_{BeO} antibond and the vacant n^*_{Be} orbital (sp hybrid). The calculated interaction energy amounts to -26.8 kJ mol^{-1}.

1.5.5 Quantum Theory of Atoms in Molecules

The theory of 'atoms in molecules' (AIM) of Bader [59, 60] offers criteria enabling the existence and the nature of bonds to be determined from the topological analysis of the electron density. This theory has not only provided new insights into the understanding of intramolecular bonds but has also been successful in the field of intermolecular bonds, such as hydrogen bonds [61], halogen bonds [62], van der Waals bonds [63] and more strongly bound donor/acceptor complexes [64].

The definitions sufficient to understand the topology of a molecule, or in our case a complex, are illustrated by Figure 1.1 and given in the following:

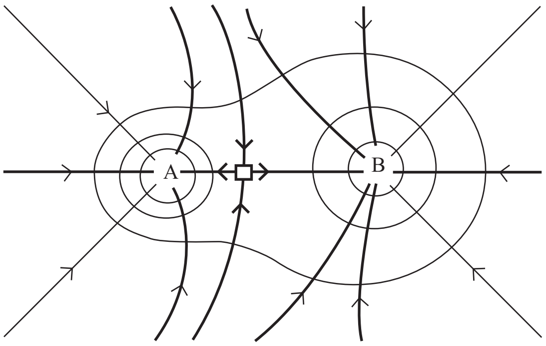


Figure 1.1 *Electron density contour of a diatomic molecule AB overlaid with trajectories of* $\nabla\rho$*. The bond path is defined by two trajectories starting at the bond critical point (denoted by a square) and ending at the nuclei. The atomic basins* $\Omega(A)$ *and* $\Omega(B)$ *are separated by a pair of trajectories originating at infinity and terminating at the bond critical point.*

- Electron density function $\rho(r)$: a three-dimensional function defined such that $\rho(r)\mathrm{d}\tau$ is the probability of finding an electron in the elemental volume $\mathrm{d}\tau$ at point r. This function may be determined experimentally by analysing X-ray diffraction data of solids.
- Gradient of the electron density $\nabla\rho(r)$: a vector that points in the direction of maximum increase in the density.
- Gradient vector field of the electron density: obtained by the trajectories traced out by the gradient vectors.
- Critical point: special point where $\nabla\rho(r)$ vanishes (for instance, a nucleus).
- Nucleus: attractor of the gradient vector field of $\rho(r)$ where trajectories starting at infinity terminate.
- Basin: space containing all trajectories leading to an attractor.
- Atom: union of a nucleus and its basin.
- Bond critical point: critical point found between nuclei that appear linked by a saddle in $\rho(r)$. There is a unique pair of trajectories that originate at such a critical point and terminate, each one, at the neighbouring nuclei. They define the bond path along which the electron density is a maximum with respect to any lateral displacement.
- Laplacian of the electron density, $\nabla^2\rho(r)$: scalar derivative of the gradient vector field of $\rho(r)$. It determines where electronic charge is locally concentrated, $\nabla^2\rho < 0$, and depleted, $\nabla^2\rho > 0$. The Laplacian can be partitioned into energy densities. It can be demonstrated that there is a local virial theorem

  $$\frac{1}{4}\nabla^2\rho(r) = 2G(r) + V(r) \tag{1.49}$$

  (in atomic units), where $G(r)$ is the kinetic energy density and $V(r)$ the potential energy density. The local energy density $H(r)$ is the sum of the kinetic and the potential energy density.
- Important properties that can be evaluated at the bond critical point (b): ρ_b, $\nabla^2\rho_\mathrm{b}$, G_b, V_b and H_b.
- Atomic properties requiring an integration over the atomic basin (Ω): $E(\Omega)$ (energy), $N(\Omega)$ (electron population) and $v(\Omega)$ (volume).
- Bond order (BO) can be calculated according to Angyan *et al.* [65]

The topological AIM properties have been extensively used for rationalizing Lewis acid/base reactions. A few examples follow.

The Lewis basic site of a species is identified as a critical point where $-\nabla^2\rho$ is maximum (local charge concentration) with high potential energy, while the Lewis acidic site is identified as a critical point where $-\nabla^2\rho$ is minimum (local charge depletion) with high kinetic energy. A Lewis acid/base reaction corresponds to the combination of a charge concentration (a 'lump' in the zero value surface of $\nabla^2\rho$) in the valence shell of the base with a charge depletion (a 'hole' in the zero value surface of $\nabla^2\rho$) in the valence shell of the acid. The alignment of the two critical points (i.e. the complementarity of the 'lump' and 'hole') provides a guide to the relative angle of approach of the acid and base molecules.

A set of criteria have been proposed to establish weak intermolecular bonding interactions, such as $CH_4\cdots OH_2$ (hydrogen bond?), $F_2\cdots CO$ (halogen bond?) or $Ar\cdots CO_2$ (van der Waals bond). For example, the criteria necessary to conclude that a hydrogen bond $X{-}H\cdots B$ is present are as follows [61]: (i) the existence of a bond critical point and a bond path $H\cdots B$, (ii) an appropriate value of ρ_b (the typical range is between 0.002 and 0.034 au),

(iii) an appropriate value of $\nabla^2\rho_b$ (a range of $+0.05$ au for the π-complex FH$\cdots$HC≡CH to $+0.14$ au for the O complex FH$\cdots$OH$_2$ can be found in ref. [62]), (iv) mutual penetration of hydrogen and acceptor atom, (v) loss of charge of the hydrogen atom, (vi) energetic destabilization of the hydrogen atom and (vii) decrease in the hydrogen atom's volume. Hydrogen bonds (like ionic bonds, van der Waals bonds and halogen bonds) are considered as closed-shell interactions because they show $\nabla^2\rho_b > 0$. Hence they differ from covalent bonds, metallic bonds and dative bonds considered as shared-shell interactions with $\nabla^2\rho_b < 0$. However, strong hydrogen bonds are also characterized by $\nabla^2\rho_b < 0$. Thus, hydrogen bonding can cover the spectrum of bonding interactions, from closed- to shared-shell.

Numerous correlations have been established between ρ_b, $\nabla^2\rho_b$, G_b, V_b, BO and so on and the electronic interaction energy. However, good correlations are generally restricted to structures in which the same pair of atoms are interacting. Multivariate correlations are required to obtain good family-independent correlations [66].

The carbonyl complexes of Cr, Fe and Ni and the metallocene complexes of Fe, Al^+ and Ge have been studied [64] to illustrate the complementary nature of the quantum theory of atoms in molecules and molecular orbital theory in the understanding of the metal–carbon bonds.

An alternative partition of the molecular space is provided by topological analysis of the electron localization function [67], which yields basins related to the local pairing of electrons. By this method, Silvi *et al.*, investigated the 1 : 1 complexes of the first series transition metals and various ligands [68], and hydrogen bonding [69]. They also studied the protonation site of simple bases and established the following rule [70]: protonation occurs in the most populated basin of the base that yields the least topological change of the localization gradient field.

1.6 Measurement of Lewis Basicity

According to the glossary of terms used in physical organic chemistry published by the International Union of Pure and Applied Chemistry [71], Lewis basicity is defined as follows:

> *The thermodynamic tendency of a substance to act as a Lewis base. Comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis bases with a common reference Lewis acid.*

Thus, the Lewis basicity of a series of bases B^i will be measured by the thermodynamic equilibrium constants K of the equilibria

$$B^i + A^\circ \rightleftharpoons B^iA^\circ \tag{1.50}$$

where A° is a reference Lewis acid. These equilibrium constants are referred to as complex formation, complexation, association, stability or binding constants. The reciprocal quantity is a dissociation or instability constant:

$$B^iA^\circ \rightleftharpoons B^i + A^\circ \tag{1.51}$$

A Lewis basicity scale can be constructed from this set of equilibrium constants. The basicity scale may be expressed as K, or as pK or as ΔG. In order that the definition and notation of Lewis scales be the same as those of the aqueous Brönsted scale $\mathrm{p}K_{\mathrm{BH}^+}$, the Lewis basicity towards the acid A° is, at this point, defined as

$$\mathrm{p}K_{\mathrm{BA}^\circ} = -\log_{10} K_{\mathrm{BA}^\circ} = -\log K(\text{reaction 1.51}) = +\log K(\text{reaction 1.50}) \qquad (1.52)$$

In this way, a Lewis base will be strong if it forms a complex with a large association constant, that is, a low dissociation constant, and a large positive value of $\mathrm{p}K_{\mathrm{BA}_0}$ will describe a strong Lewis base towards A°.

1.6.1 Gas-phase Reactions

For the ideal-gas (a good approximation for real gas mixtures at relatively low pressures) reaction $\mathrm{A(g)} + \mathrm{B(g)} \rightleftharpoons \mathrm{AB(g)}$, the *standard pressure equilibrium constant* K_p° is

$$K_\mathrm{p}^\circ = \frac{(P_\mathrm{AB}/P^\circ)}{(P_\mathrm{B}/P^\circ)(P_\mathrm{A}/P^\circ)} \qquad (1.53)$$

where P_AB, P_A and P_B are the partial pressures at equilibrium in bar of the complex, the acid and the base, respectively, and the standard pressure P° is taken to be 1 bar. The total pressure of the system at equilibrium, P, is given by the sum of the partial pressures:

$$P = P_\mathrm{A} + P_\mathrm{B} + P_\mathrm{AB} \qquad (1.54)$$

From the stoichiometry of the reaction, P_A and P_B can be related to the initial pressures $P_{0,\mathrm{A}}$ and $P_{0,\mathrm{B}}$. In the manometric method, the pressures $P_{0,\mathrm{A}}$, $P_{0,\mathrm{B}}$ and P are successively measured in a vacuum line kept at a fixed temperature using a precision manometer. Thus, the equilibrium constant can be calculated using the equation

$$K_\mathrm{p}^\circ = \frac{\left(P_{0,\mathrm{A}} + P_{0,\mathrm{B}} - P\right)}{\left(P - P_{0,\mathrm{B}}\right)\left(P - P_{0,\mathrm{A}}\right)} P^\circ \qquad (1.55)$$

Examples of determinations of pressure equilibrium constants by the manometric method can be found in the literature [52, 72] for the complexes of $\mathrm{B(CH_3)_3}$ and $\mathrm{CH_3OH}$ with amines.

The equilibrium constant can also be expressed in terms of concentration C by using the ideal-gas relation:

$$P = \frac{n}{V} RT = CRT \qquad (1.56)$$

where R is the ideal-gas constant (0.083 145 l bar $\mathrm{mol^{-1}\,K^{-1}}$), n the number of moles, T the temperature (K) and V the volume (l). We have

$$K_\mathrm{p}^\circ = \frac{C_\mathrm{AB}}{C_\mathrm{A} C_\mathrm{B}} \left(\frac{RT}{P^\circ}\right)^{-1} = K_\mathrm{c}^\circ \left(\frac{C^\circ RT}{P^\circ}\right)^{-1} \qquad (1.57)$$

where K_c° is the *standard concentration equilibrium constant*

$$K_\mathrm{c}^\circ = \frac{(C_\mathrm{AB}/C^\circ)}{(C_\mathrm{A}/C^\circ)(C_\mathrm{B}/C^\circ)} \qquad (1.58)$$

and C° is taken to be 1 mol $\mathrm{l^{-1}}$.

Since the standard state of an ideal gas is defined as having 1 bar pressure, the standard complexation Gibbs energy ΔG° is directly related to K_p°:

$$\Delta G^\circ = -RT \ln K_\mathrm{p}^\circ \tag{1.59}$$

but indirectly related to K_c° through (1.57).

1.6.2 Solution Reactions

Most complexation reactions between neutral molecules are carried out in a solvent since it is easier to work on solutions than on gases. Moreover, the number of neutral systems that can be studied by gas-phase techniques is limited. The ion–molecule reactions in the gas phase are treated in Chapter 6.

For the reaction A(solution) + B(solution) $\rightleftharpoons$ AB(solution), the *activity equilibrium constant* K_a is defined as

$$K_\mathrm{a} = \frac{a_\mathrm{AB}}{a_\mathrm{A} a_\mathrm{B}} \tag{1.60}$$

where a_AB, a_A and a_B are the activities at equilibrium of the complex, the acid and the base, respectively. Practical expressions for the activities depend on the scale chosen to specify the composition of the solution.

If the mole-fraction scale is used for the solutes, then the mole-fraction scale activity is

$$a_x = \gamma_x x \tag{1.61}$$

where γ_x is the mole-fraction scale activity coefficient and x the mole fraction. The equilibrium constant K_a becomes

$$K_x = \frac{x_\mathrm{AB}}{x_\mathrm{A} x_\mathrm{B}} \frac{\gamma_{x,\mathrm{AB}}}{\gamma_{x,\mathrm{A}} \gamma_{x,\mathrm{B}}} \tag{1.62}$$

and the standard Gibbs energy of complexation is

$$\Delta G_x^\circ = -RT \ln K_x \tag{1.63}$$

The subscript x on K and ΔG° indicates that the mole-fraction scale is used.

The concentration scale is most commonly used for determining equilibrium constants of Lewis acid/base reactions in organic solvents. The concentration scale activity of a solute is

$$a_\mathrm{c} = \gamma_\mathrm{c} C / C^\circ \tag{1.64}$$

where γ_c is the concentration-scale activity coefficient and $C^\circ = 1\ \mathrm{l\ mol^{-1}}$. The equations for K_c° and ΔG° are

$$K_\mathrm{c}^\circ = \frac{C_\mathrm{AB}/C^\circ}{(C_\mathrm{A}/C^\circ)(C_\mathrm{B}/C^\circ)} \frac{\gamma_\mathrm{c,AB}}{\gamma_\mathrm{c,A} \gamma_\mathrm{c,B}} \tag{1.65}$$

$$\Delta G_\mathrm{c}^\circ = -RT \ln K_\mathrm{c}^\circ \tag{1.66}$$

In non-electrolyte solutions, if the solution is dilute, it is a good approximation to set the activity coefficients equal to one. The equilibrium constants K_x in (1.62) and K_c° in (1.65) then reduce to the expressions (1.67) and (1.68) for ideally dilute solutions:

$$K_x \approx \frac{x_{\mathrm{AB}}}{x_{\mathrm{A}} x_{\mathrm{B}}} \tag{1.67}$$

$$K_{\mathrm{c}}^{\circ} \approx \frac{(C_{\mathrm{AB}}/C^{\circ})}{(C_{\mathrm{A}}/C^{\circ})(C_{\mathrm{B}}/C^{\circ})} \tag{1.68}$$

It is often convenient to work with an equilibrium constant that omits the C° in (1.68). We define the *concentration equilibrium constant* K_{c} as

$$K_{\mathrm{c}} = \frac{C_{\mathrm{AB}}}{C_{\mathrm{A}} C_{\mathrm{B}}} \tag{1.69}$$

K_{c} has the dimensions of l mol^{-1}. The validity of the approximations (1.67) and (1.68) decreases as the complexation constant is small, owing to the high base and/or acid concentration that should be used to shift the equilibrium towards the complex formation. Unfortunately, it is very difficult, and for practical purposes impossible, to measure all the individual activity coefficients γ_{AB}, γ_{A} and γ_{B}. Thus, it is hoped that the ratio $\gamma_{\mathrm{AB}}/\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}$ remains close to unity, or at least constant. For example, the complexation reaction

$$\mathrm{CH_3CON(CH_3)_2 + I_2 \rightleftharpoons (CH_3)_2NC(CH_3){=}O \cdots I_2} \tag{1.70}$$

of complexation constant $K_{\mathrm{c}} = 6.8$ l mol^{-1} has been studied [73] in CCl_4 over the concentration range 0.002–0.40 mol l^{-1} of base for solutions of 10^{-3} mol l^{-1} of I_2. The activity coefficient of $CH_3CON(CH_3)_2$ in this concentration range varies from 1.0 to 0.77. Since I_2 is very dilute and non-polar, $\gamma_{I_2} = 1$. One cannot measure γ_{AB}. Consequently, since the values of K_{c} do not show a concentration dependence on going from 0.002 to 0.40 mol l^{-1}, it may be assumed that $\gamma_{\mathrm{AB}}/\gamma_{\mathrm{B}}$ is approximately one, or at least constant.

1.6.3 Standard State Transformations

The relationship between the mole fraction x_i and the concentration C_i (mol l^{-1}) of a solute i (A, B and AB) in a solvent S is given by

$$x_i = \frac{C_i}{1000\,d}\left(\frac{\sum n_j M_j}{\sum n_j}\right) \tag{1.71}$$

or, in terms of molar volumes $\overline{V}$ (l mol^{-1}),

$$x_i = C_i\left(\frac{\sum n_j \overline{V_j}}{\sum n_j}\right) \tag{1.72}$$

where d is the density of the solution in g cm^{-3}, $\sum n_j$ is the sum of the number of moles (j = A, B, AB and S) and M_j (g mol^{-1}) is the molar mass of constituent j. In very dilute solutions of solute i, Equation 1.71 becomes

$$x_i \approx \frac{C_i M_{\mathrm{s}}}{1000\,d_{\mathrm{s}}} \tag{1.73}$$

where d_s and M_s are the density and the molar mass of the solvent, respectively. For constituent i in a solution containing high concentrations of solute B, Equation 1.72 becomes

$$x_i \approx C_i \left[\overline{V_s} + x_B \left(\overline{V_B} - \overline{V_s}\right)\right] \tag{1.74}$$

Thus, K_c and K_x are related by expressions

$$K_c \approx K_x \left[\overline{V_s} + x_B \left(\overline{V_B} - \overline{V_s}\right)\right] \tag{1.75}$$

when x_B is appreciable, or

$$K_c \approx K_x \overline{V_s} = K_x \frac{M_s}{1000\, d_s} \tag{1.76}$$

when all solutes are very dilute. Consequently, the standard Gibbs energies ΔG_x° and ΔG_c° are related by

$$\Delta G_c^\circ \approx \Delta G_x^\circ - RT\ln\left(\overline{V_s}/1\,\mathrm{mol\,l^{-1}}\right) \tag{1.77}$$

The conversion factor $\overline{V_s}$ relating K_x to K_c, and the correction term $-RT\ln\overline{V_s}$ relating ΔG_x° to ΔG_c° are given in Table 1.8.

1.6.4 Choice of Solvent

The criteria for choosing a solvent fall into three classes: (i) the solubility of A, B and AB, (ii) those specific to the experimental technique, for example IR or UV transparency when using IR or UV spectrometric methods, and (iii) the avoidance of specific solvation effects. In fact, if a solvent S is specifically associated with species A, B and AB as shown by the equilibrium

$$\mathrm{AS}_a + \mathrm{BS}_b \rightleftharpoons \mathrm{ABS}_p + q\mathrm{S} \tag{1.78}$$

where $q = a + b - p$, the equilibrium constant is defined by

$$K_c = \frac{[\mathrm{ABS}_p]\, x_\mathrm{S}^q}{[\mathrm{AS}_a][\mathrm{BS}_b]} \tag{1.79}$$

where brackets signify equilibrium concentrations and x_s is the mole fraction of solvent S. In this description of the formation of the complex in the 'active' solvent S, the constant K_c appears to be in error by the factor x_S^q. It therefore appears necessary to choose solvents as 'inert' as permitted by criterion (i). Very roughly, the 'inertness' of a solvent without significant hydrogen-bond acceptor site(s) is indicated by a low relative permittivity, a low refractive index and a low value of Reichardt's parameter $E_\mathrm{T}(30)$ (low hydrogen-bond acidity) [75]. These solvent parameters are listed in Table 1.8 for the most often used solvents in determinations of complexation constants.

1.7 Measurement of Lewis Affinity

A number of groups (Drago [76, 77], Gutmann [78, 79], Maria and Gal [80], Arnett *et al.* [81]) have proposed measuring Lewis (Brönsted) basicity from the negative enthalpies of the complexation (protonation) reactions (1.50). In order to follow the IUPAC definition of

Table 1.8 *Properties of common solvents*[a] *(at 25°C unless otherwise stated): density d_S (g cm^{-3}), molar mass M_S (g mol^{-1}), molar volume $\bar{V}_S$ (l mol^{-1}), thermal expansivity α (10^{-3} K^{-1}), relative permittivity ε (at 20°C), refractive index n (at 20°C), Reichardt's $E_T(30)$ and correction terms $RT\ln\bar{V}_S$ and αRT^2 (kJ mol^{-1}).*

Solvent	d_S	M_S	$\bar{V}_S$	α	ε	n	$E_T(30)$	$-RT\ln\bar{V}_S$	αRT^2 [b]
Heptane	0.679 46	100.203	0.1475	1.260	1.94	1.388	30.9	4.745	0.933
Cyclohexane	0.773 89	84.161	0.1088	1.22	2.02	1.426	30.8	5.500	0.902
Tetrachloroethylene	1.614 32	165.834	0.1027	1.02	2.34	1.505	31.8	5.641	0.754
Carbon tetrachloride	1.584 36	153.823	0.0971	1.229	2.30	1.460	32.4	5.781	0.908
Dichloromethane	1.316 78	84.933	0.0645	1.391	9.02	1.424	40.7	6.795	1.028
Chloroform	1.479 70	119.378	0.0807	1.26	4.89	1.446	39.1	6.240	0.931
1,2-Dichloroethane	1.2458	98.960	0.0794	1.21	10.74	1.445	41.3	6.279	0.894

[a] References [74, 75].

[b] $\alpha RT^2 = RT^2\left(\mathrm{d}\ln K_c/\mathrm{d}T\right) - RT^2\left(\mathrm{d}\ln K_x/\mathrm{d}T\right)$.

basicity [71], we recommend reserving the measurement of basicity to Gibbs energies of complexation (protonation) and using the name ‘affinity’ for the corresponding enthalpies. The names ‘enthalpy of basicity’ [26] and ‘enthalpimetric basicity’ [81] have been suggested. However, the term ‘affinity’ is in common use, mainly in the field of ion/base reactions, as exemplified by the proton affinity scale and the many scales of metal–cation affinities (see Chapter 6). Hereafter, the negative enthalpies of complexation of bases with the Lewis acids BF_3, 4-FC_6H_4OH or I_2 will be named boron trifluoride, 4-fluorophenol and diiodine affinities, respectively. However, the historical name ‘donor number’ [78, 79] will also be used for the $SbCl_5$ affinity.

The two most commonly employed techniques for obtaining complexation enthalpies are based on the temperature dependence of equilibrium constants or calorimetric procedures. In the latter, the heat evolved when the acid and base are mixed in the reaction cell of a calorimeter is measured. The molar enthalpy of complexation, ΔH°, is related to the measured heat output, Q, corrected for the heats of dilution, the equilibrium concentration of the complex, [AB], and the volume of the solution in litres, V, by the relation

$$\Delta H^\circ = \frac{Q}{[\mathrm{AB}]\,V} \tag{1.80}$$

If an undetermined number of moles of AB have been formed, and if the equilibrium constant K_c is known from a previous study (for example, by a spectrometric method), [AB] can be calculated by Equation 1.81 obtained by resolving Equation 1.82:

$$[\mathrm{AB}] = \frac{1}{2}\left[[\mathrm{A}_0] + [\mathrm{B}_0] + \left(K_c^{-1}\right) - \left\{\left([\mathrm{A}_0] + [\mathrm{B}_0] + K_c^{-1}\right)^2 - 4[\mathrm{A}_0][\mathrm{B}_0]\right\}^{\frac{1}{2}}\right] \tag{1.81}$$

$$K_c = \frac{[\mathrm{AB}]}{([\mathrm{A}_0] - [\mathrm{AB}])([\mathrm{B}_0] - [\mathrm{AB}])} \tag{1.82}$$

where $[A_0]$ and $[B_0]$ represent the initial concentrations of acid and base. The value of ΔH° can also be found without using a separately determined value of K_c. ΔH° and K_c are considered as two adjustable parameters in a series of equations obtained by varying $[B_0]$ or $[A_0]$, and determined by iterative calculations. The high sensitivity of modern solution calorimeters offers great potential for the simultaneous determination of ΔH° and K_c, but attention must be paid to the stability of these optimized values in the iterative procedure.

The alternative procedure consists in measuring the equilibrium constant at several temperatures. The temperature dependence of the pressure equilibrium constant for an ideal-gas reaction is given by the van’t Hoff Equation 1.83:

$$\Delta H^\circ = RT^2\left(\mathrm{d}\ln K_p^\circ/\mathrm{d}T\right) \tag{1.83}$$

Since $\mathrm{d}(T^{-1}) = -T^{-2}\mathrm{d}T$, Equation 1.83 can be expressed in a form convenient for plotting:

$$\frac{\mathrm{d}\ln K_p^\circ}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ}{R} \tag{1.84}$$

Assuming that ΔH° is constant over the temperature range involved, a plot of $\ln K_p^\circ$ against $1/T$ should be a straight line whose slope multiplied by $-R$ gives the enthalpy ΔH°. Having obtained ΔG° from Equation 1.59, we can calculate the value of ΔS°, the entropy of complexation, from the equation

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \tag{1.85}$$

In the case of solution studies, the van't Hoff Equation 1.83 can be applied to K_x values. We obtain the same ΔH° value as that obtained from calorimetric measurements (Equation 1.80). However, application of Equation 1.83 to K_c values leads to a different result:

$$RT^2(\mathrm{d}\ \ln\ K_c/\mathrm{d}T) \approx \Delta H^0 + \alpha RT^2 \tag{1.86}$$

A demonstration of Equation 1.86 is given in ref. [82]. In the correction term αRT^2, α is the coefficient of thermal expansion of the solvent:

$$\alpha = V^{-1}(\mathrm{d}V/\mathrm{d}T) \tag{1.87}$$

Table 1.8 gives values of the correction term at 298 K for common organic solvents. This term amounts to $\sim$1 kJ mol^{-1} and thus cannot be neglected for weak enthalpies.

When applying the van't Hoff equation, a temperature range as large as technically permitted must be used because the error δ in ΔH° is inversely proportional to the temperature range $T' - T$ as shown [83] by Equation 1.88:

$$\delta \approx 2R\frac{T'T}{T' - T}\varepsilon \tag{1.88}$$

where ε is the maximum relative error in the equilibrium constant (assuming that the slope of the van't Hoff line is controlled by the first and last points). The error σ in ΔS° calculated by Equation 1.85 may be written as [83]

$$\sigma \approx \delta\left(\frac{1}{T} + \frac{T' - T}{2TT'}\right) \tag{1.89}$$

The influence of the temperature range on the errors in ΔH° and ΔS° is shown by the numerical examples in Table 1.9.

Many correlations between the complexation enthalpy and the Gibbs energy of complexation have been proposed, for example the SbCl$_5$ complexes [78], the diiodine complexes [4] or the hydrogen-bonded complexes [84]. They have been explained either by a quasi-isoentropic behaviour of the complexation reaction or by an enthalpy–entropy compensation effect (Equation 1.90):

$$\Delta H^\circ = \beta\Delta S^\circ + \text{constant} \tag{1.90}$$

Table 1.9 *Effect of the temperature (K) range on the errors δ in the enthalpy (kJ mol^{-1}) and σ in the entropy (J K^{-1} mol^{-1}).*

ε	T	T'	δ	σ	Remark
5%	293	313	3.8	13.4	Inadequate range
5%	268	328	1.2	5.0	Technically permitted range for CCl$_4$
5%	268	343	1.0	4.2	Technically permitted range for C$_2$Cl$_4$

This linear relationship, in which the slope β has the dimension of temperature, gives

$$\Delta G^\circ = \frac{\beta - T}{\beta} \Delta H^\circ + \text{constant} \tag{1.91}$$

There is a danger of misuse of these extrathermodynamic relationships for essentially two reasons.

First, they are often obtained from incorrect statistical treatments. When the primary experimental quantities are the equilibrium constants, which are measured at different temperatures, any error that makes ΔH° greater also makes ΔS° greater, as indicated by Equation 1.89. The propagation of errors will tend to distribute enthalpy and entropy estimates along a line characterized by a slope equal to the harmonic mean of the experimental temperatures [85]. This artefact has been pointed out many times [86–88]. Several correct statistical treatments have been advanced [85–89]. For example, the fair value of the correlation coefficient (0.951) of the enthalpy–entropy correlation (plotted in Figure 1.2) for the complexation of seven amines with I_2 has been taken to imply a chemical causation [90]. A correct statistical treatment shows [85] that the 95% confidence interval for β is (850, 147) and includes the harmonic mean of the experimental temperatures, 298 K. Thus, the hypothesis that the observed enthalpy–entropy compensation is just a consequence of the propagation of experimental errors cannot be rejected at the 5% level of significance.

The second reason is that the enthalpy–entropy compensation is generally limited to (i) acid complexes of specific base types (i.e. correlations are family dependent) and (ii) unhindered bases. An example is given for a set of complexes of boron acids with nitrogen and phosphorus bases [72, 91]. Table 1.10 shows the continuous increase in the quality of the ΔH–ΔG correlation when the sample of 31 nitrogen and phosphorus bases is gradually restricted to 21 unhindered primary and secondary amines. The limited correlation is displayed in Figure 1.3.

The molecular origin of the relations between ΔS and ΔH for a series of bases with a standard acid has been examined [92]. Investigation of the various terms contributing to ΔH in Equation 1.43 and to ΔS in Equation 1.46 suggests that the linear relations are

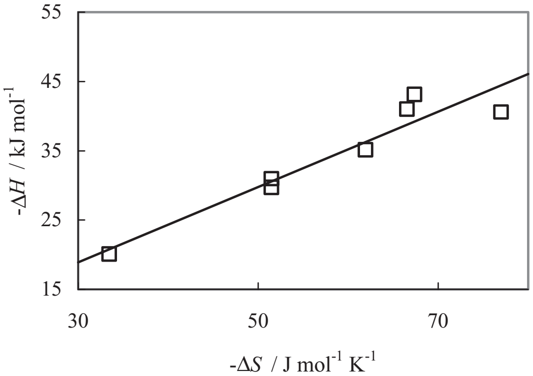


Figure 1.2 *Enthalpy–entropy plot for the complexation of diiodine with NH_3, $MeNH_2$, $EtNH_2$, $BuNH_2$, Me_2NH, Et_2NH and piperidine in heptane.*

Table 1.10 *Influence of the type of bases on the quality of the ΔH–ΔG correlation for boron acid complexes*[a].

Sample of bases	*n*	*r*	*s*[b]
Amines, pyridines and phosphines	31	0.932	3.7
Amines and pyridines	27	0.947	2.9
All amines	24	0.956	2.8
Only unhindered primary and secondary amines	21	0.966	2.6

[a] The correct regression should be of ΔH° on ΔG° evaluated at the harmonic mean of experimental temperatures, T_{hm}. Here, ΔG° is at 393 K, a temperature often close to the T_{hm}s of the 31 experiments.
[b] kJ mol^{-1}.

due to a linear relation between the vibrational entropy change, ΔS_{vib}, and the dissociation energy, D_0. The latter relation can occur if the logarithms of A–B force constants in the complex are linearly related to D_0.

1.8 The Role of the Solvent

Ideally, the reaction A + B → AB should be carried out in the gas phase in order to measure an intrinsic Lewis basicity (affinity), free of solvent effects. The development of mass spectrometric techniques has enabled many equilibrium constants of cation exchange between bases to be measured and a number of Lewis basicity scales in the gas phase [93] to be constructed. However, there are only a few determinations of equilibrium constants for the formation of uncharged complexes in the gas phase. The construction of Lewis basicity scales towards uncharged Lewis acids has essentially been carried out in solution.

It is well known that the equilibrium constant and complexation enthalpy are usually widely affected by intermolecular interactions of the species A, B and AB with the solvent

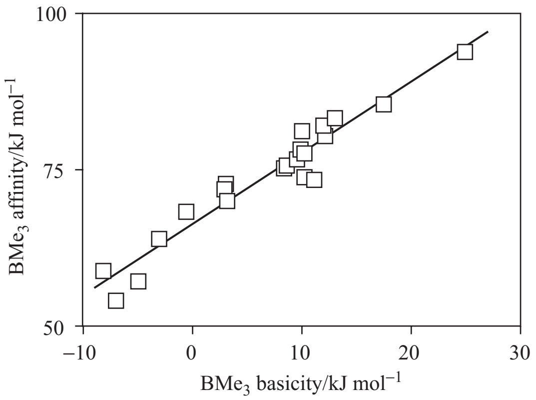


Figure 1.3 *Correlation of affinity and basicity for the complexes of BMe$_3$ with primary and secondary amines in the gas phase.*

Table 1.11 *Complexation constants (l mol^{-1}) and complexation enthalpies (kJ mol^{-1}) of some Lewis acid/base complexes in the gas phase and in certain solvents.*

		Gas phase		Solution			
Acid	Base	K_c[a]	$-\Delta H^\circ$	K_c[a]	$-\Delta H^\circ$	Solvent	Ref.
Complexes more stable in the gas phase than in solution							
SO_2	*trans*-2-Butene	3.1		0.08		Hexane	[95, 96]
TCNE[b]	*p*-Xylene	280	33.9	7.2	14.1	CH_2Cl_2	[97, 98]
I_2	Benzene	4.5	8.4	0.24[c]	6.8[c]	Heptane	[99]
I_2	Diethyl ether	6.4	18.8	0.90[c]	17.6[c]	Heptane	[99, 100]
I_2	Diethyl sulfide	226	35.1	195[c]	35.2[c]	Heptane	[101]
CH_3OH	Trimethylamine	20.8	28.9	4.6[d]	23.7[d]	C_2Cl_4	[52]
CF_3CH_2OH	Acetone	47.3	30.9	7.3	21.1	CCl_4	[102]
Complexes more stable in solution than in the gas phase							
SO_2	Trimethylamine	340	40.6	2550	46	Heptane	[103]
BF_3	Trimethylamine		111.3		129.5	CH_2Cl_2	[e]
BF_3	Trimethylphosphine		79.1		87.4	CH_2Cl_2	[e]

[a] At 25°C.
[b] Tetracyanoethylene.
[c] Chapter 5.
[d] M. Lucon, University of Nantes, personal communication.
[e] Chapter 3.

[94]. Weak complexes generally have larger complexation constants and affinities in the gas phase than in solution, while the reverse is often observed for strong complexes [94]. Numerical examples are given in Table 1.11.

The values of thermodynamic functions in the gas and solution phases can be compared in the following cycle

$$\begin{array}{ccccccc} B_g & + & A_g & \rightleftharpoons & AB_g & & \Delta H_g^o, \Delta G_g^o \\ \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \\ B_s & + & A_s & \rightleftharpoons & AB_s & & \Delta H_s^o, \Delta G_s^o \end{array} \qquad (1.92)$$

The relation between the gas-phase complexation energies, ΔH_g° orΔG_g°, and the solution complexation energies, ΔH_s° or ΔG_s°, is (where $Y = G$ or H)

$$\Delta Y_s^\circ = \Delta Y_g^\circ + \Delta Y_{g\to s}^\circ(\mathrm{AB}) - \Delta Y_{g\to s}^\circ(\mathrm{B}) - \Delta Y_{g\to s}^\circ(\mathrm{A}) \qquad (1.93)$$

where $\Delta Y_{g\to s}^\circ(i)$ denote the energies of transfer of individual species i (i = A, B or AB) from the gas phase into the solvent phase. The situation $|\Delta H_g^\circ| > |\Delta H_s^\circ|$ and $K_g > K_s$ is found when

$$\left|\Delta H_{g\to s}^\circ(\mathrm{AB})\right| < \left|\Delta H_{g\to s}^\circ(\mathrm{A}) + \Delta H_{g\to s}^\circ(\mathrm{B})\right| \qquad (1.94)$$

and

$$\left|\Delta G_{g\to s}^0(\mathrm{AB})\right| < \left|\Delta G_{g\to s}^0(\mathrm{A}) + \Delta G_{g\to s}^0(\mathrm{B})\right| \qquad (1.95)$$

The reverse situation, $|\Delta H_g^\circ| < |\Delta H_s^\circ|$ and $K_g < K_s$, is observed when inequalities converse to (1.94) and (1.95) apply. The latter solvent effect has been attributed [103] mainly to the existence of a strong dipole–(induced) dipole interaction between the very polar complex AB (for example $\mu = 4.95$ D for $Me_3N–SO_2$ and 6.02 D for $Me_3N–BF_3$) [103, 104] and the polar (polarizable) solvent; solute dipole/solvent forces are not so stabilizing for the weakly polar monomers A and B (for example $\mu = 0.86$ D for Me_3N, 1.6 D for SO_2 and 0 D for BF_3).

The question now is: 'In spite of significant solvent effects, are the solution Lewis basicity scales closely related to the intrinsic gas-phase Lewis basicity scales?' This is an important question for computational chemists who need to identify the computational methods that yield reliable basicities. A relative comparison of gas-phase computed basicities with solution experimental basicities would avoid the difficult and approximate modelling of the solvent effect [105]. However, this comparison requires that experimental gas-phase and solution basicities (affinities) be strongly correlated. This correlation appears to exist for BF_3 affinities and hydrogen-bond basicities. Equation 1.96

$$\mathrm{BF_3\ affinity(gas)} = -15.8(\pm 6.0) + 1.02(\pm 0.07)\ [\mathrm{BF_3\ affinity(CH_2Cl_2)}]$$
$$n = 8, r = 0.985, s = 4.8\ \mathrm{kJ\ mol^{-1}} \tag{1.96}$$

and Figure 1.4 compare BF_3 affinities measured in the gas phase and in the solvent CH_2Cl_2 (data in Chapter 3). Equation 1.97

$$\mathrm{CF_3CH_2OH\ basicity(gas)} = 0.82(\pm 0.11) + 0.80(\pm 0.07)[\mathrm{4\text{-}FC_6H_4OH\ basicity(CCl_4)}]$$
$$n = 11, r = 0.971, s = 0.19\ \mathrm{kJ\ mol^{-1}} \tag{1.97}$$

and Figure 1.5 compare the CF_3CH_2OH hydrogen-bond basicity measured in the gas phase [106] with the 4-fluorophenol basicity scale measured in CCl_4 (data in Chapter 4). The latter comparison is not as direct as the former but is, however, correct insofar as alcohol hydrogen-bond basicities measured in CCl_4 are strongly correlated with the 4-fluorophenol basicity in CCl_4 (see Chapter 4).

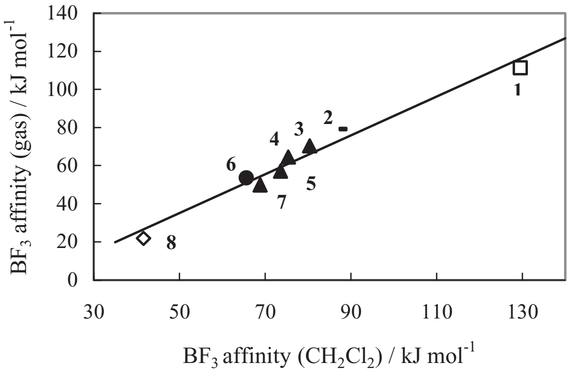


Figure 1.4 *Comparison of BF_3 affinities measured in the gas phase and in CH_2Cl_2.* ***1*** *Me_3N,* ***2*** *Me_3P,* ***3*** *tetrahydrofuran,* ***4*** *tetrahydropyran,* ***5*** *Me_2O,* ***6*** *MeCOOEt,* ***7*** *Et_2O,* ***8*** *tetrahydrothiophene.*

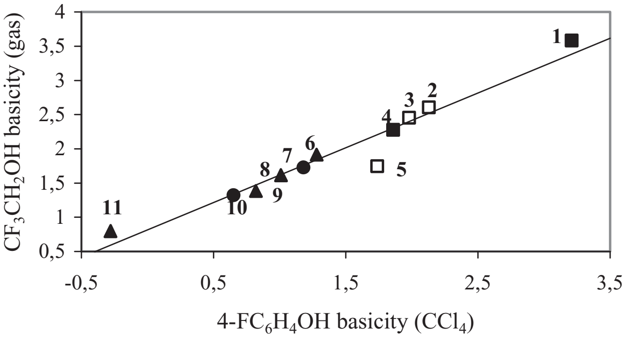


Figure 1.5 *Comparison of the trifluoroethanol basicity (as logK_c) in the gas phase with the 4-fluorophenol basicity (pK_{BHX}) in CCl_4.* ***1*** *Tetramethylguanidine,* ***2*** *Me_3N,* ***3*** *Et_3N,* ***4*** *pyridine,* ***5*** *NH_3,* ***6*** *tetrahydrofuran,* ***7*** *Me_2CO,* ***8*** *Et_2O,* ***9*** *MeOH,* ***10*** *C_2H_5COH,* ***11*** *CF_3CH_2OH. Because Me_3N and Et_3N behave well, the deviation of NH_3 is attributed to experimental errors, rather than to solvation effects.*

In the thermodynamic cycle (1.92), the Gibbs energies of transfer $\Delta G^\circ_{\mathrm{g}\to\mathrm{s}}(i)$ can be calculated by theoretical methods. Two main classes of methods have been developed for modelling solvent effects. Molecular dynamics and Monte Carlo methods use a discrete representation of the solvent molecules whereas, in the second class of so-called SCRF (self-consistent reaction field) methods, the solvent is represented as a dielectric continuum surrounding the solute cavity. These methods are outside the scope of this book. They are described in reviews [105, 107, 108] and books [109, 110]. Examples of their application to Lewis acid/base complexes can be found in the following references: hydrogen-bonded complexes [111–113], BF_3 and BH_3 complexes [114] and diiodine complexes [115].

When constructing a basicity scale in solution, the measurements must be carried out in one standard solvent because complexation constants may depend strongly on the nature of the solvent. Representative variations of complexation constants are given in Table 1.12 for hydrogen-bonded complexes [116] and in Table 1.13 for diiodine complexes [117]. It is seen that K_c [4-FC_6H_4OH–$(Me_2N)_3PO$] is 27 times larger in cyclohexane than in CH_2Cl_2, while K_c (I_2–*N*-methylimidazole) is 14 times smaller in $CHCl_3$ than in 1,2-dichlorobenzene. The

Table 1.12 *Logarithm (to base 10) of complexation constants (l mol^{-1}) of 4-fluorophenol with bases at 25°C in the indicated solvents.*

Base	*c*-C_6H_{12}	CCl_4	C_6H_5Cl	1,2-$C_6H_4Cl_2$	$ClCH_2CH_2Cl$	CH_2Cl_2
1,4-Dioxane	0.83	0.73	0.55	0.45	0.09	0.14
Triethylamine	1.99	1.98	1.84	1.93	1.70	1.67
Pyridine	2.03	1.86	1.60	1.63	1.29	1.26
N,N-Dimethylformamide	2.30	2.10	1.74	1.70	1.27	1.18
Dimethyl sulfoxide	2.56	2.54	2.20	2.18	1.65	1.44
Hexamethylphosphoric triamide	3.8	3.60	3.06	3.06	2.92	2.37

Table 1.13 *Logarithm (to base 10) of complexation constants (l mol^{-1}) of diiodine with bases at 25°C in the indicated solvents.*

Base	*n*-C_7H_{16}	CCl_4	C_6H_5Cl	1,2-$C_6H_4Cl_2$	$ClCH_2CH_2Cl$	CH_2Cl_2	$CHCl_3$
Tetrahydrofuran	0.39	0.12	−0.07	−0.24	0.10	−0.26	−0.44
N,*N*-Dimethylformamide	0.81	0.46	0.44	0.72	0.16	−0.02	−0.22
Methyl dithiovalerate	1.12	1.10	1.30	1.49	1.46	1.38	1.25
Triphenylphosphine oxide	[a]	1.38	1.17	1.27	0.96	0.97	0.89
Triphenylphosphine sulfide	[a]	2.26	2.26	2.49		2.32	2.13
N-Methylimidazole	2.86	2.67	3.10	3.35	3.18	2.65	2.19
Triphenylphosphine selenide	[a]	3.48	3.72	4.09	3.93	3.88	3.65

[a] Not soluble enough.

values of complexation Gibbs energies in two solvents S_1 and S_2 can be compared in the thermodynamic cycle (1.98):

$$\begin{array}{ccccccc} B_{S_1} + & A_{S_1} & \rightleftharpoons & AB_{S_1} & & \Delta G^{o}_{S_1} \\ \upharpoonleft\!\downharpoonright & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \\ B_{S_2} + & A_{S_2} & \rightleftharpoons & AB_{S_2} & & \Delta G^{o}_{S_2} \end{array} \tag{1.98}$$

Equation 1.99 shows that the difference $\Delta G^{\circ}_{S_2} - \Delta G^{\circ}_{S_1}$ depends on the Gibbs energies of transfer:

$$\Delta G^{\circ}_{S_2} = \Delta G^{\circ}_{S_1} + \Delta G^{\circ}_{S_1 \to S_2}(AB) - \Delta G^{\circ}_{S_1 \to S_2}(B) - \Delta G^{\circ}_{S_1 \to S_2}(A) \tag{1.99}$$

$\Delta G^{\circ}_{S_1 \to S_2}(i)$, of species i (i = A, B, AB) from the solvent S_1 to the solvent S_2. These Gibbs energies of transfer can themselves be considered to have five components

$$\Delta G^{\circ}_{S_1 \to S_2}(i) = \Delta G^{\circ}_{S_1 \to S_2}(i)(\text{cavity}) + \Delta G^{\circ}_{S_1 \to S_2}(i)(\text{electrostatic}) + \Delta G^{\circ}_{S_1 \to S_2}(i)(\text{dispersion}) + \Delta G^{\circ}_{S_1 \to S_2}(i)(\text{repulsion}) + \Delta G^{\circ}_{S_1 \to S_2}(i)(\text{hydrogen bonding}) \tag{1.100}$$

The cavity term is the positive Gibbs energy required to form the solute cavity within the solvent. The other terms correspond to the intermolecular interactions already described between two molecules and generalized here to solute/solvent interactions.

Unfortunately, it is not always technically possible to study a series of complexation reactions with bases spanning a wide range of properties in the same solvent. Hence the results of measurements of an extended basicity scale are often obtained in different solvents. Since there is little hope that the various terms of Equations 1.99 and 1.100 cancel so that $\Delta G^{\circ}_{S_1} \approx \Delta G^{\circ}_{S_2}$, methods must be found to refer the data originally determined in a given solvent to the standard solvent. The transformation can be done by means of linear Gibbs energy relationships in the form of Equation 1.101:

$$\log K_c(\text{in a standard solvent } S_1) = a \log K_c\,(\text{in a given solvent } S_2) + b \tag{1.101}$$

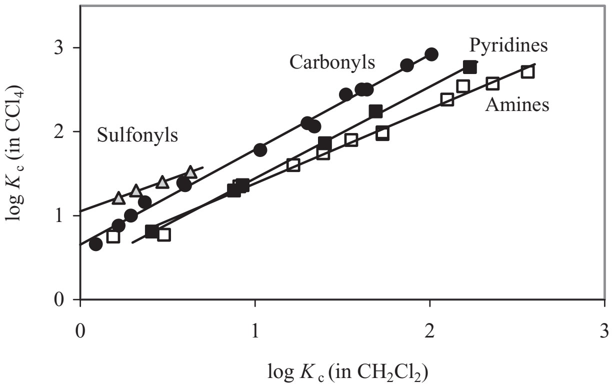


Figure 1.6 *Family-dependent transformation of 4-fluorophenol basicities in CH_2Cl_2 to 4-fluorophenol basicities in the standard solvent CCl_4. Different lines are found for sulfonyls [118], carbonyls [119], pyridines [119] and amines [120].*

These relationships have been shown to exist for hydrogen-bonded complexes [116] and for diiodine complexes (see Chapter 5), but their validity domain is limited to structurally related bases. For example, the plot of logK_c (in CCl_4) versus logK_c (in CH_2Cl_2) for the hydrogen-bonded complexes of 4-fluorophenol with bases does not give a single linear relationship (Equation 1.101) but a series of lines corresponding to various families of oxygen and nitrogen bases, as shown by Figure 1.6. The secondary values calculated by Equation 1.101 are of lower accuracy than the primary values measured in the standard solvent, since the standard deviation of the estimate (often about 0.05–0.10 log$K$ unit) must be added to the experimental uncertainty (often about 0.05 log$K$ unit for hydrogen bonding).

On the other hand, it has been observed [80] that the relative BF_3 affinities for 13 representative bases are almost insensitive to the change of measurement medium from dichloromethane to nitrobenzene (see Chapter 3).

A few scales of Lewis affinity and some spectroscopic scales of Lewis basicity (see below) have been constructed by carrying out the reaction $A + B \rightleftharpoons AB$ on a dilute solution of the acid in pure, liquid base as solvent. This pure base method will be studied in Chapter 4. It gives ‘solvent basicity scales’ which are not strictly equivalent to ‘solute basicity scales’ measured on a dilute solution of the acid and the base in an ‘inert’ solvent.

1.9 Spectroscopic Scales of Basicity (Affinity)

Besides direct measurement of the thermodynamic quantities K and ΔH discussed above, spectroscopic estimates of basicity (affinity) have been proposed. Their main attraction is the ease with which they can be carried out. Moreover, many systems that do not possess the physical properties needed for a thermodynamic study can be characterized by spectroscopic parameters. Spectroscopic scales of basicity (affinity) are based on the change of a spectrochemical property (NMR, UV–Vis, IR, etc.) of the Lewis acid upon complexation with a series of Lewis bases, and on the assumption that this change is dominated by the strength of the interaction. Factors other than those that control the intermolecular bond strength, such as coupling of vibrational modes or neighbour anisotropic effects, are assumed negligible or quasi-constant along the studied series of complexes. Other conditions required for such spectrochemical data to acquire the status of a spectroscopic scale of basicity (affinity) are as follows:

(i) measurement in standard conditions of medium and temperature;
(ii) reference to a numerous and diversified sample of bases;
(iii) correlation to the Gibbs energy of complexation, for a spectroscopic scale of Lewis basicity or to the enthalpy of complexation, for a spectroscopic scale of Lewis affinity.

NMR data [116, 121] for the limiting ^{19}F chemical shift of 4-fluorophenol upon hydrogen bonding with Lewis bases fulfil these conditions:

(i) They have been measured in dilute solutions of 4-FC_6H_4OH and base in CCl_4 at 25 °C.
(ii) They have been obtained for about 60 oxygen, nitrogen and sulfur bases.
(iii) 96% of the variance of the ^{19}F chemical shift is explained by the thermodynamic basicity (as $\log K_c = pK_{BHX}$; see Chapter 4), as shown in Figure 1.7.

Unfortunately, many spectroscopic scales are not as rigorously defined as the ^{19}F chemical shift scale and are flawed by a number of shortcomings. The first of these comes from measurements that have not been thermoregulated, notwithstanding that the system is temperature dependent. For example, in the domain of UV–Vis measurements, thermochromism goes together with solvatochromism [122]. A second weakness comes from the supposed equivalence of solvent scales with solute scales on the basis of a poor interpretation of statistics. For example, the change in the OH infrared stretching frequency

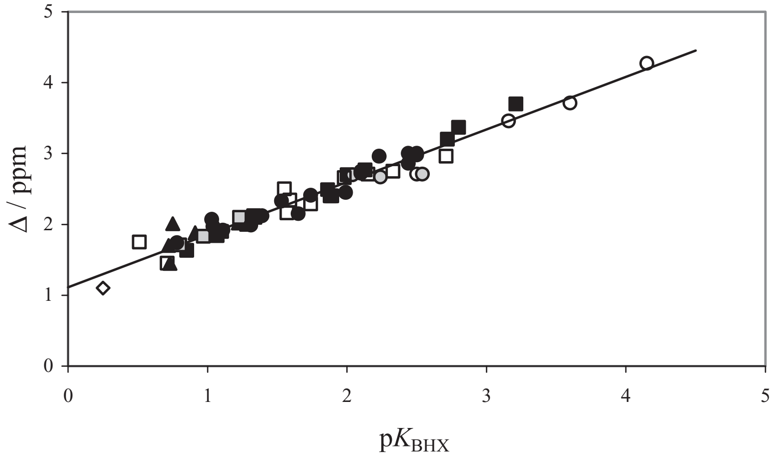


Figure 1.7 *Plot of the limiting ^{19}F chemical shift versus the logarithm of the complexation constant for hydrogen-bonded complexes of 4-FC_6H_4OH with 59 diversified bases ($r = 0.978$, $s = 0.13$ ppm).*

of methanol, $\Delta\nu$(OH), upon complexation with a series of bases can be measured in the pure bases or in dilute solutions of the bases in some inert medium. The two scales are apparently satisfactorily correlated ($r = 0.97$, $n = 72$) [123]. However, their differences are not randomly distributed. They are significantly correlated ($r = 0.94$, $n = 26$) with a parameter measuring the polarity of the pure base [123]. Thus, infrared $\Delta\nu$(XH) spectroscopic scales measured in the pure bases are contaminated by the polarity of the pure base. Methods such as the solvatochromic comparison method [122], the pure base calorimetric method [124], the solvatovibrational comparison method [125] and the solvatomagnetic comparison method [126] have been developed for subtracting the non-specific effects of the base. However, the scales constructed in this way are still not strictly equivalent to solute scales. This important point can be illustrated [126] by the comparison between the ^{19}F enhanced chemical shift of 4-fluorophenol hydrogen-bonded to bases in CCl_4, Δ_2, and the same quantity measured in the media of pure bases by the solvatomagnetic comparison method, Δ_1. For 19 diverse bases, only 72% of the variance of Δ_1 is explained by Δ_2. Moreover, the $\Delta_2 - \Delta_1$ differences are not randomly distributed. They are related ($n = 19$, $r = 0.9$) to the Onsager function, $(\varepsilon - 1)/(2\varepsilon + 1)$, that is, to the reaction field of the medium. Clearly, the solvent NMR spectroscopic scale of hydrogen-bond basicity, Δ_1, is not equivalent to the solute one, Δ_2. Two other examples concerning the complexation enthalpy of 4-fluorophenol and the solvatochromism of 4-nitrophenol, given in Chapter 4, support this conclusion.

The last shortcoming concerns the relationships between spectroscopic and thermodynamic scales of basicity (affinity). It appears that they often have a more limited validity domain than claimed by their advocates. As shown in Chapters 4 and 5, these relationships are often family dependent, that is, they are limited to bases that are structurally related. In the correlation of two basicity-dependent properties, it is often found that the organic bases separate into families that are distinguished by their basic sites as follows:

(a) aromatic carbon bases;
(b) nitriles and oxygen bases, which have a rather high dipole moment in common;
(c) sp^2 nitrogen bases;
(d) sp^3 nitrogen bases;
(e) single-bonded sulfur bases (generally distinct from double-bonded sulfur bases).

The family (b) contains the most often encountered Lewis bases in chemistry: nitriles, nitros, carbonyls, sulfonyls, sulfinyls, phosphoryls and ethers. Samples of bases heavily loaded with such highly dipolar bases may show an apparently general relationship between spectroscopic and thermodynamic scales. For example, the acetylacetonato-*N*,*N*,*N*′,*N*′-tetramethylethylenediaminocopper(II) perchlorate complex (Figure 1.8) has been proposed [127] as a solvatochromic indicator of Lewis basicity. Indeed, the wavenumber $\tilde{\nu}$ of the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition [128] of this square-planar complex at about 550 nm is blue shifted when the basicity of the axial ligands increases, and a satisfactory relationship ($n = 12$, $r = 0.966$) exists between the donor number (see Chapter 2) of the ligands and $\tilde{\nu}$. However, 11 ligands out of 12 belong to the family (b). The relationship of Figure 1.8 must therefore be limited to the estimation of the donor number of ligands in this family. Any extrapolation to other families could be unreliable.

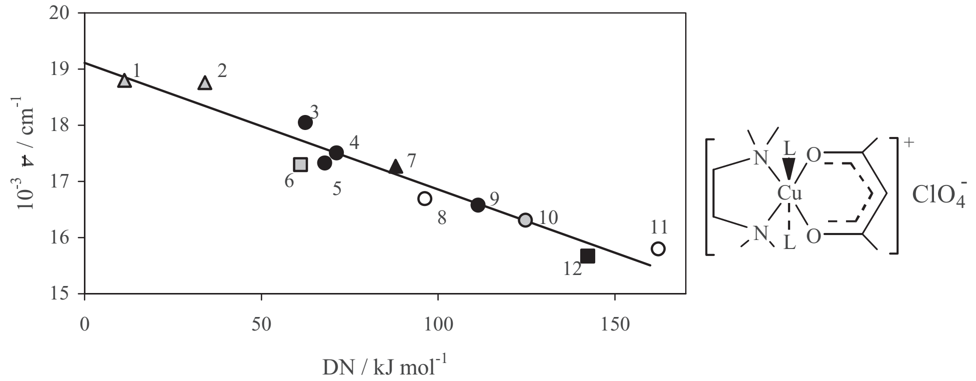


Figure 1.8 *Relationship between the wavenumber of the highest energy transition of Cu(tmen)(acac)L_2ClO_4 and the donor number (DN) of ligands L.* ***1*** *CH_3NO_2,* ***2*** *$C_6H_5NO_2$,* ***3*** *propylene carbonate,* ***4*** *CH_3COCH_3,* ***5*** *$CH_3COOC_2H_5$,* ***6*** *CH_3CN,* ***7*** *c-$(CH_2)_4O$,* ***8*** *$(MeO)_3PO$,* ***9*** *$HCONMe_2$,* ***10*** *Me_2SO,* ***11*** *$(Me_2N)_3PO$,* ***12*** *C_5H_5N.*

Other types of family dependence may be found between two basicity-dependent properties that are very dissimilar. For the complexes of SO_3 with Lewis bases [129], the comparison of the frequency shift of the asymmetric stretching vibration of the SO bonds upon coordination, $\Delta\nu_{as}(SO_3)$, with the proton affinity, PA, splits the sample of bases into families of first- and second-row bases (Figure 1.9). For the spectroscopic nucleophilicity, *N*, defined [130, 131] from the force constant of the hydrogen bond X—H$\cdots$B, the family of sp nitrogen bases (N_2, C_2N_2, HCN, HCCCN, MeCN, *t*-BuCN) exhibits a behaviour different from that of oxygen bases (Figure 1.10).

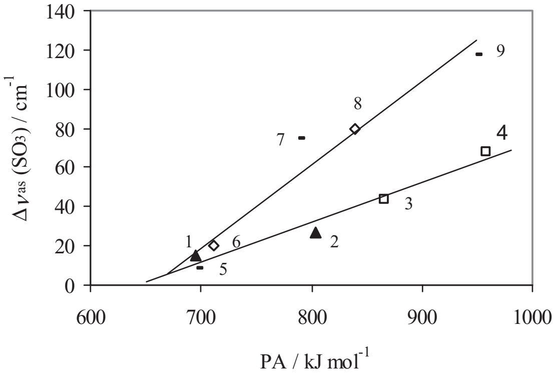


Figure 1.9 *Two regression lines are found in the comparison of $\Delta\nu_{as}(SO_3)$ with the proton affinity, the line of first-row bases (**1** H_2O, **2** Me_2O, **3** NH_3, **4** NMe_3) and that of second-row bases (**5** PF_3, **6** H_2S, **7** PH_3, **8** Me_2S, **9** PMe_3).*

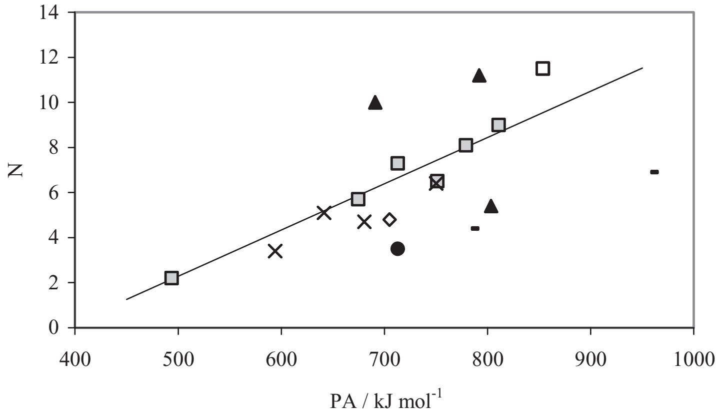
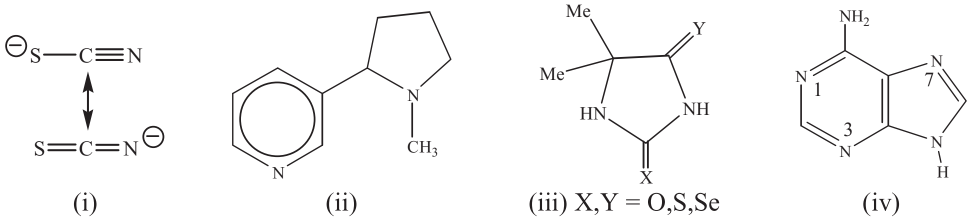


Figure 1.10 *Lack of a general relationship between the spectroscopic nucleophilicity N and the proton affinity PA (n = 18, r = 0.585). The line is a least-squares fit (r = 0.974) to the data of six sp nitrogen bases (□).*

1.10 Polybasic Compounds

Many Lewis bases bear more than one possible Lewis acid acceptor site. They are called polyfunctional bases, polybases or, in coordination chemistry, multidentate ligands. For instance (Scheme 1.1), (i) coordination of the ligand SCN^- to cations may occur at the nitrogen or at the sulfur atom, (ii) nicotine may be hydrogen bonded on the amino nitrogen or on the pyridine nitrogen [132], (iii) there is competition between the two chalcogen atoms X and Y of the shown compounds to coordinate diiodine [133] and (iv) BF_3 may form a dative bond with each nitrogen N1, N3 or N7 of adenine [134]. In order to measure the basicity of such polyfunctional compounds, it is necessary to determine the relative stability of the various possible isomeric complexes.

Consider, as the simplest example, the interaction of a base B_1B_2 which has two binding sites, B_1 and B_2, with a Lewis acid A which has a single binding site. Two 1 : 1 complexes can be formed by the interaction of the Lewis acid at either of the sites B_1 or B_2, giving the isomeric 1 : 1 complexes C_1 (A–B_1B_2) and C_2 (B_1B_2–A) of equilibrium



Scheme 1.1 *Examples of polyfunctional bases.*

constants K_1 and K_2:

$$B_1B_2 + A \rightleftharpoons C_1 \quad K_1 = \frac{[C_1]}{[B_1B_2][A]} \tag{1.102}$$

$$B_1B_2 + A \rightleftharpoons C_2 \quad K_2 = \frac{[C_2]}{[B_1B_2][A]} \tag{1.103}$$

A 1 : 2 (1 Base:2 Acids) complex may be formed by the addition of a second Lewis acid to either of the 1 : 1 complexes. This possibility can be ruled out if the concentration of base is chosen in large excess to the concentration of the acid.

Most experimental methods are not able to determine the equilibrium concentrations $[C_1]$ and $[C_2]$ separately and furnish only the sum $[C_1] + [C_2]$. It follows that experimental methods yield only the total (or gross) equilibrium constant K_t:

$$K_t = \frac{[C_1] + [C_2]}{[B_1B_2][A]} \tag{1.104}$$

Its relationship to the individual complexation constants K_1 and K_2 is evidently

$$K_t = K_1 + K_2 \tag{1.105}$$

This can be generalized to any number of isomeric 1 : 1 complexes:

$$K_t = \sum_{i=1}^{n} K_i \tag{1.106}$$

Three cases are encountered for the determination of the various K_is: all sites have the same basicity, one site is significantly more basic than the other(s) and more than one site contributes significantly to the total constant.

If all sites have the same basicity, then $K_t = nK_i$ and each individual constant is

$$K_i = \frac{1}{n}K_t \quad \text{and} \quad \log K_i = \log K_t - \log n \tag{1.107}$$

The coefficient $1/n$ is called a statistical factor: when the 1 : 1 complex is formed there are n possibilities of placing the Lewis acid, but in the dissociation there is only one possibility of losing it. Values for some nitrogen bases are given in Table 1.14. The statistical factor represents a correction which should be applied to the experimental constant in order to obtain a true constant for a single functional group. Since the statistical factor is independent of temperature, it is a correction to the entropy of complexation:

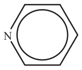
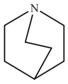
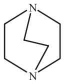
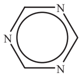
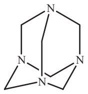
$$\Delta S_i^\circ = \Delta S_t^\circ - R \ln n \tag{1.108}$$

The statistical factor can also be deduced from the symmetry numbers [135, 136] by the equation

$$\frac{1}{n} = \frac{\sigma_e(C)\,\sigma_i(C)}{\sigma_e(A)\,\sigma_i(A)\,\sigma_e(B_1B_2)\,\sigma_i(B_1B_2)} \tag{1.109}$$

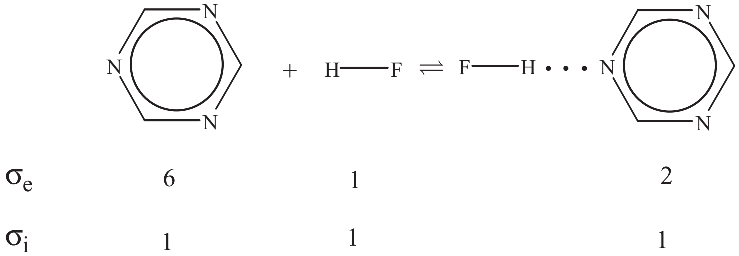
(in the absence of a racemic mixture), where σ_e is the external symmetry number (the number of different ways in which the molecule can be rotated around symmetry axes into a configuration indistinguishable from the original) and σ_i the internal symmetry number

Table 1.14 *Statistical factors for the complexation constant of N-heteroaromatics and amines.*

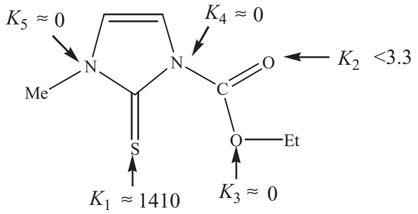
Lewis base	1/*n*	Lewis base	1/*n*
	1		1
	1/2		1/2
	1/3		1/4

(the number of equivalent positions that a molecule can attain by rotation of its parts around single bonds). For instance, in the hydrogen bonding of 1,3,5-triazine (Scheme 1.2), the statistical factor $1/n = (2.1)/(1.1)(6.1) = 1/3$. The result would be the same if phenol was used instead of hydrogen fluoride, by considering the hydroxyl group as freely rotating and having the symmetry of a cone. In the complexation of the same base with diiodine, the statistical factor becomes 1/6 because $\sigma_e(I_2) = 2$. However, for the complexation of diiodine, the contribution $\frac{1}{2}$ brought by diiodine to the statistical factor is often neglected when only diiodine complexes are being compared with each other (see the pK_{BI_2} scale in Chapter 5).

If one complex, say C_1, is significantly more stable than the others, K_1 dominates and $K_t \approx K_1$ and $\log K_t \approx \log K_1$. Consider, for example, the diiodine complexation of the antithyroid drug carbimazole (Scheme 1.3). There are five possible locations that might be considered as diiodine acceptor sites: the two nitrogen atoms, the two oxygen atoms and the sulfur atom. Three of them, the two nitrogens and the ether oxygen, may be ruled out because of the strong electron-withdrawing effects of the thiocarbonyl and carbonyl groups. From the value $K_c = 3.3\,\mathrm{l\,mol^{-1}}$ of the diiodine complexation constant of $Me_2NCOOEt$, it is clear that the contribution of the carbonyl group to the measured value $K_t = 1411\,\mathrm{l\,mol^{-1}}$ (in CCl_4) is negligible. IR and UV studies confirm that diiodine binds almost exclusively to



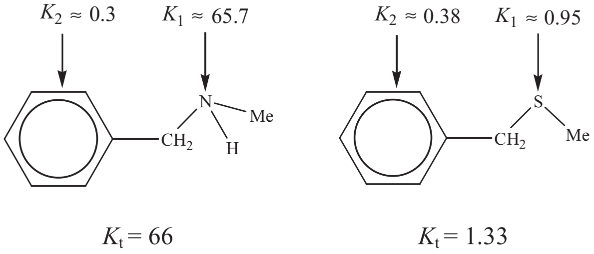
Scheme 1.2 *External and internal symmetry numbers of 1,3,5-triazine, HF and their complex.*



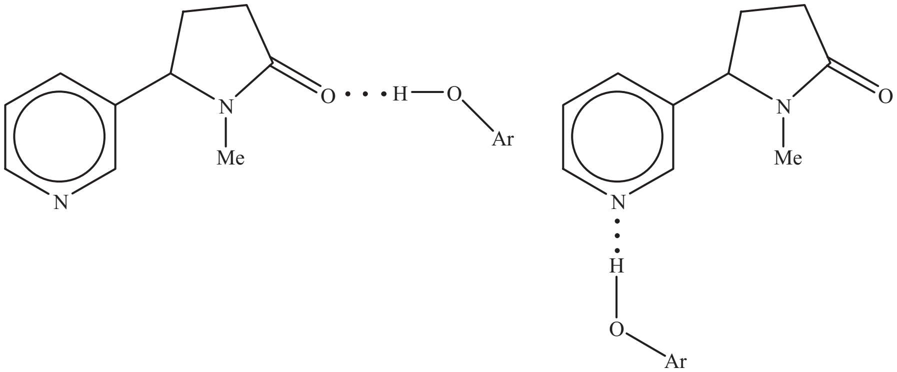
Scheme 1.3 *Diiodine basicities (as K in l mol^{-1}) of the various basic sites of carbimazole.*

the thiocarbonyl group [137]. This conclusion cannot be extended to other types of carbimazole complexes. The IR spectrum of the 4-fluorophenol–carbimazole complex shows the presence of two hydrogen-bonded complexes, OH···O(=C) and OH···S, each contributing significantly to the total complexation constant [137]. Similarly, the contribution of the phenyl basicity can be neglected in the 4-fluorophenol basicity of *N*-methylbenzylamine but not of benzyl methyl sulfide (Scheme 1.4) (see Tables 4.3, 4.5 and 4.24 in Chapter 4).

When several 1 : 1 complexes coexist, the determination of the various K_is must be achieved by either direct or indirect methods. The gas-phase protonation of some polybases has been measured and the various GB_is estimated [138–140]. The majority of experimental studies are found, however, in the field of hydrogen bonding [132, 141–145]. In fact, the smaller Gibbs energies of hydrogen-bond formation compared with protonation or complexation to strong Lewis acids make the selectivity lower in hydrogen bonding than in the formation of strong complexes, and multiple hydrogen bonds are fairly common. It must be recalled that selectivity in complexation is governed by the Gibbs energy change and that theoretical calculations of the electronic energy change cannot give a firm answer to the question of the basicity of each possible site. An example is given by the hydrogen-bonding basicity of nicotine (ii in Scheme 1.1). While calculated $\Delta E_{i,\mathrm{el}}$s give a small preference for hydrogen bonding to the amino nitrogen, experimental ΔG_is show that 90% of the 1 : 1 hydrogen-bonded complexes are formed to the pyridine nitrogen because here the selectivity is driven by entropy [132].



Scheme 1.4 *4-Fluorophenol basicities (as K in l mol^{-1}) of the π and N sites of PhCH$_2$NHMe (left) and π and S sites of PhCH$_2$SMe (right).*



Scheme 1.5 *O (left) and N (right) 1 : 1 hydrogen-bonded complexes of cotinine.*

In direct spectroscopic methods, measurement of the various K_is requires the existence of a signal characteristic of each complex C_i. For instance, in the complexation of a phenol with cotinine [143] (Scheme 1.5), the carbonyl stretching vibration at 1703 cm^{-1} and the breathing of the pyridine ring at 1026 cm^{-1} allow the calculation of $K_1 = 145 \pm 10\,l\,mol^{-1}$ for the oxygen site and $K_2 = 42 \pm 12\,l\,mol^{-1}$ for the pyridine nitrogen site. The sum $K_1 + K_2 = 187 \pm 16\,l\,mol^{-1}$ compares well with the value $K_t = 197 \pm 14\,l\,mol^{-1}$ determined from the OH stretching vibration at 3614 cm^{-1}.

Indirect methods depend on the establishment of family-dependent (site-dependent) relationships of the log K_is with quantum chemical descriptors of basicity (e.g. electrostatic potentials), Hammett substituent constants or IR frequency shifts of Lewis acids [132, 142–145].

One must realize that the logarithmic quantity $\log K_t$ is deprived of any thermodynamic significance since no thermodynamic function can be calculated from it. The term $-RT\ln K_t$ is not simply related to the ΔG_is, since the logarithm of a sum is not equal to the sum of logarithms. For the same reason, the derivative $d\ \ln K_t/d(1/T)$ is not simply related to the individual ΔH_is. Only calorimetric methods can yield an experimental heat related simply to the various ΔH_is and K_is, since the heat evolved by forming one mole of complexes C_i (that is, $V\sum[C_i] = 1$ in a cell of volume V) is equal to $\sum(K_i\Delta H_i)/\sum K_i$. In the domain of calorimetry, a procedure has been devised [146] that allows the determination of the individual BH_3 affinities of the arsenic and phosphorus sites of the bifunctional base $Ph_2AsCH_2CH_2PPh_2$.

1.11 Attempts at a Quantitative Formulation of the Lewis Definition of Acids and Bases

1.11.1 Hard and Soft Acids and Bases

A scale of Lewis basicity (acidity) can be determined, in principle, by measuring the stabilities of complexes formed with a reference Lewis acid (base). This approach fails in

Table 1.15 *Lewis basicity of halide ions in aqueous solution*[a].

	LogK_1			
Acid	F^-	Cl^-	Br^-	I^-
Fe^{3+}	6.04	1.41	0.49	
In^{3+}	3.78	2.36	2.01	1.64
Zn^{2+}	0.77	−0.19	−0.6	−1.3
Ag^+	0.36	3.04	4.38	8.13
Hg^{2+}	1.03	6.74	8.94	12.87

[a] Selected by Arhland *et al.* [147] from the stability constants compiled in refs [148, 149].

practice because the order of stability constants is not invariant when the reference acid (base) is changed. For example, the relative basicities of halide ions towards the acids Zn^{2+}, In^{3+} and Fe^{3+} is $F^- > Cl^- > Br^- > I^-$, whereas towards Ag^+ and Hg^{2+} it is $I^- > Br^- > Cl^- > F^-$ (Table 1.15).

Pearson [150–155] has explained reversals in basicity (acidity) such as those illustrated in Table 1.15 by qualifying the acids and bases by their so-called hardness (or softness, which is the inverse of hardness), in addition to their strength. Hard and soft acids and bases were originally defined as follows:

- **Soft bases**: the donor atoms are of high polarizability, low electronegativity, easily oxidized and associated with low-lying empty orbitals suitable for π back-donation.
- **Hard bases**: the donor atoms are of low polarizability, high electronegativity, difficult to oxidize and associated with empty orbitals of high energy.
- **Soft acids**: the acceptor atoms are of low positive charge, large size, high polarizability and have several easily excited outer electrons.
- **Hard acids**: the acceptor atoms are of high positive charge, small size, low polarizability and do not have easily excited outer electrons.

Accordingly, acids and bases were divided into three classes, labelled hard, soft and borderline. This classification is shown in Table 1.16. Its usefulness arises from the generalization that hard acids prefer to coordinate to hard bases and soft acids to soft bases, all things being otherwise equal. This is the so-called Hard and Soft Acid and Base (HSAB) principle. A possible quantitative statement of the HSAB principle would be the four-parameter Equation 1.110:

$$\log K = S_A S_B + \sigma_A \sigma_B \tag{1.110}$$

where K is the equilibrium constant of the acid/base reaction, S_A is a strength factor for the acid and S_B for the base and σ_A and σ_B are parameters that measure the softness of the acid and of the base, respectively. In spite of many efforts, the lack of *ad hoc* experimental data for establishing separate scales of strength and of softness has prevented a numerical evaluation of Equation 1.110.

The HSAB principle was, originally, entirely empirical. Its first theoretical rationale was given by Klopman's perturbation theory [3, 33]. It was proposed [2, 3] to equate the strength and softness terms of Equation 1.110 to the charge-controlled and orbital-controlled terms

Table 1.16 *Classification of some Lewis acids and bases into hard, borderline and soft.*

Hard	Borderline	Soft
	Acids	
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	Pd^{2+}, Pt^{2+}
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	$B(Me)_3$, GaH_3	Cu^+, Ag^+, Au^+, Hg^+, Hg^{2+}, $HgCl_2$
Sc^{3+}, La^{3+}, Ce^{4+}, $UO_2{}^{2+}$	R_3C^+, NO^+, Bi^{3+}	BH_3, $Ga(Me)_3$
Ti^{4+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	SO_2	π Acceptors (trinitrobenzene, quinones, tetracyanoethylene)
BF_3, BCl_3, Al^{3+}, $Al(Me)_3$, Ga^{3+}		Br_2, Br^+, I_2, I^+, ICN
CO_2, RCO^+, Si^{4+}		
SO_3		
HX (hydrogen-bond donor)		
	Bases	
NH_3, RNH_2	C_5H_5N, $N_3{}^-$	H^-
H_2O, OH^-, ROH, R_2O	$NO_2{}^-$, $SO_3{}^{2-}$	C_2H_4, C_6H_6, CN^-, CO
CH_3COO^-, $CO_3{}^{2-}$, $NO_3{}^-$, $SO_4{}^{2-}$	Br^-	SCN^-, R_2S, RSH, RS^-
F^-, Cl^-		R_3P, R_3As
		I^-

of Equation 1.39, respectively. In short, quoting Jensen [2, 3], 'soft acids are characterized by low-lying acceptor orbitals and soft bases by high-lying donor orbitals. Hard acids and hard bases 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'. Nevertheless, this interpretation does not give a precise definition of hardness and does not enable a numerical scale of hardness to be established. This has been done by Parr and Pearson [156] within the framework of density functional theory.

Thus, the hardness of a chemical system (atom, molecule, supermolecule, ion, radical) has been identified [156] as the partial second derivative of the electronic energy E with respect to the number of electrons N, keeping constant the potential v due to the fixed nuclei:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \tag{1.111}$$

Remember that the electronegativity χ is rigorously defined [157] as the negative of the first derivative of the $E(N)$ curve:

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_v \tag{1.112}$$

Using the energies of N, $(N + 1)$ and $(N - 1)$ electron systems, operational and approximate definitions of η and χ are obtained [156] as

$$\eta \approx \frac{1}{2}(\mathrm{IE} - \mathrm{EA}) \tag{1.113}$$

$$\chi \approx \frac{1}{2}(\mathrm{IE} + \mathrm{EA}) \tag{1.114}$$

where IE and EA are the ionization energy and electron affinity, respectively. Whereas the electronegativity defines whether a compound is a net electron acceptor or donor and must be constant everywhere in the chemical system, the hardness determines how easily the number of electrons can be changed and it need not be constant, that is it can have local values [158]. Local values determine which parts of a compound are the most reactive.

Values of χ and η, calculated from experimental values of IE and EA, are given in Table 1.17 for some atoms, monoatomic cations and organic molecules. A more extensive list can be found in ref. [159] for inorganic species and ref. [160] for organic species. For anions and polyatomic cations, see ref. [161]. For molecules, the entries in Table 1.17 are arranged in order of decreasing electronegativity so that Lewis acids start the list and bases are at the bottom (see below). Cations are ordered by decreasing hardness (increasing softness) and atoms by atomic number.

Because electronegativity and hardness are intimately related to the gain and loss of electrons by chemical compounds, they are fundamental properties for studying Lewis acid/base reactions. Examples are given below.

The numerical values of η are generally satisfactory when compared with the qualitative HSAB classification of Table 1.16. For instance, the cations classified hard acids, such as Li^+, Mg^{2+} and Al^{3+}, have large η values, those classified borderline, such as Ni^{2+} and Cu^{2+}, have intermediate values, and those classified soft, such as I^+, Pd^{2+} and Ag^+, have small values. Moreover, the expected increased hardness with increased oxidation state is shown by the η values of Fe, Fe^{2+} and Fe^{3+}.

The electronegativity determines which of two molecules, C and D, is the electron donor and which the acceptor when they form a complex. The direction of electron transfer is given by the difference

$$(\mathrm{IE_C} - \mathrm{EA_D}) - (\mathrm{IE_D} - \mathrm{EA_C}) = 2(\chi_\mathrm{C} - \chi_\mathrm{D}) \tag{1.115}$$

A positive value for the difference means that it costs less energy to transfer an electron from D to C. Thus, any molecule high in the list in Table 1.17 is a Lewis acid towards a molecule lower in the list, and vice versa. Hence the electronegativity of HF shows that it is an acid towards NH_3, by forming the hydrogen bond $F—H\cdots NH_3$, but a base towards BF_3, by forming the complex $HF–BF_3$.

A rigorous proof of the HSAB principle has been given [162], provided a restriction be added: hard likes hard and soft likes soft, *among potential partners of a given electronegativity*. A partial and approximate deduction of the HSAB principle can be found by considering the energy decrease, ΔE, resulting from the transfer of electron density from the base B to the acid A when a complex AB is formed. This transfer is driven by the electronegativity difference, $\chi_\mathrm{A} - \chi_\mathrm{B}$, and inhibited by the sum of hardness, $\eta_\mathrm{A} + \eta_\mathrm{B}$ [156]. The principle of electronegativity equalization [163] states that electron density flows until a single average value of electronegativity exists everywhere in the complex.

Table 1.17 *Some experimental values of electronegativity and hardness in eV.*

Atom	χ	η	Cation	χ	η	Molecule	χ	η
H	7.17	6.42	Al^{3+}	74.2	45.8	SO_3	7.2	5.5
Li	3.00	2.38	Li^{+}	40.5	35.1	N_2	7.0	8.6
B	4.29	4.01	Mg^{2+}	47.6	32.5	Cl_2	7.0	4.6
C	6.27	5.00	Sc^{3+}	49.3	24.6	SO_2	6.7	5.6
N	7.27	7.27	Na^{+}	26.2	21.1	Br_2	6.6	4.0
O	7.53	6.08	Ca^{2+}	31.6	19.7	O_2	6.3	5.9
F	10.41	7.01	La^{3+}	34.6	15.4	BF_3	6.2	9.7
Na	2.85	2.30	Fe^{3+}	43.7	13.1	CO	6.1	7.9
Al	3.21	2.77	Ba^{2+}	22.8	12.8	I_2	6.0	3.4
Si	4.76	3.38	Rb^{+}	15.8	11.7	HF	5.0	11.0
P	5.62	4.86	Zn^{2+}	28.8	10.8	CH_3I	4.9	4.7
S	6.22	4.12	Tl^{3+}	40.3	10.5	CH_3Br	4.8	5.8
Cl	7.31	4.70	Cd^{2+}	27.2	10.3	HCl	4.7	8.0
K	2.41	1.92	Mn^{2+}	24.4	9.3	C_2H_4	4.4	6.2
V	3.64	3.11	Ni^{2+}	26.7	8.5	C_5H_5N	4.4	5.0
Cr	3.76	3.05	Pb^{2+}	23.5	8.5	C_2H_2	4.4	7.0
Fe	4.03	3.87	Cu^{2+}	28.6	8.3	C_6H_6	4.0	5.2
Co	4.26	3.60	Hg^{2+}	26.5	7.7	PH_3	4.0	6.0
Ni	4.44	3.24	Fe^{2+}	23.4	7.3	CH_3Cl	3.8	7.5
Cu	4.48	3.25	Ti^{2+}	20.6	7.0	CH_3F	3.2	9.4
Se	5.89	3.86	Ag^{+}	14.6	6.9	H_2O	3.1	9.5
Br	7.60	4.24	Pd^{2+}	26.2	6.8	NH_3	2.9	7.9
Rb	2.34	1.85	Cu^{+}	14.0	6.3	$(CH_3)_3As$	2.8	5.5
Zr	3.63	3.21	Au^{+}	14.9	5.7	$(CH_3)_3P$	2.8	5.9
Nb	3.88	2.99	Br^{+}	16.7	4.9	$(CH_3)_2S$	2.7	6.0
Mo	3.92	3.17	I^{+}	14.8	4.3	$(CH_3)_2O$	2.0	8.0
Rh	4.30	3.16				$(CH_3)_3N$	1.5	6.3
Pd	4.44	3.88						
Ag	4.44	3.14						
Sn	4.30	3.05						
Sb	4.84	3.79						
Te	5.49	3.52						
I	6.76	3.70						
Ba	2.6	2.6						
Pt	5.6	3.5						
Au	5.8	3.5						

An approximate value of ΔE is given [156] by

$$\Delta E \approx -\frac{(\chi_A - \chi_B)^2}{4\,(\eta_A + \eta_B)} \tag{1.116}$$

If both A and B are soft, $\eta_A + \eta_B$ is a small number and, for a given reasonable electronegativity difference, ΔE is substantial and stabilizing. This explains the HSAB principle in part: soft acids prefer soft bases. Equation 1.116 refers only to the first step of the interaction between A and B. A complete expression for the interaction energy, within the framework of the local HSAB principle, can be found in the literature [164, 165].

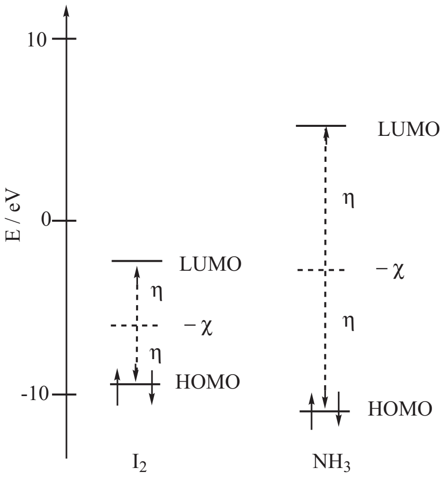


Figure 1.11 *Frontier orbital energy diagram for I_2 and NH_3.*

The concepts of hardness and electronegativity can be considered within the framework of the frontier molecular orbital theory. According to Koopmans' approximation, the frontier orbital energies are given by

$$-E_{\mathrm{HOMO}} \approx \mathrm{IE} \quad \text{and} \quad -E_{\mathrm{LUMO}} \approx \mathrm{EA} \tag{1.117}$$

Therefore, further estimates of η and χ may be written as

$$\eta \approx \frac{1}{2}\left(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}\right) \tag{1.118}$$

$$\chi \approx -\frac{1}{2}\left(E_{\mathrm{LUMO}} + E_{\mathrm{HOMO}}\right) \tag{1.119}$$

Figure 1.11 shows the HOMO, the LUMO, the electronegativity and the hardness for the molecules I_2 and NH_3. It is seen that ammonia will readily transfer electrons to I_2 (since $\chi_{I_2} - \chi_{NH_3} = 3.1$ eV), leading to the halogen-bonded complex $I\text{–}I\cdots NH_3$. Equation 1.118 identifies the hardness with half the energy gap between HOMO and LUMO. This identification agrees with the earlier empirical definition of softness [150–155], which emphasizes polarizability. Indeed, the theory of polarizability shows that a small HOMO-LUMO difference corresponds to a high polarizability.

1.11.2 The ECW and ECT Models

The reversals that occur in affinity scales for a series of Lewis bases with a change in the reference Lewis acid inspired Drago *et al.* [6, 76, 77] to formulate the double-scale enthalpy Equation 1.120:

$$-\Delta H = E_A E_B + C_A C_B \tag{1.120}$$

where ΔH is the enthalpy of the reaction A + B → AB measured in the gas phase or in 'inert' solvents such as alkanes or CCl_4. The Lewis affinity of each neutral acid A is measured by two empirically determined parameters, E_A and C_A (E stands for 'electrostatic' and C for 'covalent'), and the Lewis affinity of each neutral base B by two parameters, E_B and C_B. The E and C Equation 1.120 relates to the HSAB principle in that, for there to be a strong enthalpy of complexation, the two molecules must 'match' in the sense that both must have a large E parameter or a large C.

Theoretically, the E and C model is consistent [3] with Klopman's perturbation theory of intermolecular interactions, with the E_AE_B and C_AC_B terms corresponding to the charge-controlled and orbital-controlled contributions to Equation 1.39, respectively. Marks and Drago [166] have shown that, by starting with the Mulliken valence-bond model (which yields the energy of the complex AB as the sum of electrostatic and covalent terms), an equation of the form of Equation 1.120 can be obtained by introducing certain approximations. The E_AE_B and C_AC_B terms also show [167] some correspondence with, respectively, the electrostatic, ΔE_{ES}, and polarization plus charge transfer, $\Delta E_{POL} + \Delta E_{CT}$, terms of the Morokuma analysis. These comparisons give some support to relating the E and C parameters to electrostatic and covalent interactions, respectively.

A detailed description of how the E and C parameters are determined is presented in the literature [76, 168–170]. The E and C values which best reproduce several hundreds of experimental enthalpy data are summarized in Table 1.18. They are expressed in $(\text{kJ mol}^{-1})^{1/2}$ by multiplying the literature values, in $(\text{kcal mol}^{-1})^{1/2}$, by $\sqrt{4.184}$. With diiodine arbitrarily chosen as the reference acid and assigned parameters $E_A = 1.02$ and $C_A = 4.09\ (\text{kJ mol}^{-1})^{1/2}$, the C_A and C_B values cannot be compared directly with the E_A and E_B values. However, the relative magnitudes of the C_B (E_B) parameters give an indication of the relative covalent (electrostatic) affinities of the Lewis bases.

In some cases [171, 172], a constant term must be added to the E and C equation, which takes the form

$$-\Delta H = E_AE_B + C_AC_B + W \qquad (1.121)$$

The term W, which is usually zero for bases, is a constant contribution to the enthalpies of reaction for a particular acid that is independent of the bases with which it reacts. For example, in the case of the dimeric acid Al_2Cl_6 reacting to form B–$AlCl_3$ adducts, W corresponds to half the enthalpy of cleaving the dimer; in the case of the acid $(CF_3)_3COH$ forming hydrogen-bonded complexes $(CF_3)_3COH\cdots B$, W incorporates the enthalpy of breaking an $OH\cdots F_3C$ intramolecular hydrogen bond. Thus, the E and C portion of Equation 1.121 corresponds to the exothermic interaction of the base with the monomeric acid or the free OH group of the hydrogen-bond donor.

One can attempt [169, 170, 173] to interpret basicity scales or spectroscopic scales of basicity with the ECW model by rewriting Equation 1.121 as

$$\Delta G \text{ or } \Delta \nu = eE_B + cC_B + w \qquad (1.122)$$

where ΔG is a Gibbs energy of complexation and $\Delta \nu$ a spectral shift upon complexation of a reference Lewis acid with a series of Lewis bases; e and c are the responses of the quantity measured to the electrostatic and covalent parameters of the bases; the constant w can arise from a variety of effects.

Table 1.18 *Selected parameters* $(\mathrm{kJ\ mol^{-1}})^{1/2}$ *of the ECW model.*

Acid	E_A	C_A	Acid	E_A	C_A
I_2	1.02	4.09	$B(CH_3)_3$	5.93	7.36
IBr	2.45	6.73	$Al(CH_3)_3$	17.71	7.53
ICl	5.97	3.40	$Ga(C_2H_5)_3$	14.22	3.03
C_6H_5OH	4.64	2.19	$In(CH_3)_3$	13.50	4.40
4-FC_6H_4OH	4.70	2.27	$(CH_3)_3SnCl$	5.87	1.45
CF_3CH_2OH	4.23	2.17	BF_3(g)	12.48	5.87
c-$(C_4H_4)NH$	2.82	1.39	SO_2	1.04	3.19
$CHCl_3$	3.19	0.90			
Base	E_B	C_B	**Base**	E_B	C_B
Carbonyl, thionyl, phosphoryl compounds			*Nsp bases*		
CH_3COCH_3	3.56	2.58	$ClCH_2C\equiv N$	3.42	0.68
c-$(CH_2)_4CO$	4.13	1.80	$CH_3C\equiv N$	3.35	1.45
CH_3COOCH_3	3.33	1.94	$C_6H_5C\equiv N$	3.38	1.53
$CH_3COOC_2H_5$	3.31	2.00	$(CH_3)_2NC\equiv N$	3.93	1.88
$CH_3CON(CH_3)_2$	4.81	2.68	*Nsp*^{2} *bases*		
$HCON(CH_3)_2$	4.48	2.68	*N*-Methylimidazole	2.37	10.06
$(CH_3)_2SO$	4.91	3.01	4-$(CH_3)_2NC_5H_4N$	3.93	9.06
c-$(CH_2)_4SO$	4.99	3.35	4-$CH_3OC_5H_4N$	3.74	7.83
$(C_6H_5)_3PO$	5.30	3.42	4-$CH_3C_5H_4N$	3.74	7.63
$(C_2H_5O)_3PO$	5.13	2.25	3-$CH_3C_5H_4N$	3.70	7.51
$[(CH_3)_2N]_3PO$	5.87	3.11	C_5H_5N	3.64	7.24
N-Oxides			3-ClC_5H_4N	3.40	6.30
C_5H_5NO	4.68	4.77	4-$N\equiv CC_5H_4N$	3.13	6.01
4-$CH_3C_5H_4NO$	4.75	5.26	*Nsp*^{3} *bases*		
4-$CH_3OC_5H_4NO$	4.79	6.18	$HC(C_2H_4)_3N$	1.64	13.75
Ethers			$(C_2H_5)_3N$	2.70	11.72
$(C_2H_5)_2O$	3.68	3.33	$(CH_3)_3N$	2.48	11.48
$(C_4H_9)_2O$	3.87	3.42	$(CH_3)_2NH$	3.68	8.61
$O(C_2H_4)_2O$	3.80	2.64	*c*-$(CH_2)_5NH$	2.95	10.08
c-$(CH_2)_4O$	3.35	4.46	CH_3NH_2	4.42	6.38
$(CH_3)_2O$	3.44	3.07	$C_2H_5NH_2$	4.79	6.75
Thioethers			NH_3	4.73	4.17
$(CH_3)_2S$	0.51	7.67	*Miscellaneous bases*		
$(C_2H_5)_2S$	0.49	8.02	$(CH_3)_3P$	0.51	11.88
c-$(CH_2)_4S$	0.53	8.33	$(CH_3O)_3P$	0.27	9.88
c-$(CH_2)_5S$	0.70	7.79	$(CH_3)_2Se$	0.10	8.67
			$(C_6H_5)_3PS$	0.72	7.47
			CH_3Cl	5.20	0.20
			C_6H_6	1.43	0.92

The ECW equation does not apply to gas-phase cation affinities. According to Drago *et al.* [174], a transfer-energy component is significant in the enthalpy of cation/molecule reactions

$$M^+(g) + B(g) \rightarrow MB^+(g)$$

and is accommodated by replacing W with a separate $R_A T_B$ term:

$$-\Delta H = E_A E_B + C_A C_B + R_A T_B \tag{1.123}$$

where R_A is called the receptance of the cation and T_B the transference of the Lewis base. An extensive list of R_A values for cations and T_B values for bases can be found in ref. [174]. Semi-empirical justifications for adding an electron-transfer term are presented in refs [174–176]. Equation 1.123 generally fits well the H^+, Li^+, K^+, Mg^+, Al^+, Mn^+, $CH_3{}^+$, $(CH_3)_3Sn^+$, $CpNi^+$ (Cp = cyclopentadiene), NO^+, H_3O^+ and various ammonium cation affinities, but there are a number of systems that are not correlated by the ECT model. An example of a good fit is given by the proton affinity of dimethyl ether:

$$\text{PA}(\text{Me}_2\text{O})\ \text{experimental} = 792\,\text{kJ mol}^{-1}$$
$$\text{PA}(\text{Me}_2\text{O})\ \text{calculated} = E_A E_B(316.3) + C_A C_B(81.8) + R_A T_B(397.7) = 796\,\text{kJ mol}^{-1}$$

whereas a bad fit is provided by the potassium cation affinity of dimethyl sulfoxide:

$$\text{KCA}(\text{Me}_2\text{SO})\ \text{experimental} = 146\,\text{kJ mol}^{-1}$$
$$\text{KCA}(\text{Me}_2\text{SO})\ \text{calculated} = E_A E_B(37.9) + C_A C_B(0.6) + R_A T_B(56.5) = 95\,\text{kJ mol}^{-1}$$

The ECT model has been little used in the analysis of gas-phase ion chemistry. In contrast, the ECW model is generally found helpful in many fields of solution chemistry and biochemistry, as shown in several reviews [77, 173, 177–179] and in a book [6] and by its introduction in many textbooks of (mainly inorganic) chemistry (e.g. ref. [180]). The ECW model is particularly useful for showing that there is no inherent one-parameter order of Lewis affinity. Factoring and rearranging Equation 1.121 (with $W = 0$) lead to [179]

$$\frac{-\Delta H}{C_A + E_A} = \frac{C_B + E_B}{2} + \frac{(C_B - E_B)}{2}\left(\frac{C_A - E_A}{C_A + E_A}\right) \tag{1.124}$$

Equation 1.124 shows that if $-\Delta H/(C_A + E_A)$ is plotted against $R_A = (C_A - E_A)/(C_A + E_A)$, each base of Table 1.18 is represented by a straight line of slope $(C_B - E_B)/2$ and intercept $(C_B + E_B)/2$. The lines for quinuclidine, dimethyl selenide, diethyl sulfide, triphenylphosphine sulfide, pyridine, pyridine *N*-oxide, tetrahydrofuran, hexamethylphosphoric triamide, dimethyl sulfoxide, *N*,*N*-dimethylformamide, acetone, acetonitrile and benzene (representative of Nsp^3, Nsp^2, Nsp, O, S, Se and C bases) are drawn in Figure 1.12. The quantity R_A on the horizontal axis ranges from $+1$ for $E_A = 0$, that is, for a purely covalent (virtual) acid, to -1 for $C_A = 0$, that is, for a purely electrostatic (virtual) acid. Among common neutral Lewis acids, the hydrogen-bond donor $CHCl_3$ ($R_A = -0.56$) is very electrostatic and the halogen-bond donor I_2 ($R_A = +0.60$) very covalent. The affinity order of bases toward any reference acid whose R_A value is known can be determined from the plot of Figure 1.12. By just drawing a vertical line at the R_A value, the proper sequence of affinity is observed as the intersections of the various lines. In Figure 1.12, vertical lines have been drawn for the acids $CHCl_3$ and I_2. The affinity orders towards $CHCl_3$ and I_2 are listed in Table 1.19, together with the experimental enthalpy data for comparison. When the lines drawn for two different bases cross, the affinity order changes toward acids on opposite sides of the intersection. Due to the large number of intersections of base lines, it is immediately apparent that the ranking of Lewis bases will often change from acid to acid. However, if the base lines do not cross over the range of R_A from -1 to $+1$, the affinity

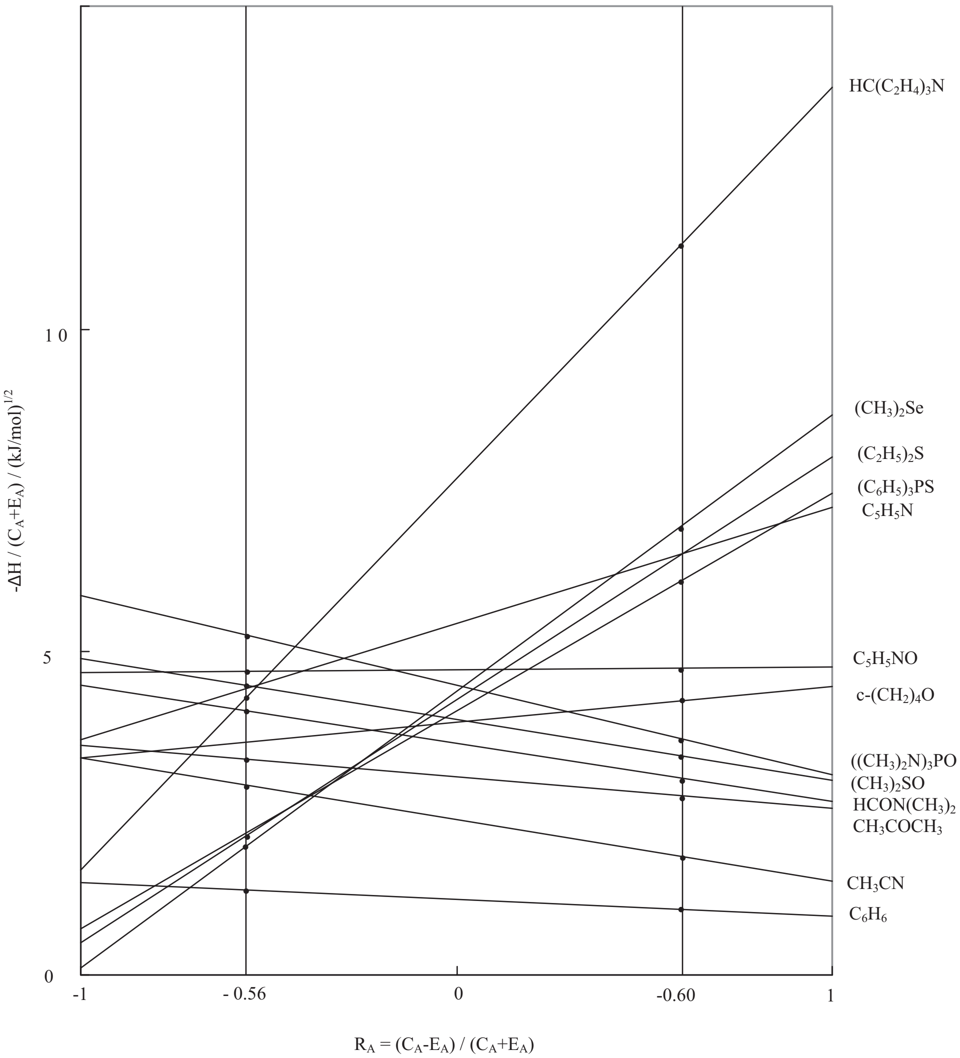


Figure 1.12 *The E and C plot of Equation 1.124 for a series of different bases.*

order for these bases will never change. For example, towards any neutral Lewis acid, the affinity order of the following bases is predicted to remain the same:

$$(Me_2N)_3PO > Me_2SO > HCONMe_2 > Me_2CO > MeC \equiv N > C_6H_6$$

Although useful, the ECW model is not always successful. For example, it cannot incorporate the acid $SbCl_5$ [181], which is unfortunate because $SbCl_5$ is the reference Lewis acid of the donor number scale (see Chapter 2). A number of *E* and *C* values are also contaminated by model and/or experimental errors. A regrettable example concerns the E_B

Table 1.19 *Orders of affinity of Lewis bases towards the reference acids $CHCl_3$ and I_2 given by the E and C plot. Comparison with experimental affinities (kJ mol^{-1}).*

Chloroform		Diiodine		
EC ranking	$CHCl_3$ affinity[a] In C_6H_{12}	*EC* ranking	I_2 affinity[b] In heptane	In CCl_4
$[(CH_3)_2N]_3PO$	20.5	$HC(C_2H_4)_3N$	43.1[c]	
C_5H_5NO		$(CH_3)_2Se$		36.0
$(CH_3)_2SO$		$(C_2H_5)_2S$	35.2	34.6
C_5H_5N		C_5H_5N	32.8	32.3
$HC(CH_2CH_2)_3N$	17.2	$(C_6H_5)_3PS$		30.5
$HCON(CH_3)_2$		C_5H_5NO		23.6
c-$(CH_2)_4O$	15.1	c-$(CH_2)_4O$	22.2	
CH_3COCH_3	9.8	$[(CH_3)_2N]_3PO$	30.5	19.9
$CH_3C{\equiv}N$		$(CH_3)_2SO$	28.8	16.9
$(C_6H_5)_3PS$		$HCON(CH_3)_2$	20.9	15.5
$(C_2H_5)_2S$	7.1	CH_3COCH_3	15.3	
$(CH_3)_2Se$		$CH_3C{\equiv}N$	13.4[d]	8.8
C_6H_6	8.4	C_6H_6	6.8	6.4

[a] From ref. [84].
[b] From Chapter 5.
[c] Value for piperidine.
[d] Value for butyronitrile.

and C_B values of the halogen base CH_3Cl, which lead to an unacceptable 4-fluorophenol affinity:

$$4\text{-}FC_6H_4OH \text{ affinity } (CH_3Cl) \text{ calc.} = (4.70 \times 5.20) + (2.27 \times 0.20) = 24.9\,\text{kJ mol}^{-1}$$

$4\text{-}FC_6H_4OH$ affinity ($C_5H_{11}Cl$) exp. = 6.96 and 8.95 kJ mol^{-1} in CCl_4 and C_6H_{12}, respectively

1.11.3 The Beta and Xi Equation

Another dual-parameter equation has been introduced by Kamlet, Taft *et al.* [182] for correlating Lewis basicity:

$$\mathrm{BDP} = b\beta + e\xi + \mathrm{BDP}_0 \qquad (1.125)$$

where BDP is a basicity-dependent property, such as a spectral shift, a Gibbs energy or an enthalpy, β is a hydrogen-bond basicity parameter, whose definition is given in Chapter 4, ξ is an empirical parameter defined to quantify the extent of family dependence observed in BDP versus β plots, b and e are the regression coefficients and BDP_0 is the intercept. Equation 1.125 formally and conceptually resembles the E and C Equations 1.120 and 1.121, with β corresponding to E_B and ξ to C_B. Indeed, hydrogen bonding is mainly electrostatic in origin and electrostatic bonding of the Lewis acid/base complexes must increase in strength with β. Further, the empirical parameter ξ can be interpreted as a coordinate covalency parameter. This follows from the increase in ξ with decrease in the charge on the hydrogen atom in BH^+ (shown in Table 1.20), since this charge decrease

Table 1.20 *Comparison of the coordinate covalency parameter ξ with the charge $q(H^+)$ on hydrogen in BH^+.*

Family	ξ	$q(H^+)^a$	$[BH]^+$
PO bases	−0.20		
CO and SO bases	0.00	0.62	$[H_2C{=}OH]^+$
Nitriles	0.10		
Single-bonded O bases	0.20	0.57	$[H_3O]^+$
Pyridines	0.60	0.55	$[C_5H_5NH]^+$
Amines	1.00	0.47	$[NH_4]^+$

[a] Mulliken charge calculated at the HF/6–31G* level.

depends on the ability of the base B to transfer a charge into the empty 1s orbital of the proton, that is, to form a coordinate covalent bond with the proton. There is, however, a difference between the parameters C_B and ξ: C_B is a property of the individual base whereas ξ is taken to be a property of a whole family of bases.

Sixteen diverse BDPs of neutral oxygen and nitrogen bases have been correlated by the β and ξ equation. These include hydrogen-bond, BF_3 and I_2 affinities and also proton affinity in the gas phase [183] and Gibbs energy of proton transfer to the aqueous bases from aqueous $NH_4{}^+$. Because steric effects, solvent effects, entropic effects and strong conjugative π-electron donation to the base centre can lead to severe deviations from Equation 1.125, this equation is not expected to be highly precise in general. The main merits of the β and ξ equation are (i) to demonstrate the usefulness of hydrogen-bond parameters as electrostatic parameters of Lewis basicity and (ii) to show that a proper separation of Lewis bases into families is a convenient way to simplify the generalized quantitative treatment of Lewis basicity. However, the parameter β, which was determined by a somewhat vague method, has to be replaced by a more clearly defined hydrogen-bond basicity parameter, such as those listed in Chapter 4.

1.11.4 A Chemometric Approach

By the method of principal component analysis (PCA), Maria, Gal *et al.* [184] determined the dimensionality of basicity scales, affinity scales and spectroscopic scales of basicity. They studied a data matrix of 22 neutral oxygen and nitrogen bases and 10 scales. These include: (i) IR and UV spectroscopic shifts upon hydrogen bonding, (ii) Gibbs energies of hydrogen bonding and halogen bonding, (iii) enthalpies of complexation with BF_3, $SbCl_5$ and I_2 and (iv) enthalpies of proton transfer. PCA shows that 95% of the total variance of the data could be accounted for by only two factors, F_1 and F_2. From the correlation of F_1 with proton affinity and F_2 with potassium cation affinity, it was proposed that F_1 represents a blend of electrostatic and covalent effects and F_2 mainly electrostatic effects. The third factor, representing in part the steric hindrance of complexation, is of marginal importance. Hence the correlation of a BDP with F_1 and F_2 by means of Equation 1.126:

$$\mathrm{BDP} = S_1F_1 + S_2F_2 + \mathrm{BDP}_0 \qquad (1.126)$$

Table 1.21 *Covalent/electrostatic character of eight affinity scales given by chemometric (θ), E and C (C_A/E_A) and β and ξ (e/b) analysis. Comparison with the hardness η_A of the acid.*

Reference Lewis acid	θ (°)	C_A/E_A	*e/b*	η_A (eV)
$CHCl_3$	60	0.28		
$4\text{-}FC_6H_4OH$	42	0.47	0.31	(9.5)[c]
$SbCl_5$	40	(2.9)[a]	0.26[b]	
$(CF_3)_2CHOH$	29	0.46		
BF_3	−4	0.47	0.57	9.7
HSO_3F	−22		0.57[b]	
SO_2	−45	3.1		5.6
I_2	−51	4.0	0.84	3.4

[a] Calculated from four enthalpies only.

[b] Calculated here from data in ref. [184]:

$SbCl_5 \text{affinity} = 38.0(\pm 3.0)\beta + 9.8(\pm 1.8)\xi - 0.6(\pm 2)(n = 18; r = 0.960; s = 2.3 \text{kcal mol}^{-1})$

$-\Delta H_i = 38.6(\pm 4.1)\beta + 22.1(\pm 2.3)\xi - 0.4(\pm 3)(n = 20; r = 0.956; s = 3.2 \text{kcal mol}^{-1})$

[c] Hardness of H_2O.

yields the sensitivities S_1 and S_2 of the BDP to the factors F_1 and F_2, respectively. Any BDP may thus be represented by a point of coordinates S_1 and S_2 in a two-dimensional space. In polar coordinates, the corresponding vector has a magnitude $\rho = \left(S_1^2 + S_2^2\right)^{1/2}$ and makes an angle $\theta = \arctan(S_2/S_1)$ with the S_1-axis; ρ is related to the strength of the Lewis acid and θ to the electrostatic/covalent character of the BDP. If θ is close to 90°, the BDP presents a character like that of F_2, that is mainly electrostatic. A decrease in θ corresponds to a larger dependence on F_1, that is an increase in covalent character. θ values for eight affinity scales are summarized in Table 1.21 and compared with the covalent/electrostatic ratios of the *EC* and $\beta\xi$ models and with the acid hardness. There is good agreement between the four approaches, if one excludes $SbCl_5$ and BF_3, apparently anomalous in the *EC* model. PCA also supports the separation of bases into the same families as those of the $\beta\xi$ model, as shown by the F_1 versus F_2 plot in Figure 1.13. Hence the multiple correlation of F_1 with F_2 and ξ (Equation 1.127) is expected by the physical significance attributed to these parameters:

$$F_1 = 3.11(\pm 0.27)F_2 + 1.90(\pm 0.13)\,\xi - 0.37(\pm 0.04) \tag{1.127}$$

$$n = 20(\text{O and N bases}),\ r = 0.964,\ s = 0.12.$$

The application of Equation 1.126 to the thermodynamic functions of a variety of Lewis acid/base reactions shows [184] that their responses to the electrostatic/covalent character increase in the order $-\Delta S < -\Delta H < -\Delta G$. A rather covalent character is found for the spectroscopic scale of hydrogen-bond basicity $\Delta\nu(\text{OH})$, and the sequence $-\Delta S < \Delta\nu(\text{OH}) < -\Delta H < -\Delta G$ is observed for the formation of hydrogen bonds.

A thorough analysis [185] of hydrogen-bond basicity scales by means of Equation 1.126 yields θ values ranging from 53° (4-fluorophenol complexes in CH_2Cl_2) to 86° (Ph_2NH complexes in CCl_4), depending on the reference hydrogen-bond donor and the

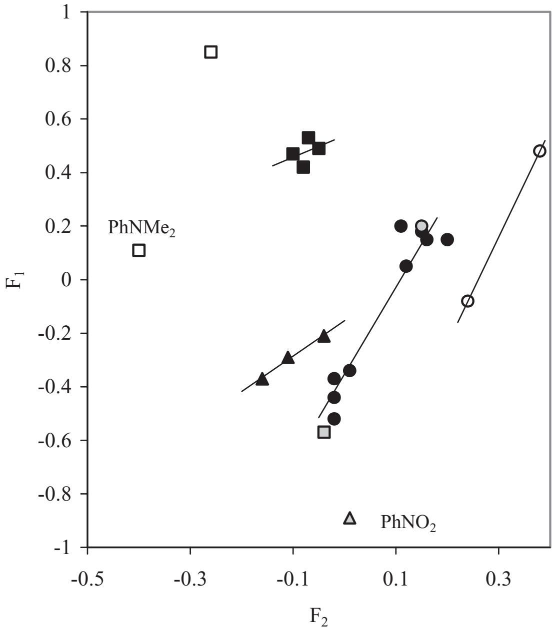


Figure 1.13 *F_1 vs F_2 plot showing the separation of bases into the families of the $\beta\xi$ treatment: PO bases (○), CO (●) and SO bases (●), nitrile (▣), ethers (▲), pyridines (■) and amine (□). The ξ parameters of $PhNO_2$ (△) and $PhNMe_2$ (□) are unknown, but the positions of $PhNO_2$ near oxygen bases and of $PhNMe_2$ near the amine appear satisfactory.*

solvent. This variation in θ precludes the construction of any general scale of hydrogen-bond basicity. However, a reasonably general scale could be set up either by choosing a reference hydrogen-bond donor having a θ value in the middle of the 53–86° range, for example 4-fluorophenol [121] in CCl_4 ($\theta = 70°$), or by averaging proper hydrogen-bond basicity scales [186]. Indeed, plots of log$K$ for bases against OH (H_2O, alcohols, phenols) and strong NH (imides, amides, HNCS) hydrogen-bond donors versus log$K$ for bases against 4-fluorophenol are family independent. Only CH ($CHCl_3$, alk-1-ynes) and weak NH (aromatic amines) hydrogen-bond donors show a moderate family dependence in such linear Gibbs energy relationships. Panchenko *et al.* found [187] that the family independence can be restored by using the two-scale Equation 1.128:

$$\log K = b\,\mathrm{p}K_{\mathrm{BHX}} + c\,\mathrm{p}K_{\mathrm{BI_2}} + \log K_0 \tag{1.128}$$

where pK_{BHX} is the 4-fluorophenol basicity (see Chapter 4), p$K_{\mathrm{BI_2}}$ is the diiodine basicity (see Chapter 5), b and c are regression coefficients and log K_0 is the intercept. For example, the application of Equation 1.128 to the diphenylamine basicity yields [187]

$$\log K = 0.73(\pm 0.06)\,\mathrm{p}K_{\mathrm{BHX}} - 0.25(\pm 0.04)\,\mathrm{p}K_{\mathrm{BI_2}} - 0.73 \tag{1.129}$$

$$n = 17, r = 0.952, s = 0.15.$$

The correlation coefficient $r = 0.952$ can be compared with the value $r = 0.767$ found in the correlation of diphenylamine basicity with the single 4-fluorophenol basicity.

In the same vein, a reasonably general hydrogen-bond acidity scale has been established [188]. Consequently, a reasonably general treatment of hydrogen-bond complexation constants (as log$K$ values) in CCl_4 has been reported [189] for more than a 1000 hydrogen-bond donor/acceptor pairs (corresponding to 89 hydrogen-bond donors and 215 hydrogen-bond acceptors) in the form of Equation 1.130:

$$\log K = 7.354(\pm 0.019)\,\alpha_2^{\mathrm{H}}\beta_2^{\mathrm{H}} - 1.094(\pm 0.007) \tag{1.130}$$

$$n = 1312, r = 0.9956, s = 0.093$$

where α_2^{H} is a hydrogen-bond acidity parameter [188] and β_2^{H} a hydrogen-bond basicity parameter [186], both scaled to zero for non-hydrogen-bonding molecules (e.g. alkanes). The subscript 2 and the superscript H indicate that these parameters are specific to the solute (that is, they are not solvent scales) and differ from their congeners α and β. Similar treatments are also successful in the gas phase [106] (Equation 1.131) and in CCl_3CH_3 [190] (Equation 1.132):

$$\log K = 9.13(\pm 0.32)\,\alpha_2^{\mathrm{H}}\beta_2^{\mathrm{H}} - 0.87(\pm 0.11) \tag{1.131}$$

$$n = 23, r = 0.987, s = 0.20$$

$$\log K = 6.86(\pm 0.15)\,\alpha_2^{\mathrm{H}}\beta_2^{\mathrm{H}} - 1.14(\pm 0.07) \tag{1.132}$$

$$n = 84, r = 0.980, s = 0.16.$$

A comparison of the slopes and intercepts of Equations 1.130–1.132 shows that hydrogen-bond complexation increases with the medium in the order $CCl_3CH_3 < CCl_4 <$ gas.

1.11.5 Quantum Chemical Descriptors for Basicity Scales

The previous $S\sigma$, EC, $\beta\xi$ and F_1F_2 two-term equations for interpreting and predicting basicities, affinities and spectroscopic scales of basicity rely on empirical parameters, either not clearly defined (S, ξ, E, C, β) or needing advanced statistical procedures for their determination (F_1, F_2). Moreover, if new systems are added to the original database, the numerical values of the parameters will change, as seen by the significant evolution of E, C and β values over the years. Lastly, since many key systems have not yet been measured or are not measurable, the number of available values is disappointingly low (22 for F_1, F_2) compared with the large number of bases that are of interest to chemists.

These shortcomings of empirical approaches and the exponential growth of computer power in the last four decades have led to empirical parameters being replaced by calculated quantum chemical descriptors of basicity. The use of computationally derived parameters in the study of basicity, or related fields, has seen much investigation. See, for example the QSPR (quantitative structure–property relationship) [191], TLSER (theoretical linear solvation energy relationship) [192], GIPF (general interaction properties function) [193] and related methods [194–196]. The analysis and prediction of Lewis basicity by a modified GIPF method [197] is presented below.

Table 1.22 *Standardized coefficients[a] and statistics of Equation 1.133.*

Property	α'	β'	γ'	ε	n	r	s
Phenol affinity	−0.659	−0.346	−0.388	3.2	25	0.979	0.4
$\Delta\nu$(OH)	−0.573	−0.341	−0.591	194	37	0.966	29
Diiodine affinity	[b]	−0.429	−0.780	17.1	26	0.950	1.0
Proton affinity	−0.266	−0.540	−0.524	206.4	36	0.975	3.6

[a] Regression coefficients have been standardized to allow direct comparisons.
[b] Not significant.

In this method, the Lewis bases are characterized by three HF/6–31G computed properties:

- The spatial minimum in the electrostatic potential, $V_{\min}$, associated with the electron-donor heteroatom. The electrostatic potential is the energy of interaction of a point positive charge with the nuclei and electrons of a molecule.
- The polarization potential, $P_{V\min}$, evaluated at the position of $V_{\min}$. It gives the energy of electronic reorganization of the molecule as a result of its interaction with a point positive charge.
- $\bar{I}_{\mathrm{S,min}}$, the surface minimum in the average local ionization energy (the molecular surface is defined by the 0.001 au contour of the electron density).

$V_{\min}$, $P_{V\min}$ and $\bar{I}_{\mathrm{S,min}}$ are closely related to the electrostatic, polarization and charge-transfer components, respectively, of the Morokuma decomposition of proton affinity. It has been shown [197] that the spectroscopic scale $\Delta\nu$(OH) (related to methanol), the phenol affinity, the diiodine affinity and the proton affinity of 42 nitrogen, oxygen and sulfur bases can be correlated by the triple-scale Equation 1.133:

$$-\Delta H \text{ (or } \Delta\nu\text{OH)} = \alpha V_{\min} + \beta P_{V\min} + \gamma \bar{I}_{\mathrm{S,min}} + \varepsilon \tag{1.133}$$

The regression coefficients α, β and γ, the intercept ε and the statistics are given in Table 1.22. Taking into account the variety of bases and BDPs, the correlations are satisfactory. The calculation of affinity scales purely from the electronic structure of bases appears a promising method.

An even better method, but of greater computational difficulty (see above), is the calculation of the properties of model complexes. For example, ΔE_{el}, ΔH or ΔG calculated for the complexation of the small hydrogen-bond donors H_2O [198] or HF [199] were found to be successful descriptors of the basicity towards larger ones (that is of greater computational cost) such as 4-FC_6H_4OH.

Ultimately, the affinity or the basicity scales themselves might be computed. This has been done successfully for the methanol affinity in the gas phase [41]. However, the MP2/aug-cc-pVTZ//B3LYP/6–31+G(d,p) costly level required to obtain good agreement with experimental affinities has limited the scale to a few small Lewis bases. Proton and cation affinities and basicities *in the gas phase* are now computed on a routine basis (see Chapter 6). Nevertheless, the size of Lewis bases and cations and the number of bases studied are inversely proportional to the level of theory, that is, to the agreement with experimental data. As far as extended *solution* basicity scales towards usual Lewis acids are concerned, it is not realistic to expect their reliable computation for a number of years or even decades, mainly because of the difficult calculation of solvent effects and the vibrational entropy of complexes. The construction of basicity scales remains a task for experimental chemists.

1.12 Concluding Remarks and Content of Chapters 2–7

There are virtually as many possible Lewis basicity scales as there are Lewis acids. This is a dramatic consequence of the Lewis definition of acids, which has considerably enlarged the number of chemical species showing an acid character and made the proton lose the status of reference acid.

Mathematically, the aqueous Brönsted basicity scale corresponds to a one-column data matrix. In fact, several columns are needed to take into account the influence of the medium but two media have been studied most, water and the gas phase. So the two most filled, and consequently most used, columns are the $\mathrm{p}K_{\mathrm{BH}^+}$ and GB scales. In the field of proton affinity, no column attains the degree of completeness and reliability of the gas-phase PA column. There is no need for spectroscopic scales of Brönsted basicity since the thermodynamic scales are satisfactory.

The mathematics of the Lewis acid/base concept is that of a data matrix of m rows and n columns. Data are complexation constants, as $\log K$ or ΔG. Each row corresponds to a Lewis acidity scale towards a reference base B_i° ($i = 1$ to m) and each column corresponds to a Lewis basicity scale towards a reference acid A_j° ($j = 1$ to n). For a rigorous treatment, the data measured in different media cannot be mixed in the same data matrix. In the matrix measuring Lewis affinity, the data are complexation enthalpies. There are extrathermodynamic relationships (isoequilibrium relationships or enthalpy–entropy compensation law) which allow transformations between blocks of the affinity and basicity matrices. In the principal component analysis of Lewis basicity, this justifies, somewhat, the mixing of affinity columns and basicity columns in a unified basicity–affinity matrix.

At first glance, the size and completeness of the currently available basicity and/or affinity data matrices are rather disappointing. It appears that much information is lacking in this fundamental field of chemistry. To give an order of magnitude, the affinity matrix supporting the EC model, limited to neutral Lewis acids and bases but mixing enthalpies measured in ‘poorly solvating solvents’ and the gas phase, had a 43 (bases) × 31 (acids) order and an occupancy rate of 21% in the 1971 version [168] and a 50 × 43 order and a rate of 23% in the 1994 version [6]. One can conclude from these figures that, whereas the number of reference Lewis acids (partially) studied appears correct for constructing basicity scales, that of Lewis bases is very low compared with the ~7000 bases of the $\mathrm{p}K_{\mathrm{BH}^+}$ database [11] and ~3000 bases of the GB database [27, 28].

There are two main reasons for the paucity of data available for constructing basicity and affinity scales. First, the observation by Lewis himself in 1938 [30] that ‘in studying acids and bases, we find that the relative strength depends not only upon the chosen solvent but also upon the particular base or acid used for reference’ very soon discouraged many chemists from measuring Lewis basicity (acidity) quantitatively, all the more so since statements similar to that of Lewis have become commonplace in the chemistry literature.

Second, there are in practice not many systems in which a Lewis reference acid reacts with a series of diversified bases for which a series of reliable equilibrium constants can be measured easily by known physicochemical techniques over a large range of values (that is, from possibly very large to possibly very low equilibrium constants), and in the same conditions of temperature and medium. This is why chemists have turned to the determination of spectroscopic scales of Lewis basicity (affinity).

Fortunately, there are a number of theoretical, statistical and empirical reasons to believe that Lewis basicity (affinity) depends on a limited number of factors. From the quantum chemical point of view, the acid/base interaction energy can be partitioned into five terms (electrostatic, dispersion, polarization, charge transfer and exchange–repulsion). By a principal component analysis [184], $\sim$99% of the variance of an affinity/basicity data matrix can be explained by three factors, the first two being by far the most important. A number of experimental affinity and basicity scales, and of spectroscopic scales of basicity, can be correlated by two parameters, using the *EC* or $\beta\xi$ equations, or three quantum chemical descriptors of basicity [197]. However, these statistical and empirical approaches are limited to systems where steric effects and π back-bonding are not important.

Due to the existence of a limited number of explanatory variables for predicting and possibly interpreting Lewis basicity, a limited number of scales should be sufficient to quantify the Lewis definitions of acids and bases. The search for these few basicity scales in the literature gave the following results.

In spite of a very large amount of data, listed in two books by Sillen and Marten (1964, second edition [148], and 1971, supplement [149]), the stability constants of metal-ion complexes with organic and inorganic ligands, measured mainly in aqueous solution, could not furnish any useful basicity scale. They did, however, help to establish the important HSAB classification and principle (Pearson, 1963–1969) [150–155].

Among numerous thermodynamic measurements on the complexes of covalent metal halides, antimony pentachloride was chosen by Gutmann (1966–1968) [78] as the reference Lewis acid for constructing an $SbCl_5$ affinity scale and developing the 'donor number' concept. This scale is critically presented in Chapter 2.

Following the use of boron acids by Brown *et al.* (1953–1955) [91] in his classical work on steric effects in the complexation of amines with trimethylboron, an extensive set of calorimetric measurements was provided by the studies of BF_3 complexes by Gal, Maria *et al.* (1970–1992) [80]. Boron trifluoride is the archetype of Lewis acids in the original Lewis definition. The promising BF_3 affinity scale is presented in Chapter 3.

The importance of hydrogen bonding in chemistry, biochemistry and physics has led to the thermodynamic and spectroscopic measurement of thousands of hydrogen-bonded systems, reviewed in an excellent book by Joesten and Schaad (1974) [84]. The largest and most reliable set of equilibrium constants for hydrogen bonding to a series of bases refers to the acid 4-fluorophenol (Taft *et al.*, 1969–1972) [116, 121]. This 4-fluorophenol basicity scale, and the corresponding 4-fluorophenol affinity scale pioneered by Arnett *et al.* (1969–1974) [23], have been considerably extended by Berthelot, Laurence *et al.* (1988–2008). The construction of the $4\text{-}FC_6H_4OH$ affinity scale enables a comparison with the $SbCl_5$ and BF_3 ones. The observation by Badger and Bauer (1937) [200] that the O—H stretching frequencies are shifted upon hydrogen bonding, and that this infrared shift is correlated with the enthalpy of hydrogen bonding, has justified the construction of several IR spectroscopic scales of hydrogen-bond basicity. Methanol is one of the most convenient reference acids for this purpose and infrared shifts, $\Delta\nu$(OH), of this probe have been systematically measured by Berthelot, Laurence *et al.* (1976–1988). By means of the solvatochromic comparison method, Kamlet and Taft (1976) [201] have set up the β scale of solvent hydrogen-bond basicity, a key parameter in the linear solvation energy relationships developed for the quantitative study of solvent effects. Improved and extended β(OH) and β(NH) scales defined from the UV shifts on hydrogen bonding of 4-nitrophenol and 4-nitroaniline, respectively, have been constructed by Laurence, Nicolet *et al.* (1986). Extended scales of 4-FC_6H_4OH basicity and affinity, $\Delta\nu$(OH), β(OH) and β(NH), are tabulated in Chapter 4.

The discovery of charge-transfer bands in the UV spectra of diiodine complexes (Benesi and Hildebrand, 1949) [202] and the development of the underlying theory (Mulliken, 1952) [31] initiated a wealth of thermodynamic and spectroscopic measurements on diiodine complexes, mainly in the period 1949–1980. Complementary measurements by Berthelot, Guiheneuf, Laurence *et al.* (1970–2002) and Abboud *et al.* (1973–2004) enabled a homogeneous scale of diiodine basicity to be constructed. In addition, recommended values of diiodine affinity have been compiled from the literature (Laurence, 2006), for comparison with the $SbCl_5$, BF_3 and 4-FC_6H_4OH affinity scales. UV and/or IR shifts upon complexation of the acids I_2, ICl and ICN have also been systematically measured by Berthelot, Laurence, Nicolet *et al.* (1981–1985). These thermodynamic and spectroscopic scales will allow the recent concept of a halogen bond to be treated quantitatively. They can be found in Chapter 5.

The development of mass spectrometric techniques has led to the construction of not only the well-known GB and PA scales, but also the lithium cation basicity scale (Taft *et al.*, 1990; Burk, Koppel, Gal *et al.*, 2000) [93] and many metal cation basicity and affinity scales in the gas phase. A selection of the most informative scales is presented in Chapter 6.

Because basicity is strongly related to the structure of complexes, Chapters 2–6 also contain a description of the main structural features of each kind of complex studied in the book. Experimental structures of complexes were taken mostly from the Cambridge Structural Database (CSD) [50] for the solid-state structures and from the MOGADOC database [49] for the gas-phase structures.

The last chapter gives examples of reliable experimental determinations of most of the scales tabulated in this book. This should allow any chemist in academia or industry, and also any graduate or upper-level undergraduate student in chemistry, familiar with IR and UV spectrometry, calorimetry and mass spectrometry, to determine new values for the scales and the molecules of interest to them.

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