CHAPTER 1

General Aspects

1.1. DEFINING ACIDITY

1.1.1. Acids and Bases

The concept of acidity was born in ancient times to describe the physiological property such as taste of food or beverage (in Latin: *acidus,* sour; *acetum,* vinegar). Later during the development of experimental chemistry, it was soon realized that mineral acids such as sulfuric, nitric, and hydrochloric acids played a key role in chemical transformations. Our present understanding of acid-induced or -catalyzed reactions covers an extremely broad field ranging from large-scale industrial processes in hydrocarbon chemistry to enzyme-controlled reactions in the living cell.

The chemical species that plays a unique and privileged role in acidity is the hydrogen nucleus, that is, the proton: H^+. Since its 1*s* orbital is empty, the proton is not prone to electronic repulsion and by itself has a powerful polarizing effect. Due to its very strong electron affinity, it cannot be found as a free "naked" species in the condensed state but is always associated with one or more molecules of the acid itself or of the solvent. Free protons exist only in the gas phase (such as in mass spectrometric studies). Regardless, as a shorthand notation, one generally depicts the proton in solution chemistry as "H^+." Due to its very small size (10^5 times smaller than any other cation) and the fact that only the 1*s* orbital is used in bonding by hydrogen, proton transfer is a very facile chemical reaction and does not necessitate important reorganization of the electronic valence shells. Understanding the nature of the proton is important while generalizing quantitative relationships in acidity measurements.[1,2]

The first clear definition of acidity can be attributed to Arrhenius, who between 1880 and 1890 elaborated the theory of ionic dissociation in water to explain the variation in strength of different acids.[3] Based on electrolytic experiments such as conductance measurements, he defined acids as substances that dissociate in water and yield the hydrogen ion whereas bases dissociate to yield hydroxide ions. In 1923, J. N. Brønsted generalized this concept to other solvents.[4] He defined an acid as a species that can donate a proton and defined a base as a species that can accept it. This

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definition is generally known as the Brønsted–Lowry concept. The dissociation of an acid HA in a solvent S can be written as an acid–base equilibrium [Eq. (1.1)].

$$\mathrm{HA} + \mathrm{S} \rightleftharpoons \mathrm{A^-} + \mathrm{SH^+} \tag{1.1}$$

The ionization of the acid HA in solvent S leads to a new acid HS^+ and a base A^-. Equation (1.1) has a very wide scope and can be very well applied to neutral and positively and negatively charged acid systems. The acid–base pair that differs only by a proton is referred to as the conjugate acid–base pair. Thus, H_2O is the conjugate base of the acid H_3O^+. An obvious consequence of the concept is that the extent to which an acid ionizes depends on the basicity of the solvent in which the ionization takes place. This shows the difficulty in establishing an absolute acidity scale. Acidity scales are energy scales, and thus they are arbitrary with respect to both the reference point and the magnitude of units chosen.

Fortunately, many of the common solvents by themselves are capable of acting as acids and bases. These amphoteric or amphiprotic solvents undergo self-ionization [e.g., Eqs. (1.2) and (1.3)], which can be formulated in a general way as in Eq. (1.4).

$$2\,\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \tag{1.2}$$

$$2\,\mathrm{HF} \rightleftharpoons \mathrm{H_2F^+} + \mathrm{F^-} \tag{1.3}$$

$$2\,\mathrm{HA} \rightleftharpoons \mathrm{H_2A^+} + \mathrm{A^-} \tag{1.4}$$

This equilibrium is characterized by the autoprotolysis constant K_{ap}, which under the usual high dilution conditions can be written as in Eq. (1.5).

$$K_{\mathrm{ap}} = [\mathrm{H_2A^+}][\mathrm{A^-}] \tag{1.5}$$

Indeed the extent of dissociation of the solvent is very small (in HF, $K_{\mathrm{ap}} \approx 10-11$; in H_2O, $K_{\mathrm{ap}} = 10-14$). The pK_{ap} value that gives the acidity range will be discussed later.

G.N. Lewis extended and generalized the acid–base concept to nonprotonic systems.[5,6] He defined an acid as a substance that can accept electrons and defined a base as a substance that can donate electrons. Lewis acids are electron-deficient molecules or ions such as BF_3 or carbocations, whereas Lewis bases are molecules that contain readily available nonbonded electron pairs (as in ethers, amines, etc.) [Eq. (1.6)].

$$\mathrm{BF_3} + :\mathrm{O(CH_3)_2} \rightleftharpoons \mathrm{BF_3{:}O(CH_3)_2} \tag{1.6}$$

Of course, in a generalized way, the proton H^+ is also a Lewis acid and the Brønsted acids and bases also fall into the Lewis categories.

Considering the general equation (1.4) for the auto-ionization of solvent HA, one can define an acid as any substance that will increase $[H_2A^+]$ and define a base as any substance that will increase $[A^-]$ and thus decrease $[H_2A^+]$. This definition, which includes both Lewis' and Brønsted's concepts, is used in practice while measuring the acidity of a solution by pH.

A number of strategies have been developed for acidity measurements of both aqueous and nonaqueous solutions. We will briefly review the most important ones and discuss their use in establishing acidity scales.

1.1.2. The pH Scale

The concentration of the acid itself is of little significance other than analytical, with the exception of strong acids in dilute aqueous solutions. The concentration of H^+ itself is not satisfactory either, because it is solvated diversely and the ability of transferring a proton to another base depends on the nature of the medium. The real physical quantity describing the acidity of a medium is the activity of the proton a_{H^+}. The experimental determination of the activity of the proton requires the measurement of the potential of a hydrogen electrode or a glass electrode in equilibrium with the solution to be tested. The equation is of the following type [Eq. (1.7)], wherein C is a constant.

$$E = C - \frac{RT}{F}\log_{10}(a_{H^+}) \tag{1.7}$$

It was Sørensen's idea[7] to use this relationship, which can be considered as a basis to the modern definition of the pH scale of acidity for aqueous solutions. The pH of a dilute solution of acid is related to the concentration of the solvated proton from Eq. (1.8). Depending on the dilution, the proton can be further solvated by two or more solvent molecules.

$$\mathrm{pH} = -\log[\mathrm{HS}^+] \tag{1.8}$$

When the acid solution is highly diluted in water, the pH measurement is convenient, but it becomes critical when the acid concentration increases and, even more so, if nonaqueous media are employed. Since a reference cell is used with a liquid junction, the potential at the liquid junction also has to be known. The hydrogen ion activity cannot be measured independently, and for this reason the equality of Eq. (1.9) cannot be definitely established for any solution.

$$\mathrm{pH} = -\log_{10}(a_{H^+}) \tag{1.9}$$

Under the best experimental conditions, the National Bureau of Standard has set up a series of standard solutions of pH from which the pH of any other aqueous solution can be extrapolated as long as the ionic strength of the solution is not higher than 0.1 M. For more concentrated solutions, the pH scale will no longer have any real significance. In extending the limit to 1 M solutions, it is apparent that the available range of acidity is directly related to the autoprotolysis constant [Eq. (1.5)], because the minimum value of pH in a solution is zero and the maximum value is $\mathrm{p}K_{\mathrm{ap}} = \mathrm{p}(\mathrm{H_2A^+}) + \mathrm{p}(\mathrm{A^-})$. Thus, the range of pH (ΔpH) is $\mathrm{p}K_{\mathrm{ap}}$ (for water, 14 pH units). These limiting conditions are rather unfortunate because many chemical transformations are achieved beyond this range and under much less ideal conditions.

1.1.3. Acidity Functions

Considering the limited applicability of the pH scale, a quantitative scale is needed to express the acidity of more concentrated or nonaqueous solutions.

A knowledge of the acidity parameter should permit one to estimate the degree of transformation of a given base (to its protonated form) in its conjugate acid. This should allow one to relate these data to the rate of acid-catalyzed reactions. Hammett and Deyrup[8] in 1932 were the first to suggest a method for measuring the degree of protonation of weakly basic indicators in acid solution. The proton transfer equilibrium in the acid solution between an electro-neutral weak base B and the solvated proton can be written as in Eq. (1.10).

$$\mathrm{B} + \mathrm{H_2A^+} \rightleftharpoons \mathrm{BH^+} + \mathrm{AH} \tag{1.10}$$

Bearing in mind that the proton is solvated (AH_2^+) and that AH is the solvent, the equilibrium can be written as in Eq. (1.11).

$$\mathrm{B} + \mathrm{H^+} \rightleftharpoons \mathrm{BH^+} \tag{1.11}$$

The corresponding thermodynamic equilibrium constant is K_{BH^+}, which is expressed as in Eq. (1.12), in which a is the activity, C the concentration, and f the activity coefficient.

$$K_{\mathrm{BH}^+} = \frac{a_{\mathrm{H}^+} \cdot a_{\mathrm{B}}}{a_{\mathrm{BH}^+}} = \frac{a_{\mathrm{H}^+} \cdot C_B}{C_{\mathrm{BH}^+}} \cdot \frac{f_{\mathrm{H}}}{f_{\mathrm{BH}^+}} \tag{1.12}$$

From this equation, Eq. (1.13) follows.

$$\frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}} = \frac{1}{K_{\mathrm{BH}^+}} \cdot a_{\mathrm{H}^+} \cdot \frac{f_{\mathrm{B}}}{f_{\mathrm{BH}^+}} \tag{1.13}$$

Because the first ratio represents the degree of protonation, Hammett and Deyrup[8,9] defined the acidity function H_0 by Eq. (1.14).

$$H_0 = -\log a_{\mathrm{H}^+} \cdot \frac{f_{\mathrm{B}}}{f_{\mathrm{BH}^+}} = -\log K_{\mathrm{BH}^+} + \log \frac{C_{\mathrm{B}}}{C_{\mathrm{BH}^+}} \tag{1.14}$$

Equation (1.14) can be written for further discussion in the more usual form of Eq. (1.15).

$$H_0 = \mathrm{pK}_{\mathrm{BH}^+} - \log \frac{[\mathrm{BH}^+]}{[\mathrm{B}]} \tag{1.15}$$

From Eq. (1.14) it is clear that in dilute aqueous solution, as the activity coefficients tend to unity, the Hammett acidity function becomes identical with pH. On the other hand, by making the fundamental assumption that the ratio $f_{\mathrm{B}}/f_{\mathrm{BH}^+}$ is the same for different bases in a given solution, Hammett postulated that the H_0 function was unique for a particular series of solutions of changing acidity. The first application was made for the H_2SO_4–H_2O system using a series of primary anilines as indicators. By starting with the strongest base B_1, the $pK_{B_1H^+}$ was measured in dilute aqueous solution. The pK of the next weaker base B_2 was then determined by measuring the ionization ratio of the two indicators in the same acid solution using the relation of Eq. (1.16).

$$pK_{B_1H^+} - pK_{B_2H^+} = \log\frac{[B_1H^+]}{[B_1]} - \log\frac{[B_2H^+]}{[B_2]} \tag{1.16}$$

The ionization ratio was measured by UV–visible spectroscopy. With the help of successively weaker primary aromatic amine indicators, the strongest base being *para*-nitroaniline (p$K = 1.40$) and the weakest trinitroaniline (p$K = -9$), Hammett explored the whole H_2O–H_2SO_4 range up to 100% sulfuric acid and the perchloric acid–water solution up to 60% of acid. Similar acidity functions such as H_-, H_+, H_{2+} were proposed related to acid–base equilibria in which the indicator is negatively, positively, or even dipositively charged. The validity of all of these functions is based on the simple assumption that the activity coefficient ratio is independent of the nature of the indicator at any given solvent composition. In this case the log $[BH^+]/[B]$ plots against H_0 should be linear with a slope of -1.00 for all neutral bases. This is not the case for groups of indicators with different structures, and especially for different basic sites, which often show significant deviations. For this reason, it is well recognized now that the above assumption does not have a general validity. The measurement of a Hammett acidity function should be limited to those indicators for which log $[BH^+]/[B]$ plotted against H_0 gives a straight line with a negative unit slope. These indicators are called Hammett bases.

Equilibria other than proton transfer have also been used to determine acidity functions. One of these is based on the ionization of alcohols (mainly arylmethyl alcohols) in acid solution following the equilibrium in Eq. (1.17).

$$\mathrm{ROH} + \mathrm{H}^+ \rightleftharpoons \mathrm{R}^+ + \mathrm{H_2O} \tag{1.17}$$

The corresponding acidity function described as H_R is then written in Eq. (1.18).

$$H_R = pK_{R^+} - \log\frac{[R^+]}{[ROH]} \tag{1.18}$$

This H_R function, also called J_0 function, has also been used to measure the acidity of the sulfuric acid–water and perchloric acid–water systems. It shows a large deviation from the H_0 scale in the highly concentrated solutions as shown in Figure 1.1.

However, all these and other acidity functions are based on Hammett's principle and can be expressed by Eq. (1.19), in which B and A are the basic and the conjugate acidic form of the indicator, respectively. They become identical with the pH scale in highly dilute acid solutions. The relative and absolute validity of the different acidity functions have been the subject of much controversy and the subject has been extensively reviewed.[1,10–14]

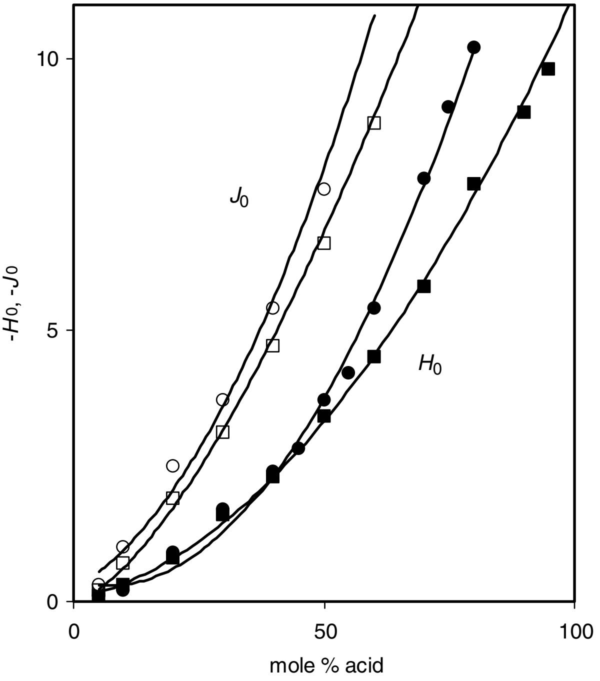


Figure 1.1. H_0 and J_0 functions for H_2SO_4–H_2O and $HClO_4$–H_2O systems. $HClO_4$: ○, ref. 11; ●, ref. 13; H_2SO_4: □, ref. 12; ■, ref. 14.

$$H_x = pK_A - \log\frac{A}{B} \tag{1.19}$$

Whatever may be the limitations of the concept first proposed by Hammett and Deyrup in 1932[8] until now, no other widely used alternative has appeared to better assess quantitatively the acidity of concentrated and nonaqueous strongly acidic solutions.[9] The experimental methods that have been used to determine acidity functions are discussed in Section 1.4.

1.2. DEFINITION OF SUPERACIDS

It was in a paper (including its title) published in 1927 by Hall and Conant[15] in the *Journal of the American Chemical Society* that the name "superacid" appeared for the first time in the chemical literature. In a study of the hydrogen ion activity in a nonaqueous acid solution, these authors noticed that sulfuric acid and perchloric acid in glacial acetic acid were able to form salts with a variety of weak bases such as ketones and other carbonyl compounds. These weak bases did not form salts with the aqueous solutions of the same acids. The authors ascribed this high acidity to the ionization of these acids in glacial acetic acid, increasing the concentration of $CH_3COOH_2^+$, a species less solvated than H_3O^+ in the aqueous acids. They proposed to call these solutions "superacid solutions." Their proposal was, however, not further followed up or used until the 1960s, when Olah's studies of obtaining stable solutions of highly electron-deficient ions, particularly carbocations, focused interest on very high-acidity nonaqueous systems.[16,17] Subsequently, Gillespie proposed an arbitrary but since widely accepted definition of superacids,[18,19] defining them as any acid system that is stronger than 100% sulfuric acid, that is, $H_0 \leq -12$. Fluorosulfuric acid and trifluoromethanesulfonic acid are examples of Brønsted acids that exceed the acidity of sulfuric acid with H_0 values of about -15.1 and -14.1, respectively.

To reach acidities beyond this limit, one has to start with an already strong acid ($H_0 \approx -10$) and add to it a stronger acid that increases the ionization. This can be achieved either by adding a strong Brønsted acid (HB) capable of ionizing in the medium [Eq. (1.20)] or by adding a strong Lewis acid (L) that, by forming a conjugate acid, will shift the autoprotonation equilibrium by forming a more delocalized counterion of the strong acid [Eq. (1.21)].

$$\mathrm{HA} + \mathrm{HB} \rightleftharpoons \mathrm{H_2A^+} + \mathrm{B^-} \tag{1.20}$$

$$2\,\mathrm{HA} + \mathrm{L} \rightleftharpoons \mathrm{H_2A^+} + \mathrm{LA^-} \tag{1.21}$$

In both cases, a remarkable acidity increase is observed from the H_0 value of the neat HA as shown in Figure 1.2 for HSO_3F.

It is this large acidity jump, generally more than 5 H_0 units, that raises a strong acid solution into the superacid region. Therefore, it is clear that the proposed reference of $H_0 = -12$ for the lower limit of superacidity is only arbitrary. It could as well be $H_0 = -15.1$ with HF or HSO_3F as solvent.

Gillespie's definition of superacids relates to Brønsted acid systems. Because Lewis acids also cover a wide range of acidities extending beyond the strength of conventionally used systems, Olah suggested the use of anhydrous aluminum chloride as the arbitrary reference and we categorize Lewis superacids as those stronger than aluminum chloride[17] (see, however, subsequent discussion on the difficulties of measuring the strength of a Lewis acid).

It should be also noted that in biological chemistry, following a suggestion by Westheimer,[20] it is customary to call catalysis by metal ions bound to enzyme systems as "superacid catalysis." Because the role of a metal ion is analogous to a proton, this arbitrary suggestion reflects enhanced activity and is in line with previously discussed Brønsted and Lewis superacids.

1.2.1. Range of Acidities

Despite the fact that superacids are stronger than 100% sulfuric acid, there may be as much or more difference in acidity between various superacid systems than between neat sulfuric acid and its 0.1 *M* solution in water.

Acidity levels as high as $H_0 = -27$ have been estimated on the basis of exchange rate measurements by NMR for an HSO_3F–SbF_5 mixture containing 90 mol% SbF_5.[21] In fact, the HF–SbF_5 is considered one of the strongest superacid system based on

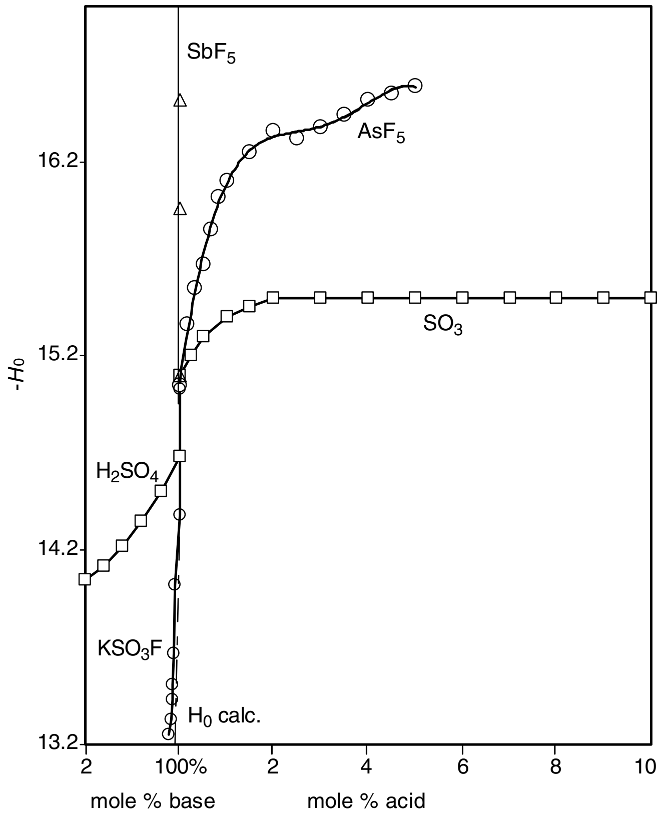


Figure 1.2. Acidity increase near the H_0 value of neat HSO_3F.[19]

various measurements. Meanwhile, however, Sommer and coworkers found that the weakest basic indicator of the *para*-methoxybenzhydryl cation family (4,4'-dimethoxy; $pK_{BH^+} \sim -23$) could not be diprotonated even in the strongest HF–SbF_5 acid.[22] For this reason it appears that one should not expect acidity levels higher than approximately $H_0 = -24$ in the usual superacid systems (Figure 1.3). Predictions of stronger acidities are all based on indirect estimations rather than direct acid–base equilibria measurements. It is important to recognize that the naked proton "H^+" is not present in the condensed phase because even compounds as weakly basic as methane or even rare gases bind the proton.[23,24]

A quantitative determination of the strength of Lewis acids to establish similar scales (H_0) as discussed in the case of protic (Brønsted-type) superacids would be most useful. However, to establish such a scale is extremely difficult. Whereas the Brønsted acid–base interaction invariably involves a proton transfer reaction that allows meaningful comparison, in the Lewis acid–base interaction, involving for example Lewis acids with widely different electronic and steric donating substituents, there is no such common denominator.[25,26] Hence despite various attempts, the term "strength of Lewis acid" has no well-defined meaning.

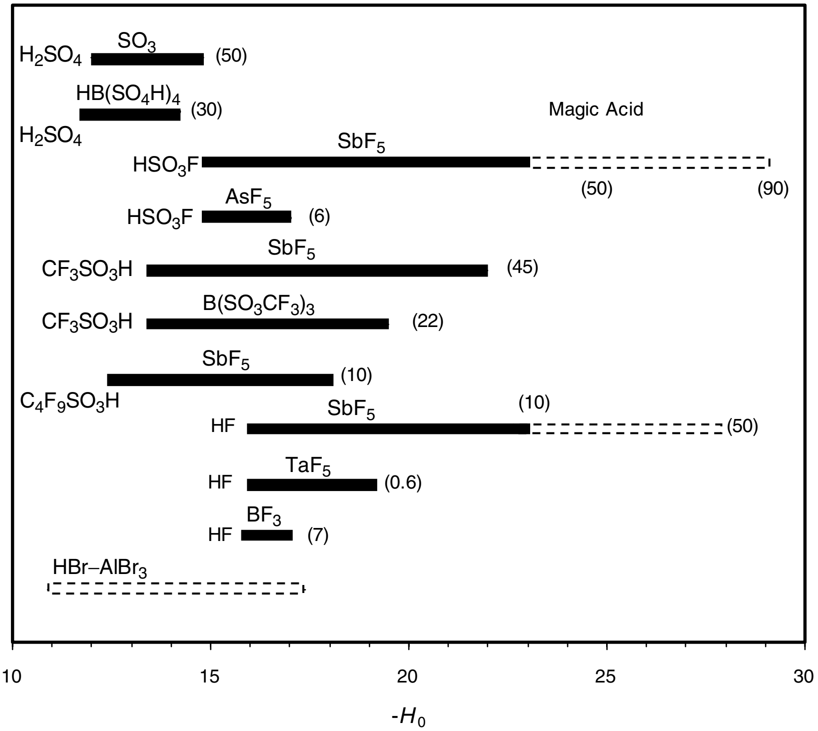


Figure 1.3. Acidity ranges for the most common superacids. The solid and open bars are measured using indicators; the broken bar is estimated by kinetic measurements; numbers in parentheses indicate mol% Lewis acid.

Regardless, it is important to keep in mind that superacidity encompasses both Brønsted and Lewis acid systems and their conjugate acids. The qualitative picture of Lewis acid strengths will be discussed in Section 1.4.7.

The acidity strength of solid acids is still not well known and is difficult to measure. Claims of superacidity in solids are numerous and will be discussed later in Chapter 2. Among the reviews related to acidity characterization of solids, those of Corma,[27] Farneth and Gorte,[28] and Fripiat and Dumesic[29] are quite significantly representative.[30]

1.3. TYPES OF SUPERACIDS

As discussed, superacids, similar to conventional acid systems, include both Brønsted and Lewis acids and their conjugate systems. Protic (Brønsted-type) superacids include strong parent acids and the mixtures thereof, whose acidity can be further enhanced by various combinations with Lewis acids (conjugate acids). The following are the most frequently used superacids.

1.3.1. Primary Superacids

1. Brønsted superacids such as perchloric acid ($HClO_4$), halosulfuric acids (HSO_3Cl, HSO_3F), perfluoroalkanesulfonic acids (CF_3SO_3H, R_FSO_3H), hydrogen fluoride, and carborane superacids [$H(CB_{11}HR_5X_6)$].
2. Lewis superacids, such as SbF_5, AsF_5, PF_5, TaF_5, NbF_5, BF_3, tris(pentafluorophenyl) borane, boron tris(trifluoromethanesulfonate), and aprotic organic superacids developed by Vol'pin and co-workers.

1.3.2. Binary Superacids

1. Binary Brønsted superacids such as HF–HSO_3F, HF–CF_3SO_3F, and $HB(HSO_4)_4$.
2. Conjugate Brønsted–Lewis superacids:
   a. Combination of oxygenated Brønsted acids (H_2SO_4, HSO_3F, CF_3SO_3H, R_FSO_3H) with Lewis acids (SO_3, SbF_5, AsF_5, TaF_5, and NbF_5);
   b. Hydrogen fluoride in combination with fluorinated Lewis acids such as SbF_5, PF_5, TaF_5, NbF_5, and BF_3;
   c. Conjugate Friedel–Crafts acids such as HBr–$AlBr_3$ and HCl–$AlCl_3$.

1.3.3. Ternary Superacids

Examples are HSO_3F–HF–SbF_5, HSO_3F–HF–CF_3SO_3H, and HSO_3F–SbF_5–SO_3.

1.3.4. Solid Superacids

The acid–base character of solids was studied very early by Tanabe's group[31,32] and was first described in a landmark volume.[33]

Solid superacids can be further divided into various groups depending on the nature of the acid sites. The acidity may be a property of the solid as part of its chemical structure (possessing Lewis or Brønsted sites; the acidity of the latter can be further enhanced by complexing with Lewis acids). Solid superacids can also be obtained by deposition on or intercalation of strong acids into an otherwise inert or low-acidity support.

1. Zeolitic acids.
2. Polymeric resin sulfonic acids including sulfonic acid resins complexed with Lewis acids and perfluorinated polymer resin acids (Nafion–H and Nafion–silica nanocomposites).
3. Enhanced acidity solids including Brønsted and Lewis acid-modified metal oxides and mixed oxides, as well as metal salts complexed with Lewis acids.
4. Immobilized superacids and graphite-intercalated superacids.

As with previous classifications, these are also arbitrary and are suggested for practical discussion of an otherwise rather complex field. The superacid character of solids is discussed later in subsequent subchapters, and individual superacid systems are discussed in Chapter 2.

1.4. EXPERIMENTAL TECHNIQUES FOR ACIDITY MEASUREMENTS (PROTIC ACIDS)

From Eq. (1.14) it is apparent that the main experimental difficulty in determining acidities is the estimation of the ratio between the free base and its protonated ionic form of a series of indicators, their so-called ionization ratios.

1.4.1. Spectrophotometric Method

In the early work of Hammett and Deyrup[8] the measurement of the ionization ratio was based on the color change of the indicator. The solutions containing the indicator were compared at 25°C in a colorimeter with a standard reference. This reference was water, when the indicator was colorless in its acid form, and 96% sulfuric acid (or 70% perchloric acid), when the indicator was colorless in the basic form.

For example, when the indicator was colored in water the authors define a stoichiometric color intensity relative to water $I_w = C_w/C_a$, where C_a and C_w are the stoichiometric concentrations of indicator in solution A and in water. On the other hand, the specific color intensity of the colored form relative to water is defined as $S_w = [B]_w/[B]_a$, where $[B]_w$ is the concentration of the colored base in water and $[B]_a$ is concentration in solution A. Because the indicator exists only in its basic form in water, $[B]_w = C_w$; and in solution A, $C_a = [B]_a + [BH^+]_a$. The ionization ratio is given by Eq. (1.22).

$$\frac{[BH^+]}{[B]} = \frac{S_w - I_w}{I_w} \tag{1.22}$$

Despite seven decades of technical and scientific progress, the original Hammett method has not become obsolete. The colorimeter has been replaced by modern spectrophotometers that can be operated at selected wavelengths extending the spectra beyond visible into the ultraviolet region of the electromagnetic spectrum. The experimental variable, which is wavelength-dependent, is the optical density D. D is related to the concentration by the Beer–Lambert law [Eq. (1.23)].

$$D_{i,\lambda} = \varepsilon_{i,\lambda} C_i \cdot l \tag{1.23}$$

C_i is the concentration of the absorbing species, l is the length of the cell, and ε_i is the molar absorptivity (or extinction coefficient). If at a given wavelength λ, ε_{BH^+}, ε_B, and ε_λ are the extinction coefficients, respectively, of acid form of the indicator, its basic form, and of the unknown solution, the ionization ratio is given by Eq. (1.24).

$$\frac{[BH^+]}{[B]} = \frac{\varepsilon_B - \varepsilon_\lambda}{\varepsilon_\lambda - \varepsilon_{BH^+}} \tag{1.24}$$

For a greater precision in this determination, λ should be chosen so as to have the maximum difference between ε_{BH^+} and ε_B. For this reason, the areas between the absorption line and the baseline of both acidic and basic forms of the indicator should be measured and compared.

Whereas the precision of the method is generally excellent, a number of drawbacks may appear with some indicators. First, Eq. (1.24) is true only with the assumption that ε_{BH^+} is solvent-independent (it is clear that ε_B and ε_{BH^+} cannot be measured separately in the same solution). The medium effect on the absorption spectrum (mainly the wavelength shift of λ_{max}) can be easily taken into account in the measurements. However, large changes in the absorption spectrum during the increase in ionization are difficult to correct. Another difficulty that might appear is the structural change of the indicator, during or after protonation. The change in temperature, however, has been shown in the H_2SO_4–H_2O system to have little effect on the H_0 value,[34] but the pK_{BH^+} and the ionization ratios are more sensitive.

The pK_{BH^+} value is easy to determine, when the ionization ratio can be measured in dilute aqueous solution [Eq. (1.25)].

$$pK_{BH^+} = \mathrm{limit}_{(HA \to 0)} \log \frac{[BH^+]}{[B]} - \log[H_3O^+] \qquad (1.25)$$

It is to be noted that when the acid solution is very dilute, the presence of the indicator modifies the acidity: $[H_3O^+] = [HA] - [B]$, and thus the concentration of the indicator has to be taken into account.

As is apparent from Eq. (1.14), an indicator is only useful over an acidity range where its ionization ratio can be measured experimentally with sufficient precision. For spectrophotometric method, this means approximately 2 log units per indicator. Accordingly, the direct determination of the pK_{BH^+} value of an indicator in concentrated solution is not possible. It is actually achieved by the method developed by Hammett in his early work using a series of indicators of overlapping range.[8] Taking into account the overlapping of each indicator with the preceding and the following one, each of which is useful for 2 log units, it appears that several indicators are necessary (approximately as many indicators as the number of desired log units). This is illustrated in Figure 1.4.

Paul and Long[35] have tabulated pK_{BH^+} values for indicators, which were used to establish Hammett acidity functions for aqueous acids between the years 1932 and 1957. The data were summarized as a set of "best values" of pK_{BH^+} for the bases. Since then, subsequent work seems to suggest that some of these values are incorrect. This is particularly the case for some of the weaker bases whose quoted pK_{BH^+} were based on a stepwise extrapolation of results of some indicators that have since been proven to be unsatisfactory based on the strict definition of H_0. These data, as well as those for weaker bases that have been studied since, covering the whole acidity range from dilute acid to the superacid media are collected in Table 1.1.

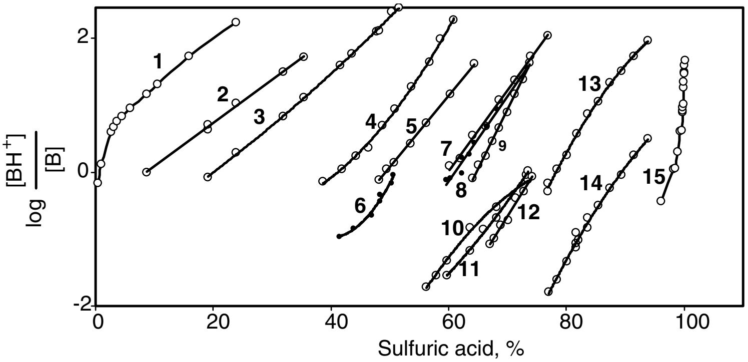


Figure 1.4. The ionization ratio as measured for a series of indicators in the 0–100% H_2SO_4–H_2O system.[8]

Up to a H_0 value of -10, all indicators are primary amines and are therefore suitable for the measurement of the Hammett H_0 function. For stronger acids, new indicators such as nitro compounds have to be used. Although the acidity function scale based upon nitro compounds as indicators may not be a satisfactory extension of the aniline indicator scale, Gillespie and Peel[18] have shown that the most basic nitro compound indicator, *para*-nitrotoluene overlaps in a satisfactory manner with the weakest indicator in the aniline series, 2,4,6-trinitroaniline. Thus, the acidity measurements using the nitro compounds may be considered to give the best semiquantitative picture of the acidity of the various superacid systems.

UV spectroscopy of adsorbed Hammett bases has also been used to estimate the acidity of solids such as zeolites.[38]

1.4.2. Nuclear Magnetic Resonance Methods

NMR spectroscopy, which was developed in the late 1950s as a most powerful tool for structural analysis of organic compounds, has also proven to be useful for acidity determinations. The measurement of the ionization ratio has been achieved by a variety of methods demonstrating the versatility of this technique. If we consider the general acid–base equilibrium Eq. (1.26) obtained when the indicator B is dissolved in the strong acid HA, then k_p, and k_d, respectively, are the rates of protonation and deprotonation.

$$\mathrm{HA} + \mathrm{B} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{BH}^+ + \mathrm{A}^- \tag{1.26}$$

The thermodynamic equilibrium constant K is related to these rates according to Eq. (1.27).

$$K = \frac{[\mathrm{BH}^+][\mathrm{A}^-]}{[\mathrm{HA}][\mathrm{B}]} = \frac{k_p}{k_d} \tag{1.27}$$

Table 1.1. Selected pK_{BH^+} Values for Extended Hammett Bases

Base	pK_{BH^+}	References
3-Nitroaniline	2.50	35
2,4-Dichloroaniline	2.00	35
4-Nitroaniline	0.99	35
2-Nitroaniline	−0.29	35
4-Chloro-2-nitroaniline	−1.03	35
5-Chloro-2-nitroaniline	−1.54	14
2,5-Dichloro-4-nitroaniline	−1.82	36
2-Chloro-6-nitroaniline	−2.46	36
2,6-Dichloro-4-nitroaniline	−3.24	36
2,4-Dichloro-6-nitroaniline	−3.29	35
2,6-Dinitro-4-methylaniline	−4.28	35
2,4-Dinitroaniline	−4.48	35
2,6-Dinitroaniline	−5.48	36
4-Chloro-2,6-dinitroaniline	−6.17	36
6-Bromo-2,4-dinitroaniline	−6.71	35
3-Methyl-2,4,6-trinitroaniline	−8.37	36
3-Bromo-2,4,6-trinitroaniline	−9.62	36
3-Chloro-2,4,6-trinitroaniline	−9.71	36
2,4,6-Trinitroaniline	−10.10	18,19
para-Nitrotoluene	−11.35	18,19
meta-Nitrotoluene	−11.99	18,19
Nitrobenzene	−12.14	18,19
para-Nitrofluorobenzene	−12.44	18,19
para-Nitrochlorobenzene	−12.70	18,19
meta-Nitrochlorobenzene	−13.16	18,19
2,4-Dinitrotoluene	−13.76	18,19
2,4-Dinitrofluorobenzene	−14.52	18,19
2,4,6-Trinitrotoluene	−15.60	18,19
1,3,5-Trinitrobenzene	−16.04	18,19
(2,4-Dinitrofluorobenzene)H^+	−17.57	18,19
(2,4,6-Trinitrotoluene)H^+	−18.36	37

In NMR spectroscopy, when a species (for example, here $[\mathrm{BH}^+]$) is participating in an equilibrium, its spectrum is very dependent on its mean lifetime (τ).[39,40] The inverse of the mean lifetime is a first-order rate constant, called the rate of exchange ($k = 1/\tau$), which can be obtained from the line-shape analysis of the NMR bands if $1\ \mathrm{s}^{-1} \leq k$ $10^3\ \mathrm{s}^{-1}$. Three cases can thus be envisaged:

1. "Slow Exchange" Conditions: $k \leq 10^{-2}\ \mathrm{s}^{-1}$. The species can be observed as if no exchange were taking place.
2. Measurable Exchange Conditions: $1\ \mathrm{s}^{-1} < k < 10^3\ \mathrm{s}^{-1}$. The rate of exchange can be calculated from the line-shape analysis of the NMR bands of the exchanging species.

3. “Fast Exchange” Conditions: $k > 10^4\ \mathrm{s}^{-1}$. The observed NMR bands appear as the weighted average of the species participating in the equilibrium.

Depending on these conditions, various NMR methods have been proposed and used to calculate the ionization ratio of weak bases in a superacid medium.

1.4.2.1. Chemical Shift Measurements. Under “slow-exchange” conditions, the ionization ratio cannot be measured. In fact, one of the major advantages of the superacidic media is the ease with which weak bases can be fully protonated and directly observed by NMR. Because it is known that the protonation rates are practically diffusion-controlled ($\sim 10^9$ liter mol^{-1} s^{-1}), under these conditions ($\leq 10^{-2}\ \mathrm{s}^{-1}$) the indicator is “totally” in the acidic form described by the NMR spectrum and no variable is available to measure the ionization ratio.

Under “fast-exchange” conditions, however, the NMR spectrum presents a weighed average of the bands of the exchanging species, and with the sensitivity limits ($\sim$5–95%) the ionization ratio can be measured taking the chemical shift as a variable. The calculation is simply based on the observed chemical shift of the average line (δ_{obs}), provided that the chemical shift of the base indicator (δ_{B}) and of its acid form ($\delta_{\mathrm{BH^+}}$) are known [Eq. (1.28)]. This is generally obtained by increasing or decreasing the acidity of the medium.

$$\delta_{\mathrm{obs}} = \frac{\delta_{\mathrm{BH^+}}[\mathrm{BH^+}] + \delta_{\mathrm{B}}[\mathrm{B}]}{[\mathrm{BH^+}] + [\mathrm{B}]} \qquad (1.28)$$

By plotting the chemical shift variation against the acidity, one observes a typical acid–base titration curve (Figure 1.5) and the $\mathrm{p}K_{\mathrm{BH^+}}$ of the indicator can be determined this way. This NMR method, which was first proposed by Grunwald et al.,[41] has been applied by Levy et al.[42] using various ketones and α-haloketones for the determination of ketone basicity and evaluation of medium acidity.

Compared with spectrophotometry, the NMR method has a number of advantages: (i) The procedure is very rapid, and it can be used by observing the variation of chemical shifts of diverse nuclei such as ^{1}H, ^{13}C, ^{19}F, and ^{17}O. (ii) It is insensitive to colored impurities and slight decomposition of the indicator. (iii) In principle, it can be used over the whole range of known acidity. The medium effect, which may be important in ^{1}H NMR, becomes negligible in the case of ^{13}C NMR spectroscopy. The method can be used with a wide variety of weak bases having a lone-pair containing heteroatoms as well as simple aromatic hydrocarbons.

However, because the measurement of the ionization ratio requires the presence of a minimum of 5% of one of the forms of the indicator, it necessitates the availability of a family of structurally similar compounds of varying basicity to cover a large domain of acidity. This condition has been met by Sommer and coworkers[22,43] using the *para*-methoxybenzhydryl cations as useful indicators for the strongest superacids.

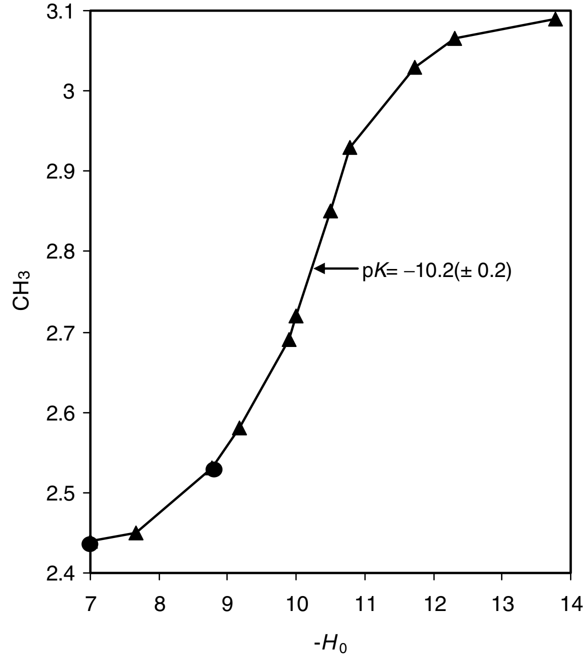
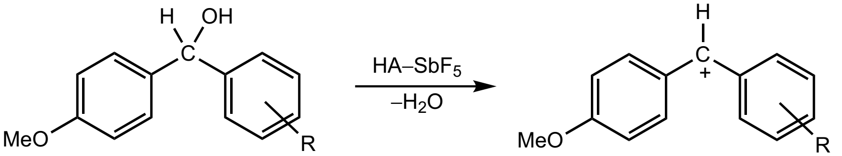
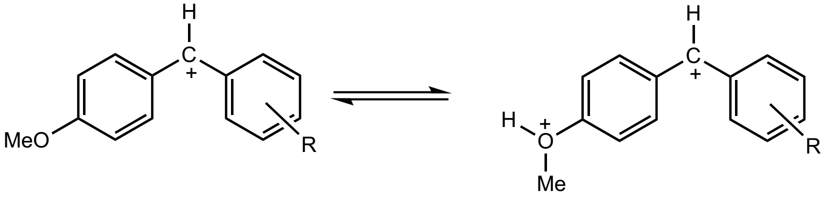


Figure 1.5. Acidity-dependent ^{1}H NMR chemical shift variations: protonation curve for acetaldehyde.[42] ● $CF_3COOH–H_2SO_4$, ▲ $CF_3COOH–CF_3SO_3H$.

The basicity of these indicators can be controlled by suitable substitution of the phenyl rings effecting ionization of the corresponding benzydrols [Eq. (1.29)]. The protonation equilibria [Eq. (1.30)] is measurable by ^{1}H or ^{13}C NMR spectroscopy.



(1.29)



R = **1**: 4'-MeO, **2**: 4'-Me, **3**: 4'-H, **4**: 4'-Br,
5: 4'-CF_3, **6**: 4'-$MeOH^+$

(1.30)

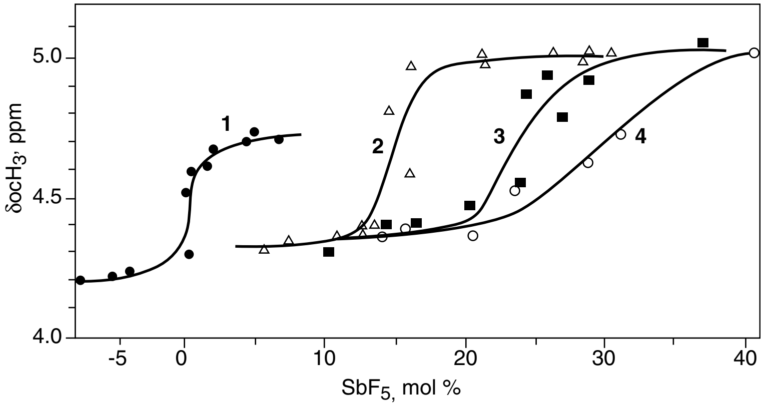


Figure 1.6. Protonation curves of indicators **1–4** in the $HSO_3F–SbF_5$ system.[22]

The protonation curves of indicators **1–4** in the HSO_3F-SbF_5 system (Figure 1.6) show how the decreasing basicity of the indicator necessitates an increasing amount of SbF_5 for half-protonation. The decreasing slope of the inflection point shows also that the increase in acidity by SbF_5 addition becomes smaller as more SbF_5 is added to the Brønsted acid (as a consequence of oligomeric anion formation).

The same indicators have been used to compare the relative acidity of the three most used superacids. As shown on Figure 1.7, the half-protonation of indicator **3** necessitates 40, 25, and 8 mol% SbF_5, respectively, in triflic acid, fluorosulfuric acid, and hydrogen fluoride systems. These results show the supremacy of the $HF–SbF_5$ system in which small concentrations of SbF_5 induce a dramatic increase in acidity (see also Section 2.2.2.7).

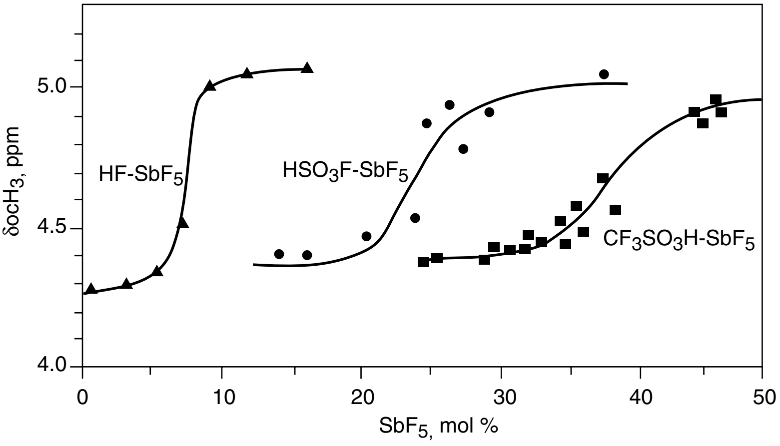


Figure 1.7. Protonation curves of indicator **3** in the superacid systems (from left to right) $HF–SbF_5$, $HSO_3F–SbF_5$, and $CF_3SO_3H–SbF_5$.[22]

1.4.2.2. Exchange Rate Measurements Based on Line-Shape Analysis (DNMR: Dynamic Nuclear Magnetic Resonance). Under the measurable exchange rate conditions, two possibilities have been considered:

1. The change in line shape can be directly related to the proton exchange.
2. The change in line shape is due to a separate exchange process related to the proton exchange.

Both methods have been exploited to determine ionization ratios.

Direct Exchange Rates. With the assumption that k_p is a constant over the range of measured acidity and k_{BH^+} of a series of overlapping bases remains measurable [Eq. (1.31)] (each base covering approximately 3 log units for a given concentration), Gold et al.[21] explored the acidity of the $HSO_3F–SbF_5$ system containing up to 90 mol% SbF_5. The highest acidity was estimated at $H_0 = -23$ approximately.[43]

$$H_0 = pK_{BH^+} - \log \frac{k_p \cdot [HA]}{k_{BH^+}} \tag{1.31}$$

Indirect Exchange Rates. In this case, the line shape is indirectly related to the acid-base equilibrium. Besides measuring intermolecular processes like the proton exchange rates, DNMR often has been used to measure intramolecular processes like conformational changes that occur on the same time scale. When the activation energy of such a process is very different in the acidic and basic forms for an indicator, DNMR can be used to measure the ionization ratio.

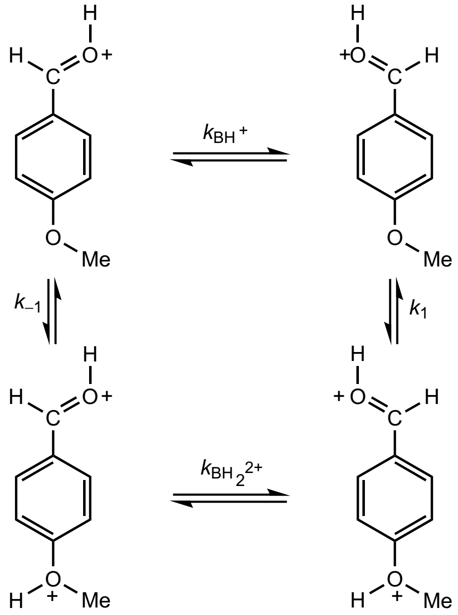
Due to a partial π-character, aromatic carbonyl compounds have an activation energy barrier for rotation around the phenyl–carbonyl bond, the value of which is substantially increased upon protonation.[44] In *para*-anisaldehyde a second protonation of the methoxy group will drastically decrease their barrier. The temperature-dependent NMR spectrum will reflect both exchange processes, intra- and intermolecular, as shown in Scheme 1.1.

A careful analysis of the NMR line shape provides the BH_2^{2+}/BH^+ ratio. Because of a large difference in activation energies between the rotation barriers in the mono- and diprotonated aldehyde, the observed rates are very sensitive to the concentration of BH^+. Thus ionization ratios of the order of 10^{-4} could be measured and approximately 4 log units of H_0 could be covered with the same indicator.[45]

By combining this method with the previously discussed chemical shift method, which is sensitive in the 0.05–20 range for the ionization ratio, the acidity could be measured over more than 5 H_0 units with the same indicator. Figure 1.8 shows the complementarity of both methods.

These are only approximate estimations, but are in reasonable agreement with more recent H_0 determination by other methods.[43]

Despite the evident advantages of the NMR methods, two points must be considered concerning the results of the acidity measurements. First, the concentration of the



Scheme 1.1.

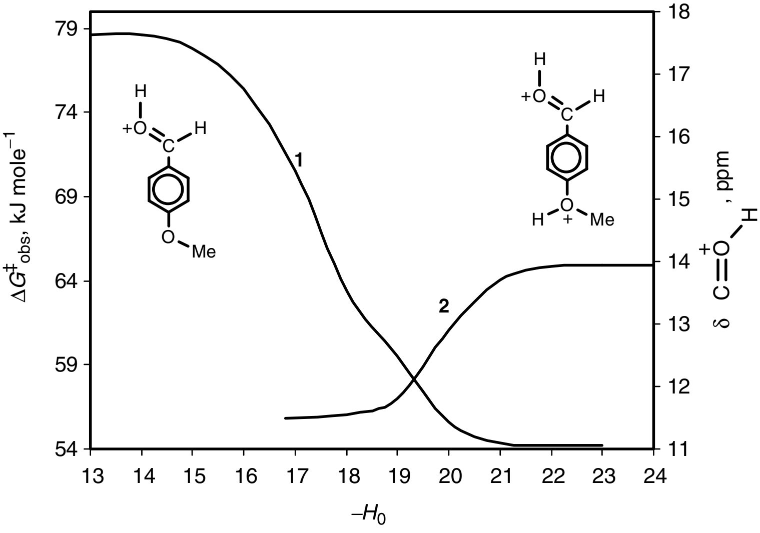


Figure 1.8. Complementarity of NMR methods in determining the variation of the acidity with the ionization of the indicator.[46] Curve **1:** line-shape analysis; curve **2:** chemical shift measurement.

indicator cannot be neglected as in the UV method, especially when the BH_2^{2+} is in low concentration. Second, aldehydes and ketones that have been generally used in the NMR methods are not true Hammett bases and the acidity that is derived should be considered only in a relative sense.

1.4.3. Electrochemical Methods

Electrochemistry provides a number of techniques for acidity measurements. The hydrogen electrode is the most reliable method in nonreducible solvents. It has been shown, however, that its reliability is limited to relatively weak acid solutions. A more general method was proposed by Strehlow and Wendt[47] in the early 1960s. They suggested a method to measure the potential variation of a pH-dependent system with respect to a reference system whose potential was solvent-independent. The measurement was made with a cell using $Pt/H_2/H_2O–H_2SO_4$, ferrocene–ferricinium (1:1)/Pt, containing sulfuric acid solution up to 100%. Strehlow defined an acidity function $R_0(H)$ [Eq. (1.32)], in which E_x and E_1 are the electromotive forces of the cell at proton activities x and unity, respectively.

$$R_0(\mathrm{H}) = \frac{F}{2.303RT} E_x - E_1 \tag{1.32}$$

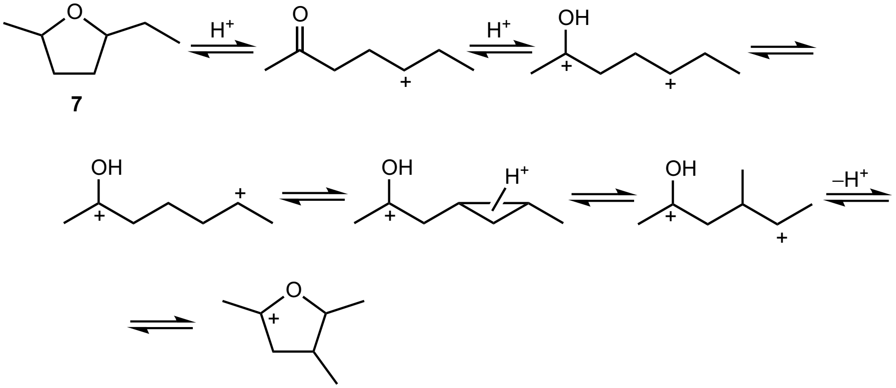
Like all the other acidity functions, $R_0(H)$ equals pH in dilute aqueous solution. In strong acids, this function should be a logarithmic measure of the proton activity as long as the normal potential of the redox system, ferrocene–ferricinium, is constant. This was, however, not the case in very strong acid solutions because ferrocene underwent protonation. Other electrochemical pH indicators have been proposed, such as quinine–hydroquinone or semiquinone–hydroquinone, the basicity of which can be modified by substitution on the aromatic ring. These electrochemical indicators have been used with success by Trémillon and co-workers[48] for acidity measurements in anhydrous HF and HF containing superacids.

In principle, the $R_0(H)$ function is of limited interest for kinetic applications because the indicators are chemically very different from the organic substrates generally used. On the other hand, as the measurements are based on pH determination, the length of the acidity scale is limited by the pK value of the solvents. However, very interesting electrochemical acidity studies have been performed in HF by Trémillon and co-workers, such as the acidity measurement in anhydrous HF solvent and the determination of the relative strength of various Lewis acids in the same solvent. By studying the variation of the potential of alkane redox couples as a function of acidity, the authors provide a rational explanation of hydrocarbon behavior in the superacid media.[48]

1.4.4. Chemical Kinetics

The idea that the acidity function may be useful in determining the rates of acid-catalyzed reactions was the main reason for development of the method first proposed by Hammett and Deyrup.[8] The parallelism between reaction rate and H_0 was noticed by Hammett in the early phase of his studies.[49] Especially when the protonation of the substrate parallels the protonation of the Hammett bases, the observed rate constant can be plotted versus $-H_0$ with unit slope. The validity of this principle for a large number of acid-catalyzed reactions and its limitation due to deviations in the protonation behavior has been reviewed extensively.[50] This method has also been applied to obtain a qualitative classification of the relative acidity of various superacid solutions.

Brouwer and van Doorn[51] used this approach in the early 1970s. In the NMR study of the interconversion rates of alkyl tetrahydrofuryl ions **7** and **8** (Scheme 1.2), proceeding via dicarbenium ion intermediates, they measured the overall rate of rearrangement in various superacid combinations of HF, HSO_3F, and SbF_5.



Scheme 1.2.

By making the assumption that the rates were only proportional to the concentration of the dication and taking into account the temperature dependence of the rate, they could estimate the relative acidity of these systems. By repeating these experiments with closely related reactions and varying the acid composition, they were able to estimate the relative acidity of 1:1 HF: SbF_5, 9:1 HF–SbF_5, 1:1 HSO_3F–SbF_5, and 5:1 HSO_3F–SbF_5 as $500:1:10^{-1}:10^{-5}$. These estimations have since been shown to be very approximate in comparison with the results obtained by other techniques. Moreover, rates can be affected by other factors than acidity such as solvation effects and temperature. Until now, however, no H_0 value has been measured for the 1:1 HF–SbF_5 medium.

The Friedel–Crafts acid systems HCl–$AlCl_3$ and HBr–$AlBr_3$ are widely used superacids of great practical significance, and various techniques have been used to rank Lewis acids such as $AlCl_3$ and $AlBr_3$ in strong Brønsted acids such as HSO_3F, CF_3SO_3H, HF, HBr, and HCl.[52,53] However, despite opposite claims, their acidity is lower than those of the fluoroacids discussed.

1.4.5. Heats of Protonation of Weak Bases

Arnett[54] had shown that several problems still exist in the currently available methods dealing with the behavior of weak bases in solution. For example, pK_A values of a wide variety of carbonyl compounds given in the literature vary over an unacceptably wide range. The variations are due not only to the activity coefficient problems, but also to practical difficulties such as the effect of media on position of the UV absorption peaks.[55] The previously discussed NMR method seems to alleviate these problems. An alternative method was proposed by Arnett and co-workers measuring the heats of protonation of number of weak bases in HSO_3F medium for which pK_A values are known from other methods. They found a good correlation of these heats of protonation with recorded pK_A values. The heat of protonation method has the advantage over the acidity function procedure that all measurements are made in the same solvent. These studies were applied to systems such as Magic Acid® ($HSO_3F–SbF_5$) but not extended to HF-based superacids.

1.4.6. Theoretical Calculations and Superacidity in the Gas Phase

The knowledge of acidities or basicities independent from solvation effects is of general interest to chemists because it gives important information on the solvent effects. It also allows the study of the intrinsic ability of the chemical structure of the acid or base to stabilize the anion/cations involved in the acid–base reaction and a quantitative structure–property relationship. In the last two decades, with the development of techniques of high-pressure mass spectrometry,[56] flowing afterglow,[57] and ion cyclotron resonance,[58] the study of ion–molecule reactions became possible in the gas phase. These techniques operating under very different conditions of pressure and time domain gave good agreement for the relative basicity measurements via proton transfer equilibria determination.

Extension of these studies in the superacid field has been reported,[59] which proposes a quantitative intrinsic superacidity scale for sulfonic acids based on measurement of the proton transfer equilibrium between the superacid and its conjugate base. The free energies (and enthalpies) of deprotonation (kcal mol^{-1}) have been estimated (within $\pm 2.5\ \text{kcal mol}^{-1}$) as follows: HPO_3 303 (311); H_2SO_4 302 (309); HSO_3F 300 (307); CF_3SO_3H 299 (306). These results show that the acidity order of the Brønsted superacids measured in the gas phase mirrors the acidity order found in solution. However, the method will be difficult to apply for measuring the large acidity domain of these acids when combined as usual with strong Lewis acids such as SbF_5.

Koppel et al.[60] have established a series of overlapping values of relative gas-phase acidities of a large number of very strong CH, OH, and SH Brønsted acids by using the pulsed FT ion cyclotron resonance (ICR) equilibrium constant method. The new intrinsic acidity scale covers a wide range from $(CF_3)_2NH$ ($\Delta G_{\text{acid}} = 324.3\ \text{kcal mol}^{-1}$) to $(C_4F_9SO_2)_2NH$ ($\Delta G_{\text{acid}} = 284.1\ \text{kcal mol}^{-1}$) and is anchored to the thermodynamic ΔG_{acid} value ($318.1\ \text{kcal mol}^{-1}$) of HBr. In several cases, the gas-phase acidity of compounds which make up the scale exceeds the acidity of such traditionally strong mineral acids as HCl, HBr, HI, or H_2SO_4 by more than 30 powers of 10. Based on these results, the acid $(C_4F_9SO_2)_2NH$ may be the strongest measured gas-phase superacid.

Subsequently, the development of both theoretical DFT methods and more sophisticated *ab initio* high-level MP2-type calculations has also spurred investigations in the superacid field.

Later, in another series of papers, Koppel et al.[61] used a theoretical approach at the G2 or G2(MP2) level/and also with the DFT method (B3LYP//6-311+G** level) to calculate the intrinsic acidities and gas-phase deprotonation enthalpies for 39 neutral strong or superstrong Brønsted acids, Brønsted–Lewis conjugate superacids, and even acidic cluster of zeolites. Comparison of the calculated gas-phase acidity with the H_0 values of the neat acid showed a fairly linear correlation. Similar DFT studies were carried out in calculating the Bronsted acidity of polycyanated hydrocarbons in the gas phase.[62]

ΔG values of deprotonation are as low as 249–250 kcal mol^{-1} for HSO_3F or HF associated with SbF_5 or SO_3. The strongest superacid was found to be dodecafluorocarborane acid $CB_{11}F_{12}H$ with a ΔG of 209 kcal mol^{-1} even suggesting that the dodeca(trifluoromethyl)carborane acid $CB_{11}(CF_3)_{12}H$ would be below the 200 kcal mol^{-1} level!

Mota and co-workers have investigated the nature of superacid electrophilic species in HF–SbF_5 by density functional theory[63] and measured the ability of the system to protonate light alkanes (methane, ethane, propane, and isobutane).[64]

More recently, Gutowski and Dixon[65] have recalculated [G3(MP2) theory] the intrinsic gas-phase acidities of a series of 21 Brønsted acids. The computed results are in excellent agreement with experimental gas-phase acidities in the range 342–302 kcal mol^{-1} to within < 1 kcal/mol for 14 out of 15 acids. However, acids with experimental acidities lower than 302 kcal mol^{-1} were found to have large deviations compared to the G3(MP2) results.

1.4.7. Estimating the Strength of Lewis Acids

A quantitative method to determine the strength of Lewis acids and to establish similar scales as discussed in the case of Brønsted acids would be very useful. However, establishing such a scale is extremely difficult and challenging. Whereas the Brønsted acid–base interaction always involves proton transfer, which allows a meaningful quantitative comparison, no such common relationship exists in the Lewis acid–base interaction. The result is that the definition of strength has no real meaning with Lewis acids.

The “strength” or “coordinating power” of different Lewis acids can vary widely against different Lewis bases. Thus, for example, in the case of boron trihalides, boron trifluoride coordinates best with fluorides, but not with chlorides, bromides, or iodides. In coordination with Lewis bases such as amines and phosphines, BF_3 shows preference to the former (as determined by equilibrium constant measurements).[66] The same set of bases behaves differently with the Ag^+ ion. The Ag^+ ion complexes phosphines much more strongly than amines. In the case of halides (F^-, Cl^-, Br^-, and I^-), fluoride is the most effective base in protic acid solution. However, the order is reversed in the case of Ag^+; iodide forms the most stable complex, whereas fluoride forms the least stable one.

The Lewis acidity with respect to strong bases such as NH_3 is greater for BCl_3 than for BF_3. In contrast, toward weak bases such as CO, BF_3 is a stronger acid than BCl_3.[67]

Despite the apparent difficulties, a number of qualitative relationships were developed to categorize Lewis acids.

Pearson proposed a qualitative scheme in which a Lewis acid and base is characterized by two parameters, one of which is referred to as strength and the other is called softness. Thus, the equilibrium constant for a simple acid–base reaction would be a function of four parameters, two for each partner. Subsequently, Pearson introduced the *hard* and *soft* acids and bases (HSAB) principle[68,69] to rationalize behavior and reactivity in a qualitative way. Hard acids correspond roughly in their behavior to class *a* acids as defined by Schwarzenbach[70] and Chatt.[66] They are characterized by small acceptor atoms that have outer electrons not easily excited and that bear considerable positive charge. Soft acids, which correspond to class *b* acids, have acceptor atoms with lower positive charge, large size, and easily excited outer electrons. Hard and soft bases are defined accordingly. Pearson's HSAB principle states that hard acids prefer to bind to hard bases while soft acids prefer to bind to soft bases. The principle has proven useful in rationalizing and classifying a large number of chemical reactions involving acid–base interactions in a qualitative manner,[71] but it gives no basis for a quantitative treatment.

There are many attempts made in the literature[72,73] to rate qualitatively the activity of Lewis acid catalysts in Friedel–Crafts-type reactions. However, such ratings largely depend on the nature of the reaction for which the Lewis acid catalyst is employed.

The classification of Lewis superacids as those stronger than anhydrous aluminum trichloride is only arbitrary. Just as in the case of Gillespie's classification of Brønsted superacids,[18,19] it is important to recognize that acids stronger than conventional Lewis acid halides exist with increasingly unique properties. Again the obvious difficulty is that reported sequences of Lewis acid strengths were established against widely varying bases. Still in applications such as ionizing alkyl halides to their corresponding carbocations, in heterocations systems, catalytic activity, and so on, Lewis acid halides such as SbF_5, AsF_5, TaF_5, and NbF_5, clearly show exceptional ability far exceeding those of $AlCl_3$, BF_3, and other conventional Lewis acid halides. Moreover, these super Lewis acid halides also show remarkable coordinating ability to Brønsted acids such as HF, HSO_3F, and CF_3SO_3H, resulting in vastly enhanced acidity of the resulting conjugate acids.

The determination of the strength of the Lewis acids MF_n, has been carried out in various solvents using the conventional methods. Numerous techniques have been applied: conductivity measurements,[74–79] cryoscopy,[80–83] aromatic hydrocarbon extraction,[53,84] solubility measurements,[85–87] kinetic parameters determinations,[52,88,89] electroanalytical techniques (hydrogen electrode),[90–93] quinones systems as pH indicators,[94–97] or other electrochemical systems,[98,99] IR,[100,101] and acidity function (H_0) determinations with UV–visible spectroscopy,[8,9,14,19,102–105] or with NMR spectroscopy.[20–22,44–46,106–108] Gas-phase measurements are also available.[109–111] Comparison of the results obtained by different methods shows large discrepancies (Table 1.2).

Table 1.2. Relative Strength of MF_n-Type Lewis Acids

Relative Strength	Solvent	Method	References
$BF_3 > TaF_5 > NbF_5 > TiF_4 > PF_5 > SbF_5 > WF_6 \gg SiF_4 \sim CrF_3$	HF	Xylene extraction by *n*-heptane	83
$SbF_5 > AsF_5$, $BF_3 > BiF_5 > TaF_5 > NbF_5 \gg SbF_3 \sim AlF_3 \sim CrF_3$	HF	Solubility and salt formation	85
SbF_5, $PF_5 > BF_3$	HF	Solubility	84
$SbF_5 > TaF_5 \sim NbF_5$	HF	Conductivity and H_0 determination	74
$SbF_5 > AsF_5 \gg PF_5$	HF	Conductivity and cryoscopy	79
$TaF_5 > SbF_5 > BF_3 > TiF_4 > HfF_4$	HF	Reactions/rates parameter selectivity	52
$OsF_5 > ReF_5 > TaF_5 > MoF_5 > NbF_5 \gg MoF_4$	HF	Conductivity and Raman spectra	81
$SbF_5 > TaF_5 > BF_3 > SO_3$	HF	Potentiometry (quinones)	95
$AsF_5 > TaF_5 > BF_3 > NbF_5 > PF_5$	HF	Potentiometry (hydrogen electrodes)	89
$SbF_5 > BF_3$	HF	Infrared spectra	99
$SbF_5 > AsF_5 > SO_3$	HSO_3F	H_0 determination	19
$SbF_5 > BiF_5 > AsF_5 \sim TiF_4 > NbF_5 \sim PF_5$	HSO_3F	Conductivity	75
$SbF_5 > AsF_5 > BF_3 > PF_5$	HSO_3F	Infrared spectra	100
$AsF_5 > BF_3 > PF_5 > SF_4$, SF_5	CH_2Cl_2	^{19}F NMR	105
$BF_3 > TaF_5$	Toluene	^{19}F NMR	106
$SbF_5 > AsF_5 > TaF_5 > NbF_5 > BF_3$	Toluene	Conductivity and cryoscopy of SeF_4–MF_n	80
$SbF_5 > AsF_5 > BF_3 > PF_5$	Gas phase	Complexing with F_3NO	108
$AsF_5 > PF_5 > BF_3 > SiF_4 > AsF_3$	Gas phase	Reaction rates: $SF_6^- + MF_n \rightarrow MF_{n+1}^- + SF_5^{\bullet}$	109
$BF_3 > SiF_4 > PF_5 > PF_3$	Gas phase	Affinity measurements for F^-	110

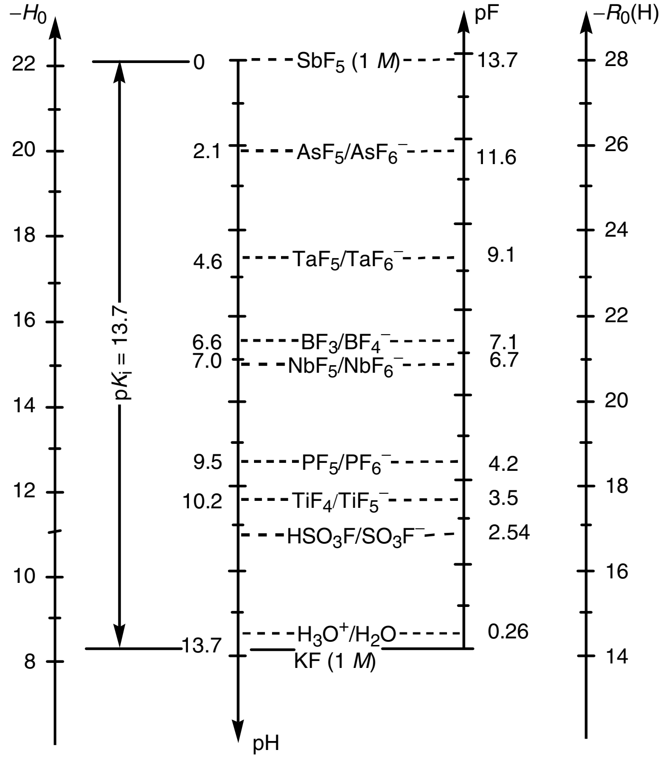


Figure 1.9. Relative strength of some strong Lewis acids as measured in HF on the pH scale by electrochemical titration.[48]

The acidity scale in anhydrous hydrogen fluoride has been the subject of electrochemical investigations by Trémillon and coworkers[48] and is presented in Figure 1.9. The figure also indicates the acidity constants of various Lewis acids allowed to buffer the medium to a pH value as calculated by Eq. (1.33), or in dilute solution by Eq. (1.34).

$$\mathrm{pH} = \mathrm{p}K_\mathrm{A} - \log \frac{{}^{a}\mathrm{MF}_n}{{}^{a}\mathrm{MF}_{n+1}} \qquad (\mathrm{p}K_A = -\log K_A) \tag{1.33}$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{A} - \log \frac{[\mathrm{MF}_n]}{[\mathrm{MF}_{n+1}]} \tag{1.34}$$

In hydrogen fluoride, the Lewis acid strength is in the following decreasing order: $SbF_5 > AsF_5 > TaF_5 > BF_3 > NbF_5$.

As in all areas, the theoretical tools developed in the last decade was also used to address this question. A theoretical approach with the semiempirical MNDO method

Table 1.3. Abbreviated pF^- Scale[26]

Compound	pF^-	Compound	pF^-
SbF_5	12.03	ClF_5	7.47
AlF_3	11.50	BrF_3	7.35
$AlFCl_2$	11.50	SiF_4	7.35
AlF_2Cl	11.47	SeF_4	7.12
$AlCl_3$	11.46	SOF_4	6.60
$TeOF_4$	10.79	$XeOF_4$	6.37
InF_3	10.75	TeF_6	6.15
GaF_3	10.70	POF_3	5.86
AsF_5	10.59	XeF_4	5.71
SnF_4	9.82	SF_4	5.67
cis-IO_2F_3	9.66	COF_2	4.99
PF_5	9.49	PF_3	4.49
$SeOF_4$	8.69	HF	3.68
TeF_4	8.34	NO_2F	1.92
BF_3	8.31	NOF	1.74
GeF_4	8.30		

combined with ^1H NMR chemical shift measurements has also been used to compare the relative acidity of 18 Lewis acids complexing crotonaldehyde.[73] However, this scale does not completely agree with the pF scale determined in HF solution by electrochemical titration (Figure 1.9).

More recently, a quantitative scale for Lewis acidity based on fluoride ion affinities was calculated using *ab initio* calculations at the MP2/B2 level of theory.[26] Due to its high basicity and small size, the fluoride ion reacts essentially with all Lewis acids; thus the fluoride affinity (or reaction enthalpy) may be considered as a good measure for the strength of a Lewis acid. An abbreviated pF^- scale is given in Table 1.3. This scale was used recently by Christe and Dixon[112] for estimating the stability of salts of complex fluoro anions and cations. The pF value represents the fluoride affinity in $kcal\,mol^{-1}$ divided by 10.

1.4.8. Experimental Techniques Applied to Solid Acids

Since solid acid catalysts are used extensively in chemical industry, particularly in the petroleum field, a reliable method for measuring the acidity of solids would be extremely useful. The main difficulty to start with is that the activity coefficients for solid species are unknown and thus no thermodynamic acidity function can be properly defined. On the other hand, because the solid by definition is heterogeneous, acidic and basic sites can coexist with variable strength. The surface area available for colorimetric determinations may have widely different acidic properties from the bulk material; this is especially true for well-structured solids like zeolites. It is also not possible to establish a true acid–base equilibrium.

Moreover, the accessibility of sites causes discrepancies in the different methods and to measure the acidity of solids. Because several reviews on this subject have been published in recent years,[27–29] we will just illustrate this problem with sulfated zirconia (SZ), probably the most studied single catalyst in the last 20 years.

SZ was claimed to be a solid superacid by Hino and Arata[113] in 1980 on the basis of its ability to isomerize *n*-butane at low temperature. Since then, various authors using all experimental techniques available tried to verify the superacidity character. Whereas the color change of Hammett indicators suggested a value of -14 to -16 on the H_0 scale,[114] the use of these indicators is considered invalid for surface acidity measurements. The color change of the indicators used (in the $\mathrm{p}K_\mathrm{a}$ range of -10 to -16) is always from colorless to yellow; this makes the visual appreciation very subjective especially on catalysts, which are generally not colorless. Moreover, the change in color may be due to sites able to transfer electrons to the aromatic ring of the indicators, and also Brønsted and Lewis sites may both contribute.

On the basis of less subjective UV spectroscopy using the same indicators, Hall and co-workers[38] concluded that neither SZ nor zeolites (such as HY, HZSM-5, and H-MOR) were superacids. However, on the basis of ^{1}H NMR spectroscopy and Raman spectroscopy, Knözinger and co-workers[115]suggested that superacidic protons were present on SZ; but here again, chemical shifts that depend on various factors should not be directly related to acidity. Early EPR studies by Vedrine and co-workers[116] have shown the formation of charge transfer complexes with benzene followed by the formation of radical cations. Since benzene has a high ionization potential, their observation was interpreted as being very probably due to strong Lewis acidity.

On the basis of its catalytic activity in isobutane conversion, this catalyst was described as zirconia-supported oleum,[117] but this hypothesis implies that the reaction mechanism is known, which is not the case. On the same basis, Fraenkel[118] suggested also that SZ was a very strong solid superacid.

In contrast, another ^{1}H NMR study suggested that the acidity was lower than that of zeolite HZSM-5.[119] Using a combination of solid-state NMR and theoretical methods, the same authors concluded on the nonsuperacidic character for SZ.[120] Similarly, CO adsorption experiments monitored by microcalorimetry and FT–IR concluded to a lower Brønsted acidity in comparison with H-zeolites[121] and showed that acidity is comparable to that of sulfuric acid.[122] On the basis of FT–IR analysis of adsorbed CO and acetonitrile, Sachtler and co-workers[123] arrived at the same conclusion and suggested that the exceptional activity of SZ can be attributed to its ability to stabilize transition states on the surface. According to a recent diffuse reflectance IR study, SZ does not exhibit higher acid strength than zeolites.[124]

Results of temperature-programmed desorption (TPD) of ammonia[125] or argon[126] were attributed to superacid sites. TPD of very weak bases such as substituted benzenes has been used successfully to compare the superacid character of a series of sulfate-treated mixed oxides.[127] However, the validity of TPD measurements and the results of IR study of adsorbed pyridine for acidity determinations have been questioned by various authors[128] as nonspecific to the acid site, considering that different probes may probe different sites providing only qualitative information and measure only an overall acidity. In fact the question whether the alleged superacidity is related to Brønsted or Lewis acid sites is still debated.

More recently, the reactivity of SZ has been assigned to its oxidizing ability,[129–131] which should not be surprising because it has often been considered as SO_3 adsorbed on zirconium oxide. However, that sulfated zirconia is not only an oxidant but also a strong protic acid has been demonstrated by Sommer, Walspurger, and co-workers[132] on the basis H/D exchange experiments with neopentane.

Concerning the acidity of zeolites, Koltunov et al.[133] have shown in a series of papers that reactions involving superelectrophiles could be achieved with excellent yields.

It appears that despite the lack of reliability of acidity determination of solid acids by spectroscopic means and in the absence of knowledge of the nature of the initial step in alkane activation by solid acids the qualification of superacid solids has been and continues to be used, despite the absence of a clear definition of solid superacidity.

Considering the impressive amount of literature on sulfated zirconia and solid superacids,[125,134–139] it will be difficult to impose a definition a posteriori. On the other hand, due to the large difference in acidity and in structure between various liquid superacids, there is no unique chemistry of hydrocarbons in liquid superacids. For this reason it is not possible to suggest a unequivocal definition of solid superacidity at the present stage. Nevertheless, it seems clear from all the data presently available that at high temperatures the chemical reactivity of the proton bound to the surface shows a close resemblance to the one observed at low temperature in liquid superacidic media as will be seen in Chapter 5.

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