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# **SUPERACID CHEMISTRY**

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**SECOND EDITION**

George A. Olah  
G. K. Surya Prakash  
Árpád Molnár  
Jean Sommer



**WILEY**

A John Wiley & Sons, Inc., Publication



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*In memory of Katherine Bogdanovich Loker, Benefactor and Friend*





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## **PREFACE TO THE SECOND EXTENDED AND UPDATED EDITION**

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More than 20 years passed since the publication of our book on Superacids. The book became out of print and much progress since was made in the field, which is gaining increasing interest and significance. Hence, it seems warranted to provide the interested reader with a comprehensively updated review and discussion of the field with literature coverage until early 2008. The title has been changed to “Superacid Chemistry” to reflect enormous progress in the field. Some aspects of superelectrophilic activation are also discussed (for more elaborate coverage, readers are referred to G. A. Olah and D. A. Klump, “Superelectrophiles and Their Chemistry” Wiley-Interscience, 2008). Our friend and colleague, Árpád Molnár joined us as a coauthor and made an outstanding contribution to the revised new edition of our book, which we hope will be of interest and use to the chemical community. Our publisher is thanked for arranging the new revised edition.

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October 2008



## PREFACE TO THE FIRST EDITION

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The chemistry of superacids, that is, of acid systems stronger than conventional strong mineral Brønsted acids such as sulfuric acid or Lewis acids like aluminum trichloride, has developed in the last two decades into a field of growing interest and importance. It was J. B. Conant who in 1927 gave the name “superacids” to acids that were capable of protonating certain weak bases such as carbonyl compounds and called attention to acid systems stronger than conventional mineral acids. The realization that Friedel–Crafts reactions are, in general, acid catalyzed with conjugate Lewis–Brønsted acid systems frequently acting as the de facto catalysts extended the scope of acid catalyzed reactions. Friedel–Crafts acid systems, however, are usually only  $10^3$  to  $10^6$  times stronger than 100% sulfuric acid. The development in the early 1960s of Magic Acid, fluoroantimonic acid, and related conjugate superacids,  $10^7$  to  $10^{10}$  times stronger than sulfuric acid, added a new dimension to and revival of interest in superacids and their chemistry. The initial impetus was given by the discovery that stable, long-lived, electron-deficient cations, such as carbocations, acidic oxonium ions, halonium ions, and halogen cations, can be obtained in these highly acidic systems. Subsequent work opened up new vistas of chemistry and a fascinating, broad field of chemistry is developing at superacidities. Because acidity is a term related to a reference base, superacidity allows extension of acid-catalyzed reactions to very weak bases and thus extends, for example, hydrocarbon chemistry to saturated systems including methane.

Some years ago in two review articles (*Science* 206, 13, 1979; *La Recherche* 10, 624, 1979), we briefly reviewed some of the emerging novel aspects of superacids. However, we soon realized that the field was growing so fast that to be able to provide a more detailed survey for the interested chemist a more comprehensive review was required. Hence, we welcomed the suggestion of our publisher and Dr. Theodore P. Hoffman, chemistry editor of Wiley-Interscience, that we write a monograph on superacids.

We are unable to thank all of our friends and colleagues who directly or indirectly contributed to the development of the chemistry of superacids. The main credit goes to all researchers in the field whose work created and continues to enrich this fascinating area of chemistry. Professor R. J. Gillespie's pioneering work on the inorganic chemistry of superacids was of immense value and inspiration to the development of the whole field. Our specific thanks are due to Drs. David Meidar and Khosrow Laali, who helped with the review of solid superacid systems and their reactions. Professor E. M. Arnett is thanked for reading part of our manuscript and for his thoughtful comments.

Finally we would like to thank Mrs. R. Choy, who tirelessly and always cheerfully typed the manuscript.

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# General Aspects

## 1.1. DEFINING ACIDITY

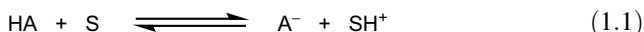
### 1.1.1. Acids and Bases

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  $1s$  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  $1s$  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.<sup>1,2</sup>

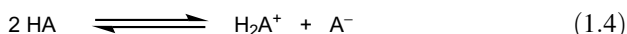
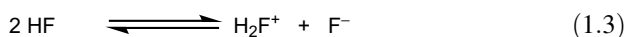
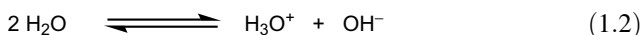
The first clear definition of acidity can be attributed to Arrhenius, who between 1880 and 1890 elaborated the theory of ionic dissociation in water to explain the variation in strength of different acids.<sup>3</sup> Based on electrolytic experiments such as conductance measurements, he defined acids 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.<sup>4</sup> He defined an acid as a species that can donate a proton and defined a base as a species that can accept it. This

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)].



The ionization of the acid HA in solvent S leads to a new acid  $\text{HS}^+$  and a base  $\text{A}^-$ . 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,  $\text{H}_2\text{O}$  is the conjugate base of the acid  $\text{H}_3\text{O}^+$ . 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).

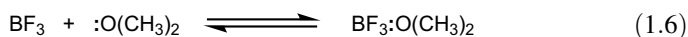


This equilibrium is characterized by the autoprotolysis constant  $K_{\text{ap}}$ , which under the usual high dilution conditions can be written as in Eq. (1.5).

$$K_{\text{ap}} = [\text{H}_2\text{A}^+][\text{A}^-] \quad (1.5)$$

Indeed the extent of dissociation of the solvent is very small (in HF,  $K_{\text{ap}} \approx 10^{-11}$ ; in  $\text{H}_2\text{O}$ ,  $K_{\text{ap}} = 10^{-14}$ ). The  $\text{p}K_{\text{ap}}$  value that gives the acidity range will be discussed later.

G.N. Lewis extended and generalized the acid–base concept to nonprotonic systems.<sup>5,6</sup> 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  $\text{BF}_3$  or carbocations, whereas Lewis bases are molecules that contain readily available nonbonded electron pairs (as in ethers, amines, etc.) [Eq. (1.6)].



Of course, in a generalized way, the proton  $\text{H}^+$  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  $[\text{H}_2\text{A}^+]$  and define a base as any substance that will increase  $[\text{A}^-]$  and thus decrease  $[\text{H}_2\text{A}^+]$ . 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.

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

It was Sørensen's idea<sup>7</sup> 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.

$$\text{pH} = -\log[\text{HS}^+] \quad (1.8)$$

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.

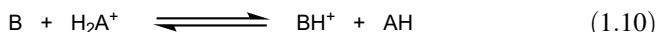
$$\text{pH} = -\log_{10}(a_{H^+}) \quad (1.9)$$

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  $\text{p}K_{\text{ap}} = \text{p}(\text{H}_2\text{A}^+) + \text{p}(\text{A}^-)$ . Thus, the range of pH ( $\Delta\text{pH}$ ) is  $\text{p}K_{\text{ap}}$  (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.

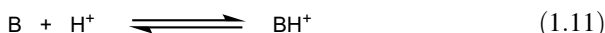
### 1.1.3. Acidity Functions

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<sup>8</sup> 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).



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).



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.

$$K_{BH^+} = \frac{a_{H^+} \cdot a_B}{a_{BH^+}} = \frac{a_{H^+} \cdot C_B}{C_{BH^+}} \cdot \frac{f_H}{f_{BH^+}} \quad (1.12)$$

From this equation, Eq. (1.13) follows.

$$\frac{C_{BH^+}}{C_B} = \frac{1}{K_{BH^+}} \cdot a_{H^+} \cdot \frac{f_B}{f_{BH^+}} \quad (1.13)$$

Because the first ratio represents the degree of protonation, Hammett and Deyrup<sup>8,9</sup> defined the acidity function  $H_0$  by Eq. (1.14).

$$H_0 = -\log a_{H^+} \cdot \frac{f_B}{f_{BH^+}} = -\log K_{BH^+} + \log \frac{C_B}{C_{BH^+}} \quad (1.14)$$

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

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \quad (1.15)$$

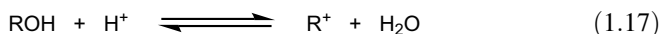
From Eq. (1.14) it is clear that in dilute aqueous solution, as the activity coefficients tend to unity, the Hammett acidity function becomes identical with pH. On the other hand, by making the fundamental assumption that the ratio  $f_B/f_{BH^+}$  is the same for different bases in a given solution, 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  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  system using a series of primary anilines as indicators. By starting with the strongest base  $\text{B}_1$ , the  $\text{p}K_{\text{B}_1\text{H}^+}$  was measured in dilute aqueous solution. The  $\text{p}K$  of the next weaker base  $\text{B}_2$  was then determined by measuring the ionization ratio of the two indicators in the same acid solution using the relation of Eq. (1.16).

$$\text{p}K_{\text{B}_1\text{H}^+} - \text{p}K_{\text{B}_2\text{H}^+} = \log \frac{[\text{B}_1\text{H}^+]}{[\text{B}_1]} - \log \frac{[\text{B}_2\text{H}^+]}{[\text{B}_2]} \quad (1.16)$$

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 ( $\text{p}K = 1.40$ ) and the weakest trinitroaniline ( $\text{p}K = -9$ ), Hammett explored the whole  $\text{H}_2\text{O-H}_2\text{SO}_4$  range up to 100% sulfuric acid and the perchloric acid-water solution up to 60% of acid. Similar acidity functions such as  $\text{H}_-, \text{H}_+, \text{H}_{2+}$  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  $\log [\text{BH}^+]/[\text{B}]$  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  $\log [\text{BH}^+]/[\text{B}]$  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).

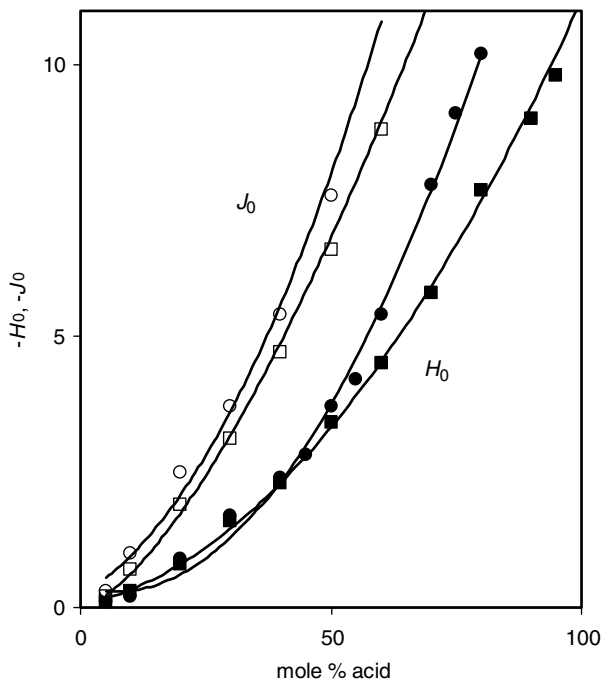


The corresponding acidity function described as  $H_{\text{R}}$  is then written in Eq. (1.18).

$$H_{\text{R}} = \text{p}K_{\text{R}^+} - \log \frac{[\text{R}^+]}{[\text{ROH}]} \quad (1.18)$$

This  $H_{\text{R}}$  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.<sup>1,10-14</sup>



**Figure 1.1.**  $H_0$  and  $J_0$  functions for  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{HClO}_4\text{-H}_2\text{O}$  systems.  $\text{HClO}_4$ :  $\circ$ , ref. 11;  $\bullet$ , ref. 13;  $\text{H}_2\text{SO}_4$ :  $\square$ , ref. 12;  $\blacksquare$ , ref. 14.

$$H_x = \text{p}K_A - \log \frac{A}{B} \quad (1.19)$$

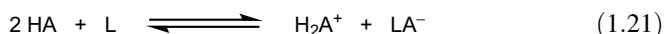
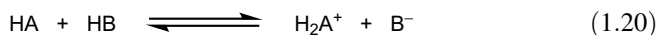
Whatever may be the limitations of the concept first proposed by Hammett and Deyrup in 1932<sup>8</sup> until now, no other widely used alternative has appeared to better assess quantitatively the acidity of concentrated and nonaqueous strongly acidic solutions.<sup>9</sup> The experimental methods that 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<sup>15</sup> 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  $\text{CH}_3\text{COOH}_2^+$ , a species less solvated than  $\text{H}_3\text{O}^+$  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.<sup>16,17</sup> Subsequently, Gillespie proposed an arbitrary but since widely accepted definition of superacids,<sup>18,19</sup> 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)].



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  $\text{HSO}_3\text{F}$ .

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  $\text{HSO}_3\text{F}$  as solvent.

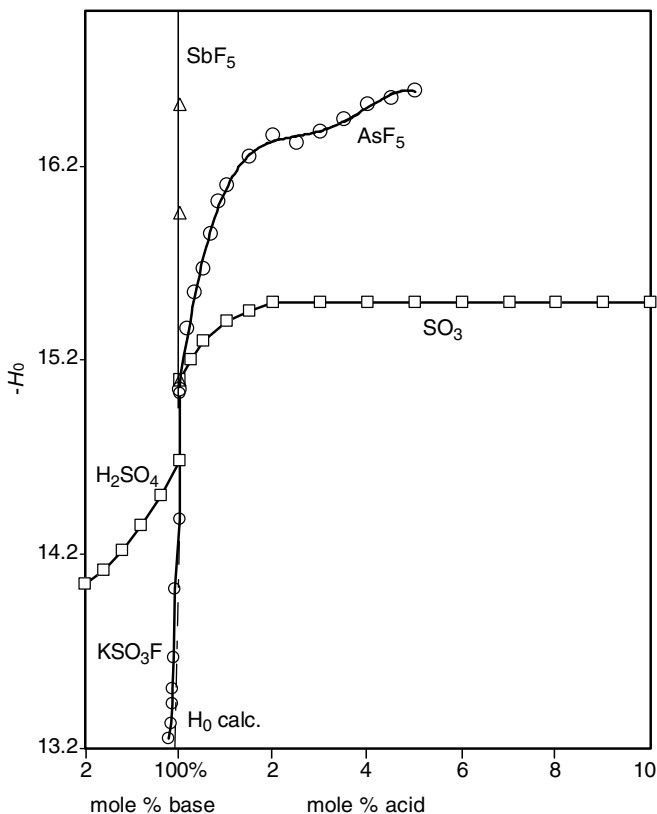
Gillespie’s definition of superacids relates to Brønsted acid systems. Because Lewis acids also cover a wide range of acidities extending beyond the strength of conventionally used systems, Olah suggested the use of anhydrous aluminum chloride as the arbitrary reference and we categorize Lewis superacids as those stronger than aluminum chloride<sup>17</sup> (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,<sup>20</sup> 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  $\text{HSO}_3\text{F}\text{--SbF}_5$  mixture containing 90 mol%  $\text{SbF}_5$ .<sup>21</sup> In fact, the  $\text{HF}\text{--SbF}_5$  is considered one of the strongest superacid system based on



**Figure 1.2.** Acidity increase near the  $H_0$  value of neat  $\text{HSO}_3\text{F}$ .<sup>19</sup>

various measurements. Meanwhile, however, Sommer and coworkers found that the weakest basic indicator of the *para*-methoxybenzhydryl cation family (4,4'-dimethoxy;  $\text{p}K_{\text{BH}^+} \sim -23$ ) could not be diprotonated even in the strongest  $\text{HF-SbF}_5$  acid.<sup>22</sup> 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 “ $\text{H}^+$ ” is not present in the condensed phase because even compounds as weakly basic as methane or even rare gases bind the proton.<sup>23,24</sup>

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.<sup>25,26</sup> Hence despite various attempts, the term “strength of Lewis acid” has no well-defined meaning.