

# **SUPERACIDS**

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# ≡ SUPERACIDS

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# ≡≡≡ PREFACE

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  $10^{19}$  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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# chapter 1

## GENERAL ASPECTS

### 1.1 DEFINING ACIDITY

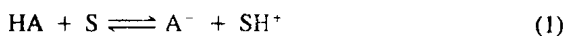
#### 1.1.1 Acids and Bases

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, i.e., 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</sup>

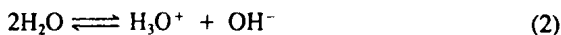
The first clear definition of acidity can be attributed to Arrhenius, who between 1880 and 1890 elaborated the theory of ionic dissociation in water to explain the

variation in strength of different acids.<sup>2</sup> Based on electrolytic experiments such as conductance measurement, he defined acids as substances that dissociate in water and yield the hydrogen ion whereas bases dissociate to yield hydroxide ion. In 1923 J. N. Brønsted generalized this concept to other solvents.<sup>3</sup> He defined an acid as a species that can donate a proton and 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.



The ionization of the acid HA in solvent S leads to a new acid HS<sup>+</sup> and a base A<sup>-</sup>. Equation (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<sub>2</sub>O is the conjugate base of the acid H<sub>3</sub>O<sup>+</sup>. 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 both with respect to the reference point and to 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, for example,



and, in a general way,

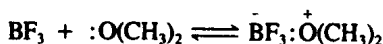


This equilibrium is characterized by the autoprotolysis constant  $K_{\text{ap}}$ , which under the usual high dilution conditions can be written as the following:

$$K_{\text{ap}} = [\text{H}_2\text{A}^+][\text{A}^-] \quad (5)$$

Indeed the extent of dissociation of the solvent is very small (in HF,  $K_{\text{ap}} \sim 10^{-11}$ ; in H<sub>2</sub>O,  $K_{\text{ap}} = 10^{-14}$ ). The p $K_{\text{ap}}$  value that gives the acidity range will be discussed later.

It was G. N. Lewis who extended and generalized the acid-base concept to nonprotonic systems.<sup>4</sup> He defined an acid as a substance that can accept electrons and a base as a substance that can donate electrons. Lewis acids are electron-deficient molecules or ions such as BF<sub>3</sub> or carbocations, whereas Lewis bases are molecules that contain readily available nonbonded electron pairs (as in ethers, amines, etc.)



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 (4) for the autoionization of solvent HA, one can define an acid as any substance that will increase  $[H_2A^+]$  and 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 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 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, wherein  $C$  is a constant.

$$E = C - \frac{RT}{F} \log_{10} (a_{H^+}) \quad (6)$$

It was Sørensen's<sup>5</sup> idea 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 equation:  $pH = -\log [HS^+]$ . Depending on the dilution, the proton can be further solvated by two or more solvent molecules.

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  $pH = -\log_{10} (a_{H^+})$  cannot be definitely established for any solution. 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 (Equation 5), as the minimum value of pH in a solution is zero and the maximum value is  $pK_{ap}$ ;  $pK_{ap} = p(HA_2^+) + p(A^-)$ . Thus, the range of pH ( $\Delta pH$ ) is  $pK_{ap}$  (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 The Acidity Functions

Considering the limited application 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>6a</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 follows:



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



The corresponding thermodynamic equilibrium constant is  $K_{BH^+}$ , which is expressed as

$$K_{BH^+} = \frac{a_{H^+} \cdot a_B}{a_{BH^+}} = \frac{a_{H^+} \cdot C_B}{C_{BH^+}} \cdot \frac{f_B}{f_{BH^+}} \quad (9)$$

in which  $a$  is the activity,  $C$  the concentration, and  $f$  the activity coefficient. From this equation, it follows that

$$\frac{C_{BH^+}}{C_B} = \frac{1}{K_{BH^+}} \cdot a_{H^+} \cdot \frac{f_B}{f_{BH^+}} \quad (10)$$

As the first ratio represents the degree of protonation, Hammett and Deyrup<sup>6</sup> defined the acidity function  $H_0$  by

$$H_0 = -\log a_{H^+} \cdot \frac{f_B}{f_{BH^+}} = -\log K_{BH^+} + \log \frac{C_B}{C_{BH^+}} \quad (11)$$

which can be written for further discussion in the more usual form:

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \quad (12)$$

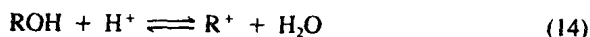


From Equation (11) it is clear that in dilute aqueous solution, as the activity coefficients tend to unity, the Hammett acidity function becomes identical with pH. On the other hand, by making the fundamental assumption that the ratio  $f_B/f_{BH^+}$  is the same for different bases in a given solution, 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  $H_2SO_4$ - $H_2O$  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

$$pK_{B_1H^+} - pK_{B_2H^+} = \log \frac{[B_1H^+]}{[B_1]} - \log \frac{[B_2H^+]}{[B_2]} \quad (13)$$

The ionization ratio was measured by uv-visible spectroscopy. With the help of successively weaker primary aromatic amine indicators, the strongest base being *p*-nitroaniline ( $pK = 1.40$ ) and the weakest trinitroaniline ( $pK = -9$ ), 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 different basic sites 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



The corresponding acidity function described as  $H_R$  is then

$$H_R = pK_{R^+} - \log \frac{[R^+]}{[ROH]} \quad (15)$$

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