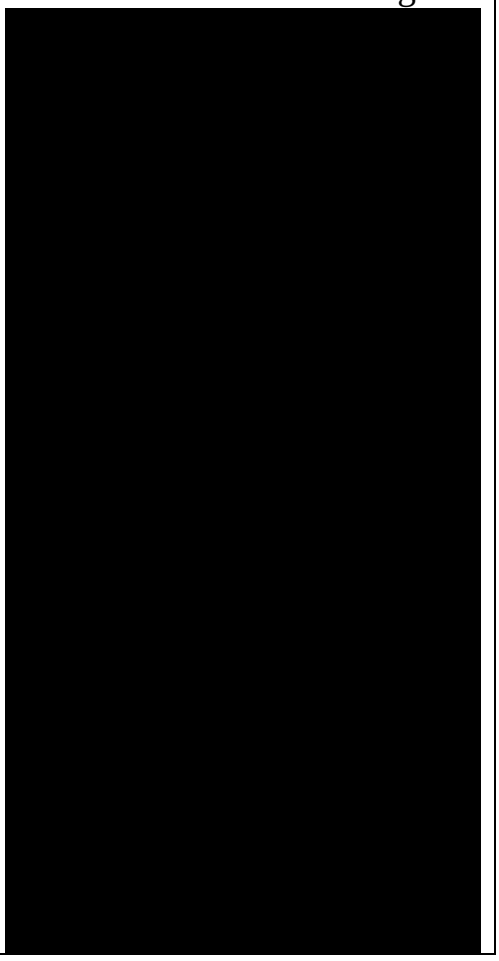
The chemistry of superacids, that is, of acid systems stronger than conventional strong mineral Brønsted acids such as sulfuric acid or Lewis acids like aluminum trichloride, has	1 h 38 Trong hai thập kỷ qua, hóa học siêu axit, tức là một hệ axit mạnh hơn các axit Brønsted vô cơ mạnh thông thường (chẳng hạn như axit sulfuric) hoặc axit Lewis (ví dụ như nhôm

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.	triclorua) đã phát triển thành một lĩnh vực nghiên cứu quan trọng và đầy sôi động. Chính J. B. Conant đã đặt tên cho axit có khả năng chuyển proton sang các bazơ yếu nhất định chẳng hạn như các hợp chất carbonyl là “siêu axit” và đã làm mọi người bắt đầu chú ý đến các hệ axit mạnh hơn axit vô cơ thông thường. Việc thực hiện thành công các phản ứng Friedel-Crafts xúc tác bằng hệ axit Lewis-Brønsted liên hợp (thường đóng vai trò là chất xúc tác tiêu chuẩn) đã mở rộng phạm vi của các phản ứng xúc tác bằng axit (đã tạo điều kiện để chúng ta có thể thực hiện nhiều phản ứng xúc tác bằng axit hơn). Tuy nhiên, các hệ axit Friedel-Crafts thường chỉ
Friedel-Crafts acid systems, however, are usually only 103 to 106 times stronger than 100% sulfuric acid. The development in the early 1960s of Magic Acid, fluoroantimonic acid, and related conjugate superacids, 107 to 1010 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

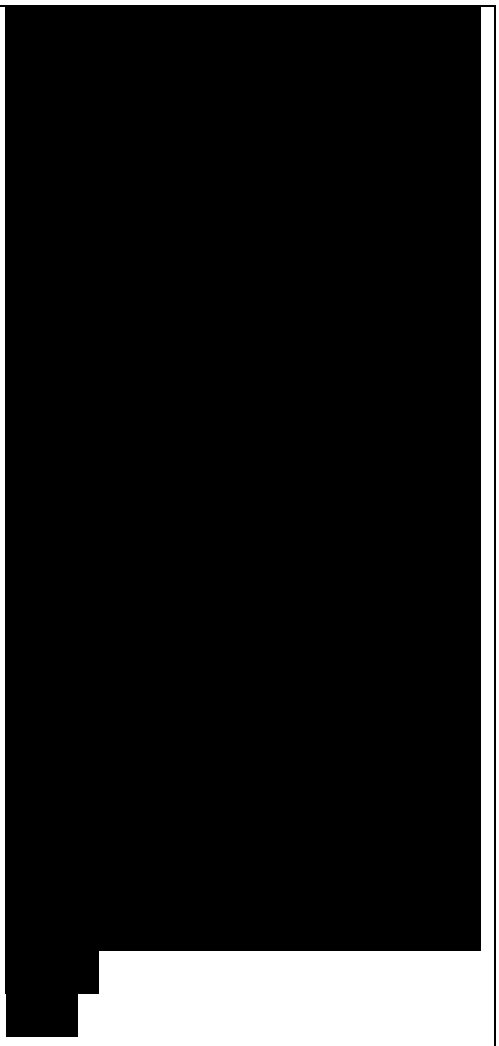
ranging from large-scale industrial processes in hydrocarbon chemistry to enzyme-controlled reactions in the living cell.

The chemical species that plays a unique and privileged role in acidity is the hydrogen nucleus, 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 (105 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

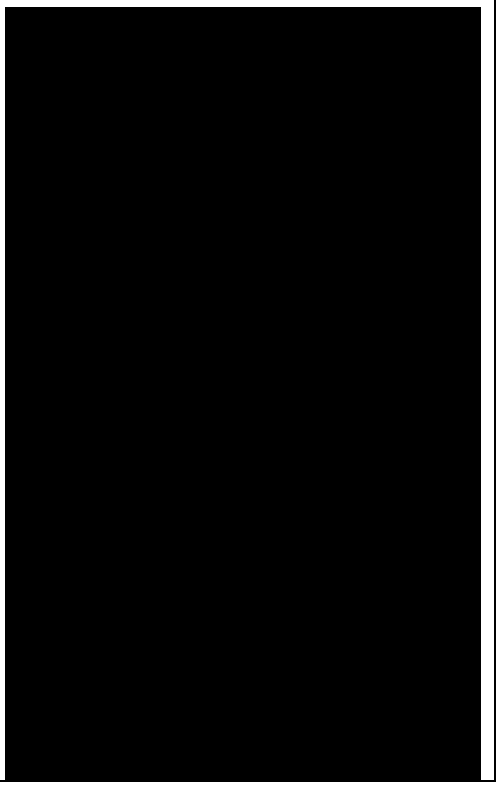
The first clear definition of acidity can be attributed to

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 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)].

(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, H2O is the conjugate base of the acid H3O+. 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).

(1.2)

(1.3)

(1.4)

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

(1.5)

Indeed the extent of dissociation of the solvent is very small (in HF, Kap « 10-11; in H2O, Kap = 10-14). The pKap 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 BF3 or carbocations, whereas Lewis bases are molecules that contain

readily available nonbonded electron pairs (as in ethers, amines, etc.) [Eq. (1.6)].
(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 [H2A+] and define a base as any substance that will increase [A~] and thus decrease [H2A+]. 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 aH +. 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.

(7)

It was S0rensen's idea7 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.

(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 areference cell is used with aliquid 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.

(1-9)

Under the best experimental conditions, the National Bureau of Standard has setup 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 signifi¬cance. 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 pKap = p(H2A+) + p(A~). Thus, the range of pH (DpH) is pKap (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 Deyrup8

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 equilibri¬um in the acid solution between an electro-neutral weak base B and the solvated proton can be written as in Eq. (1.10).

(1-10)

Bearing in mind that the proton is solvated (AH2+) and that AH is the solvent, the equilibrium can be written as in Eq. (1.11).

(1-11)

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

(1-12)

From this equation, Eq. (1.13) follows.

(1-13)

Because the firstratio represents the degree of protonation, Hammett and Deyrup8’9 defined the acidity function H0 by Eq. (1.14).

(1-14)

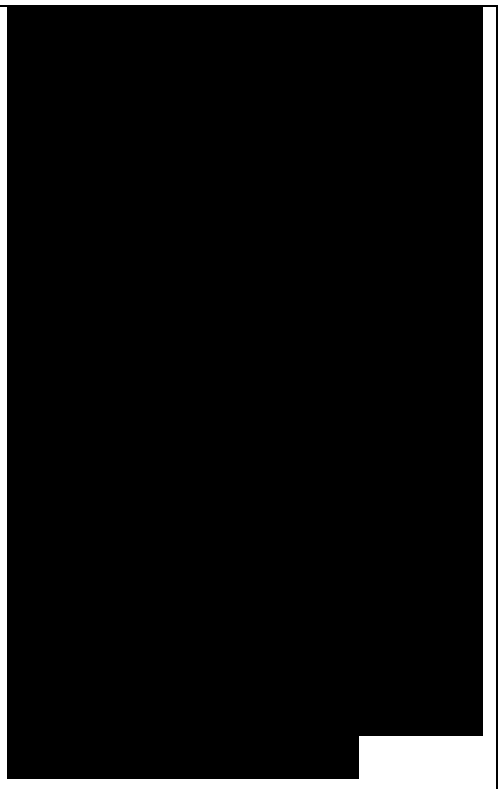
Equation (1.14) can be written for further discussion in the more usual form of Eq. (1.15).

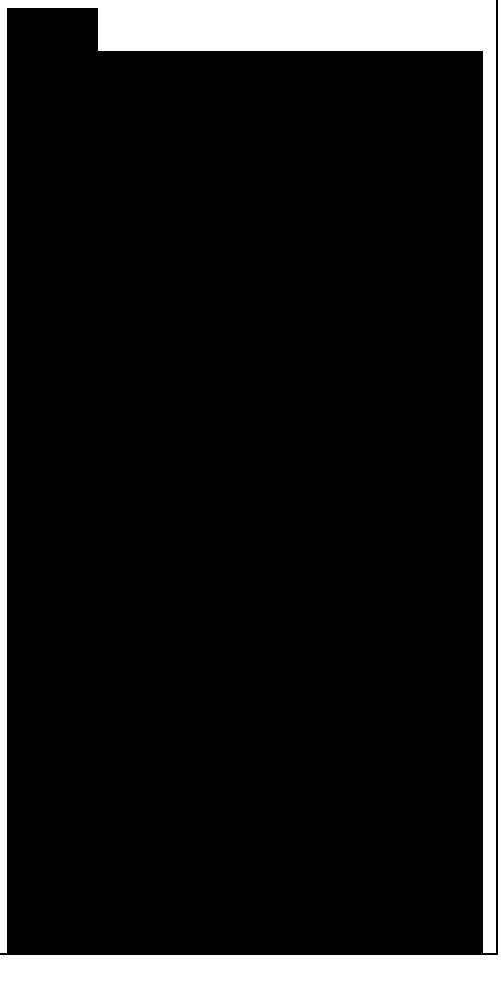
(1.15)

FromEq. (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 fB/fBH + is the same for different bases in a given solution, Hammett postulated that the H0 function was unique for a particular series of solutions of changing acidity. The first application was made for the H2SO4-H2O system using a series of primary anilines as indicators. By starting with the strongest base Bj, the pKB[H + was measured in dilute aqueous solution. The pK of the next weakerbase B2 was then determined by measuring the ionization ratio of the two indicators in the same acid solution using the relation of Eq. (1.16).

(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 (pK = 1.40) and the weakest trinitroaniline (pK = — 9), Hammett explored the whole H2O-H2SO4 range up to 100% sulfuric acid and the perchloric acid-water solution up to 60% of acid. Similar acidity functions such as H—, H+, H2+ 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 H0 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 [BH1]/ [B] plotted against H0 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).

(1.17)

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

(1.18)

This Hr function, also called J0 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 H0 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

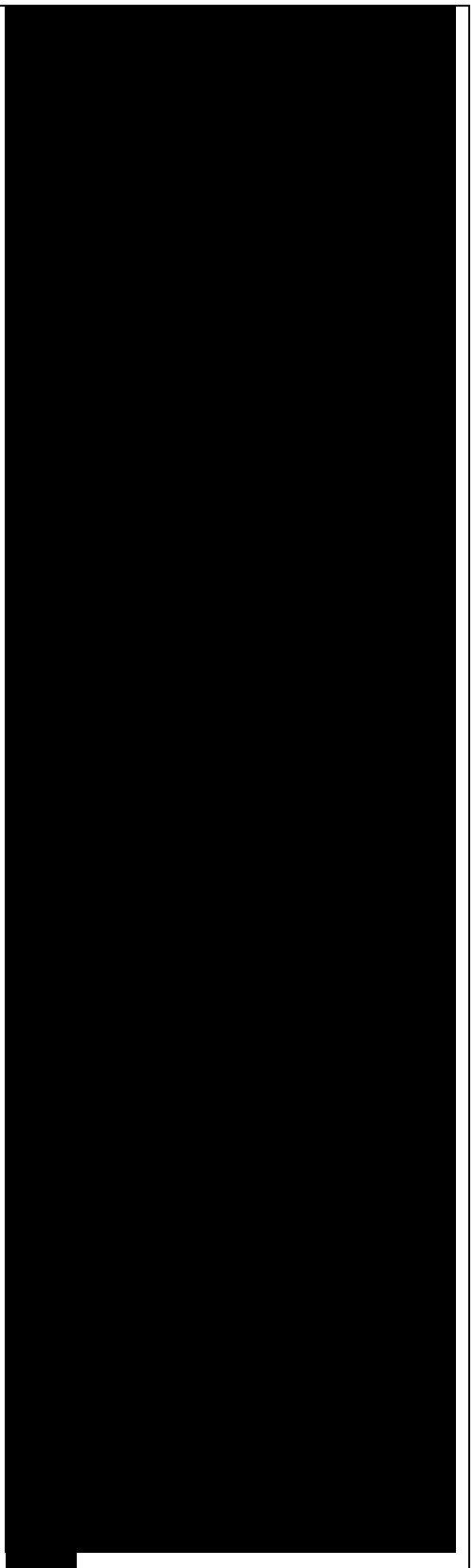
(1.19)

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 Conant15 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, $H_0 < -12$. 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 ($H_0 \ll -10$)

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)].

(1.20)

(1.21)

In both cases, a remarkable acidity increase is observed from the H0 value of the neat HA as shown in Figure 1.2 for HSO3F.

It is this large acidity jump, generally more than 5 H0 units, that raises a strong acid solution into the superacid region. Therefore, it is clear that the proposed reference of H0 = —12 for the lower limit of superacidity is only arbitrary. It could as well be H0 = —15.1 with HF or HSO3F 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

chloride17 (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 H0 = —27 have been estimated on the basis of exchange rate measurements by NMR for an HSO3F-SbF5 mixture containing 90 mol% SbF5.21 In fact, the HF-SbF5 is considered one of the strongest superacid system based on various measurements. Meanwhile, however, Sommer and coworkers found that the weakest basic indicator of the para-methoxybenzhydryl cation family (4,4'- dimethoxy; pKBH+ ~ —23) could not be

diprotonated even in the strongest HF-SbF5 acid.22 For this reason it appears that one should not expect acidity levels higher than approximately H0 = —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 (H0) 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.

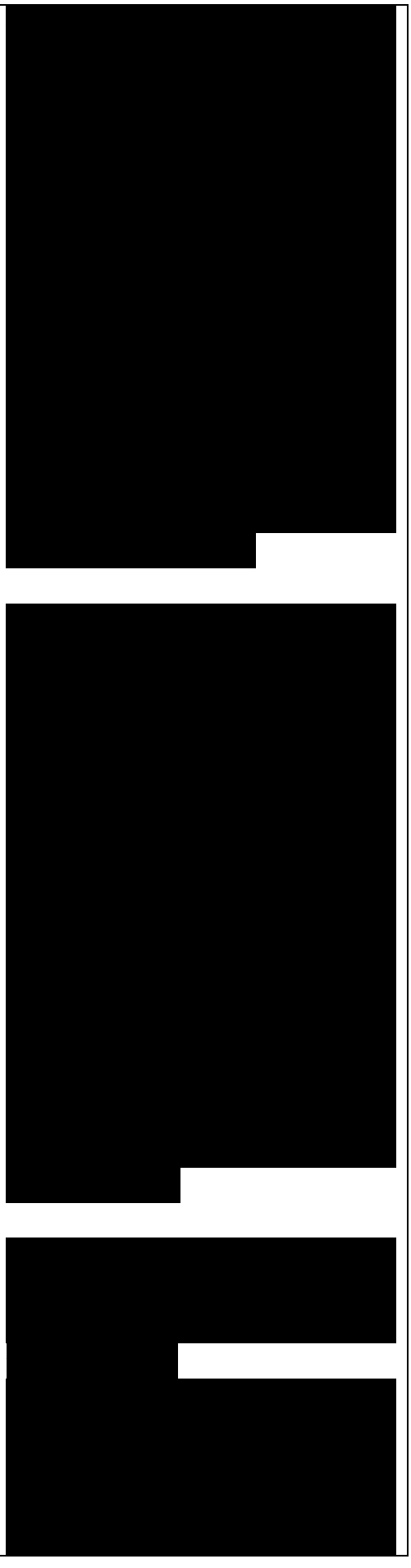


Figure 1.3. Acidity ranges for the most common superacids. The solid and open bars are measured using indicators; the broken bar is estimated by kinetic

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, Farneth and Gorte, and Fripiat and Dumesic 9 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

(CF3SO3H, RFSO3H), hydrogen fluoride, and carborane superacids [H(CB11HR5X6)].

2. Lewis superacids, such as SbF5, AsF5, PF5, TaF5, NbF5, BF3, tris(pentafluoro- phenyl) 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-HSO3F, HF-CF3SO3F, and HB(HSO4)4.
2. Conjugate Brønsted-Lewis superacids:
   a. Combination of oxygenated Brønsted acids (H2SO4, HSO3F, CF3SO3H, RfSO3H) with Lewis acids (SO3, SbF5, AsF5, TaF5, and NbF5);
   b. Hydrogen fluoride in combination with fluorinated Lewis acids such as SbF5, PF5, TaF5, NbF5, and BF3;
   c. Conjugate Friedel-Crafts acids such as HBr-AlBr3 and HCl-AlCl3.

1.3.3. Ternary Superacids

Examples are HSO3F-HF-SbF5, HSO3F-HF-CF3SO3H, and HSO3F-SbF5-SO3.

1.3.4. Solid Superacids

The acid-base character of solids was studied very early by Tanabe's group31,32 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

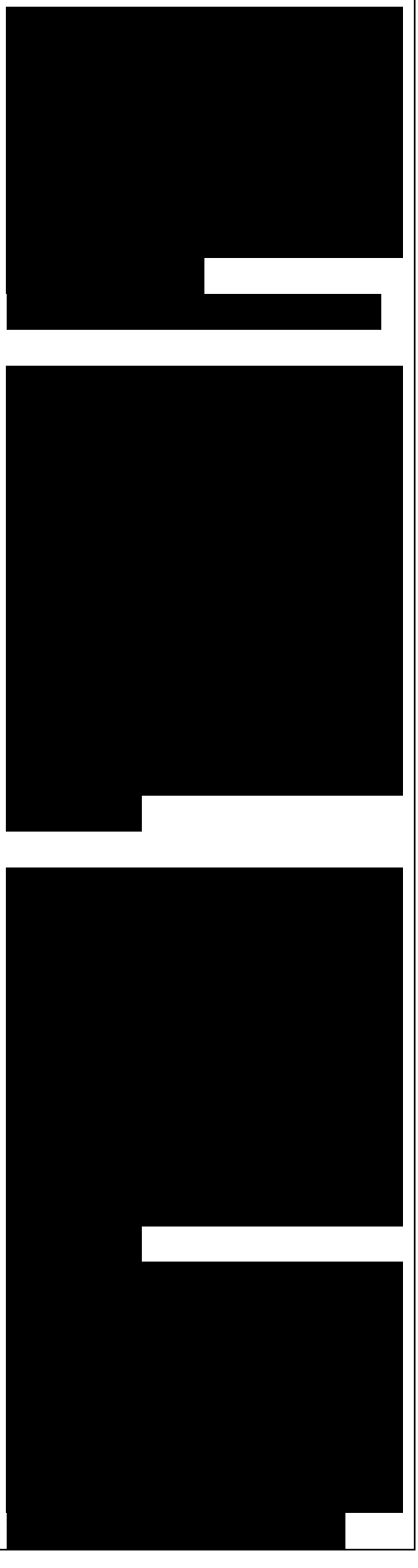
ACIDS)

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 Deyrup8 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 Iw = Cw/Ca, where Ca and Cw 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 Sw = [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 = Cw; and in solution A, Ca = [B]a + [BH+]a. The ionization ratio is given by Eq.



(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)].

Cj is the concentration of the absorbing species, I is the length of the cell, and s, is the molar absorptivity (or extinction coefficient). If at a given wavelength A, sBH +, sB, and sA 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).