

Is the world basic?  
Lessons from surface science\*

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In this work the authors review various definitions of acids and bases. Furthermore, the application of these theories to surface and adhesion science is discussed. It is clear that application of various acid-base theories may not always lead to consistent conclusions on the acid-base character of surfaces. Possible reasons for the inconsistency include the nature of the scale, the choice of reference points, and the use of either poor or inconsistent statistical procedures in addition to experimental difficulties. The present authors recommend a future careful study and comparison of the various acid-base theories when applied to surface and adhesion science. The limited studies already performed suggest this activity would be worthwhile.

## 1. INTRODUCTION

From antiquity chemists and alchemists realized the fundamental importance of acid-base reactions and interactions in a variety of chemical and physico-chemical processes. The development of molecular based and quantitative definitions of acidity and basicity has not been fully completed despite a couple of centuries of work by notable scientists.

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\* Dedicated to Prof. Emil Chibowski on the occasion of his 65<sup>th</sup> birthday

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Lavoisier[1] is responsible for the first molecular based definition of acids. He incorrectly thought acids must contain oxygen. Indeed, the name oxygen refers to the ability to make acids. Lavoisier was not aware of hydrohalic acids or indeed the presence of hydrogen in sulfuric or nitric acids as they were prepared from the gases not containing hydrogen. Justus von Liebig [1] around 1838 suggested that acids must contain hydrogen. Von Liebig's theory [2] differs from modern thought in a number of respects. Arrhenius [1] suggested that the ability to produce hydrogen or hydroxide ions established a compound as an acid or base, respectively. Sorensen [3-5], in 1909, established the pH scale and its measurement both electrochemically and by the use of indicators. The pH scale is the first popular quantitative scale for acidity. A competing and similar scale was the "Rational" scale proposed by Giribaldo (see, for instance, Bates [6]). Bates [6] has discussed more fully the development and use of pH scales. The usual pH scale applies exclusively to dilute aqueous solutions. Similar scales can be and have been used in other protic solvents. Relating pH scales for various solvents is at best difficult.

In 1923 Brønsted and Lowry[1] developed a theory of acids and bases based on the ability of molecules to donate or accept protons (Hydrogen ions). Also in 1923 Gilbert Lewis[1] devised a scale which is based on the ability of compounds to accept or donate electrons. The Brønsted and Lowry definition can be subsumed into the Lewis definition. The Lewis definition serves as a basis for many of acid-base theories used in surface science such as those advanced by Drago [1] and Gutmann[8].

Pearson and Parr (see Pearson [9]) have more recently (when compared to the work of Lewis) explored the concept of Hard-Soft Acids and Bases (HSAB).

Morra [10] compared the results of two methods of investigating the acid-base properties of solids. His results suggest that the assessment of acid-base character of surfaces may be different depending on the acid-base scale chosen. In this work, the authors review various acid-base scales used in the literature to assess the acid-base character of surfaces. Experimental approaches used to assess the acid-base character of solids are also reviewed. This work provides an assessment of the current state-of-the-art.

## 2. ACID-BASE SCALES USED IN SURFACE SCIENCE

### 2.1. Overview

Several approaches have been used to study the acid-base character of solids. Generally they employ either pH type scales, or Lewis acid-base scales to assess the acid-base character. pH scales are linear and continuous with acid character lying at one end of the scale and base character at the other end. Materials are said to be basic or acidic based on the scale value relative to the neutral value

(typically pH=7). Bates [6] has reviewed in detail the development of pH scales and their determination by electrochemical and indicator methods.

Various Lewis acid-base scales have also been used for assessment of acid-base character. In general, two scales have been used – one to assess acidity and the other to assess basicity. Materials may thus have both acid and base properties. These two scales may be based on different criteria and may not be of the same range of values.

Drago [7] has proposed a scale where a molecule must be considered as either an acid or a base but cannot have amphoteric character.

## 2.2. pH scales

The pH scale for dilute aqueous solutions was suggested by Sorensen [3-5] in 1909. For aqueous systems the scale runs from 0–14 with 7 being neutral. pH scales for other protic solvents and mixed solvents have also been suggested. The range of pH values in these other solvents differs as to the points of neutrality and the length of the scale. There are thus many pH scales. Comparison of pH values determined on one scale to those determined on another scale is at best difficult as they do not share a common standard state, range of values or neutral point. Bates [6] has discussed the comparison of various pH scales extensively.

Fowkes [11] has reviewed various wet chemical methods for determining the acidity of surfaces. Methods employing pH type scales are discussed further below.

### 2.2.1. pH indicator dyes

pH indicator dyes adsorbed on surfaces have been used to assess surface acidity [11]. An acidity scale can be defined as follows:

$$H_0 = pK_a + \log \left\{ \frac{[B]}{[BH^+]} \right\} \quad (1)$$

where  $pK_a$  is the value for the indicator dye in aqueous media. The ratio  $[B]/[BH^+]$  may be determined spectrophotometrically. Titration of the surface with different bases is known to give different responses so that a unique acidity scale cannot be found. Fowkes [11] more fully reviews this topic.

### 2.2.2. Isoelectric pH

Bolger [12] has proposed that the use of isoelectric pH in water could be used to assess surface acidity. For monopolar acids and bases, such as silica and

aluminum oxide, this approach seems appropriate. For amphoteric materials like iron oxide the use of a single number fails to tell the complete story. A single value assessment of acid or base character appears to be an inadequate descriptor of the acid-base character of surfaces. (Also see Chehimi et al. [13]).

### 2.3. Hard and Soft Acids

Pearson [9] has proposed scales for acidity based on the numerical values of equilibrium constants ( $K$ ) of nucleophilic reactions. In this model acids (A) and bases (B) are considered to be either hard or soft. Hard acids have positive charge, are difficult to reduce and have small size. Soft acids are easy to reduce, may not be charged and are of large size. Hard bases (nucleophiles) are often negatively charged, are difficult to oxidize and have small size. Soft bases are easy to oxidize, do not need to have negative charge and are large size.

According to Pearson

$$\log K = S_A S_B + \sigma_A \sigma_B \quad (2)$$

where  $S$  is a hardness factor and  $\sigma$  is a softness factor. Lee [14] has, in particular, contributed to the use of HSAB theory.

HSAB theory introduces the use of separate scales for acidity and basicity. Compounds are classified as acids or bases but cannot have amphoteric properties.

### 2.4. Drago

In a manner not dissimilar to HSAB theory Drago [7] proposed that the heat of acid-base adduct formation can be expressed as:

$$-\Delta H_{AB} = (E_A E_B + C_A C_B) \quad (3)$$

where  $E$  and  $C$  are susceptibilities to electronic and covalent interactions. Fowkes [11,15-20], in particular, has exploited Drago's model to determine acid-base character of polymer and metal surfaces using calorimetric heats of adsorption. Oldak and Pearson [21] have recently commented on the determination of Drago constants using infrared spectroscopy.

For common materials  $E$  and  $C$  values are in the range of  $\sim 1-10$ .  $E_b$  values, however, only range from  $\sim 0.5$  to  $1.7$ . The lengths of the acid and base scales thus may not be of equal ranges.

## 2.5. Gutmann

Gutmann[8] also proposed a scale for estimation of  $\Delta H_{AB}$ . His equation is

$$-\Delta H_{AB} = \frac{(AN \cdot DN)}{100} \quad (4)$$

where AN is referred to as the acceptor number and DN the donor number. DN is defined by the enthalpy of interaction between  $SbCl_5$  and a base. Thus

$$DN = -\Delta H(SbCl_5 : base) \quad (5)$$

The acceptor number, AN, is defined as the  $^{31}P$  NMR shift when triethylphosphine is dissolved in the acid of interest. AN is defined to be 0 when hexane is used and 100 when  $SbCl_5$  in 1,2 dichloroethane is used. Riddle and Fowkes [22] realized that the  $^{31}P$  NMR shift had a significant contribution from van der Waals interactions. These authors suggested an alternate scale,  $AN^*$ , with units of kcal/mole. Here

$$AN^* = 0.228(AN - AN^d) \quad (6)$$

AN and  $AN^d$ , the dispersion or van der Waals component, have units of ppm.

For common tested materials the values of  $AN^*$  and DN range from approximately 0 to 38, indicating that the scales are of nearly equal lengths.

## 3. SURFACE SCIENCE MODELS INCORPORATING ACID-BASE CONCEPTS

### 3.1. Fowkes

Earlier Fowkes [23] suggested that surface free energy could be expressed as a summation of components. Over the past few decades several authors have proposed acid-base scales based to determine of surface free energy. These authors include Fowkes; van Oss, Chaudhury and Good (see van Oss [24]) as well as Chang [25]. Each of these approaches considers the surface free energy to be the summation of Lifshitz-van der Waals interactions and Lewis acid-base interactions. They differ with respect to how Lewis acid-base interactions are considered. (Also see Etzler [26])

Fowkes considers:

$$W_a = W_a^{LW} + W_a^{AB} \quad (7)$$

where  $W_a$  is the work of adhesion and the superscripts LW refers to Lifshitz-van der Waals interactions and AB refers to Lewis acid-base interactions.  $W_a^{AB}$  is expressed as follows:

$$W_a^{AB} = -f \cdot N \cdot \Delta H_a^{AB} \quad (8)$$

where N is the number of adsorption sites per unit area and

$$f = \left[ 1 - \frac{\partial \ln W_a^{AB}}{\partial \ln T} \right]^{-1} \quad (9)$$

and

$$f \approx 0.2 \dots 1.0 \quad (10)$$

When using the Fowkes approach some authors have taken  $f$  as unity although this does not seem to be a good approximation [27]. Because  $f$  and N are generally not known, direct calculations of the work of adhesion are often not made. Determination of  $\Delta H^{AB}$  for multiple probe liquids on a given solid together with models by Drago [7] or Gutmann [8,28] can be used to assess the acid-base nature of the surface (also see [22]).

The Fowkes approach is particularly suitable for use with data ( $\Delta H^{AB}$ ) collected using either IGC or flow microcalorimetry.

### 3.2. Van Oss, Chaudhury and Good

According to the van Oss, Chaudhury and Good model [24,29] the Lewis acid-base component is modeled as follows

$$\gamma_i^{AB} = 2(\gamma_i^+ \gamma_i^-)^{1/2} \quad (11)$$

where  $\gamma^+$  is the Lewis acid parameter and  $\gamma^-$  the Lewis base parameter. van Oss, Chaudhury and Good further choose

$$\gamma_i^+ = \gamma_i^- \equiv 0 \quad (12)$$

for alkanes, methylene iodide and  $\alpha$ -bromonaphthalene which presumably interact only through Lifshitz-van der Waals interactions. For water

$$\gamma_{H_2O}^+ = \gamma_{H_2O}^- \equiv 25.5 \text{ mJ / m}^2 \quad (13)$$

Based on these above numerical choices,  $\gamma^+$  and  $\gamma^-$  have been experimentally determined for a variety of liquids. van Oss [24] has compiled and reviewed the determination of these values (also see Etzler [26]).

The range of  $\gamma^-$  values for known liquids is 0-77, while the range of  $\gamma^+$  values is 0-25 with most being less than 10. The idea of the neutrality of pure water in this scale is like the pH scale. It also appears that the acid and base scales may not be of equal range.

### 3.2.1. Della Volpe

Della Volpe [30] has criticized the choices of van Oss and co-workers. Della Volpe suggests that  $\gamma^{LW} = 26.25$ ,  $\gamma^+ = 48.5$  and  $\gamma^- = 11.2 \text{ mJ/m}^2$  for water. Della Volpe also suggests that the  $\gamma^{LW}$  estimate made earlier by Fowkes [31] is incorrect. The neutrality of water must be questioned in general because ordinary water contains dissolved carbon dioxide. A different choice of acid and base parameters is mathematically permitted and Della Volpe argues that his choice yields acid and base parameters for solid surfaces that are more consistent with chemical intuition.

Whether or not Della Volpe's scale offers advantages over that of van Oss and co-workers has not been resolved. van Oss [32] claims that the choice of numerical values for acid and base parameters is arbitrary and unimportant. DellaVolpe [30] claims that his choice of parameters is more consistent with chemical intuition and is more appropriate for statistical reasons as well.

### 3.3. Chang-Chen

The Chang-Chen model [25,33] for interfacial free energy is largely based on the same principles which govern the van Oss, Chaudhury and Good model. Both models treat Lifshitz-van der Waals interactions in the same way. Calculation of the surface free energy components requires the knowledge of the same experimental data. The two models, however, differ in the way that Lewis acid-base interactions are modeled.

In the Chang-Chen model

$$W_a^{LW} = W_a^L = 2(\gamma_1^{LW} \gamma_2^{LW})^{1/2} = P_1^L P_2^L \quad (14)$$

where

$$P_i^L = (2\gamma_i^L)^{1/2} \quad (15)$$

$P_i^L$  is the dispersion parameter. The superscript L is equivalent to LW.

Like the van Oss, Chaudhury and Good model the acid-base interaction is modeled using two parameters. These parameters,  $P_i^a$  and  $P_i^b$ , are referred to as principal values. The acid-base work of adhesion can be represented using the following relation:

$$W_a^{AB} = -\Delta G_a^{AB} = -(P_1^a P_2^b + P_1^b P_2^a) \quad (16)$$

Where  $\Delta G_a^{AB}$  is the acid-base free energy of adhesion. Tabulated  $P_i^a$  and  $P_i^b$  values are substituted into Eqn. (16) such that the work of adhesion is maximized and the free energy of adhesion is minimized.

The acid-base character of a material is determined by the sign of  $P_i^a$  and  $P_i^b$ . If  $P_i^a = P_i^b = 0$  then the material is neutral (or non-polar). If  $P_i^a$  and  $P_i^b$  are both positive then the material is monopolar acidic and if both negative then the material is monopolar basic. If  $P_i^a$  and  $P_i^b$  are of opposite sign then the material is amphoteric.

#### 4. EXPERIMENTAL METHODS USED TO EVALUATE ACID-BASE CHARACTER OF SURFACES

##### 4.1. Contact Angles

Contact angle measurements have often been used for the determination of solid surface free energies. Acid-base character can be determined using the models proposed by van Oss, Chaudhury, and Good as well as those by Chang or Della Volpe.

Contact angles can be obtained using sessile drops, Wilhelmy plate method, wicking or much less popular heats of immersion [26]. The use of ASDA (Axisymmetric Drop Shape Analysis) is particularly useful for determining the quality of contact angle. Chibowski [34], Dalal [35] and Etzler [26] have separately commented on the importance of obtaining quality contact angle data. Carre [36] has recently commented on the effect of probe liquid choice on the calculated value of the van Oss, Chaudhury and Good parameters. Chibowski [37,38] has recently commented on the application of different models for determination of surface free energies from contact angle data. It is likely that



much of the literature data are inappropriate for determination of surface free energies.

The following criteria must be met in order for contact angle data to be used for calculation of surface free energies.

1. Young's equation is valid.
2. Probe liquids are pure compounds. Mixtures are likely to exhibit selective surface adsorption. See Adamson [39], for instance.
3. The surface free energy of materials is independent of the test conditions at fixed T and P. ( i. e. the surface free energy of a solid is not modified by the probe liquid.
4.  $\gamma_l > \gamma_s$  or more generally  $\cos(\theta) > 0$
5.  $\gamma_{sv}$  is not influenced by probe liquids.

Chibowski [40] has recently discussed some of the experimental issues in determining good contact angle data.

Contact angle titrations can also be performed. Contact angles of aqueous solutions will vary with pH depending on the ionization state of the surface.

#### 4.2. Inverse Gas Chromatography (IGC)

The Fowkes approach is most often used with IGC. Either Drago or Gutmann parameters are thus generated. Figure 1 illustrates how IGC may be implemented. The free energies of adsorption near infinite vapor dilution of a series of alkanes are determined. These free energies of adsorption show a linear relation with the number of carbons in the probe alkane. Figure 1 follows the model of Dorris and Gray [41] which is often employed. From the slope of the alkane data  $\gamma^{LW}$  can be determined. For the adsorption of materials with acid-base properties the  $\Delta G^{AB}$  is determined from the difference between the measured value and that of an alkane at the same value of  $a(\gamma_L^{LW})^{1/2}$ . Here  $a$  is molecular area. This difference is illustrated by the vertical line in Figure 1. If  $\Delta G^{AB}$  is known for at least three temperatures then  $\Delta H^{AB}$  can be calculated using the usual thermodynamic relations. If  $\Delta H^{AB}$  is known for several acid-base probes then the Gutmann or Drago parameters can be determined. Similarly from  $\Delta G^{AB}$  van Oss acid-base parameters could be determined.

The acid-base component values are often larger than they might be using contact angle data. This is presumably so as data are taken for a very low surface coverage, thus adsorption largely occurs on high energy sites. Acid-base characterization may differ from that determined via contact angle data for experimental reasons.

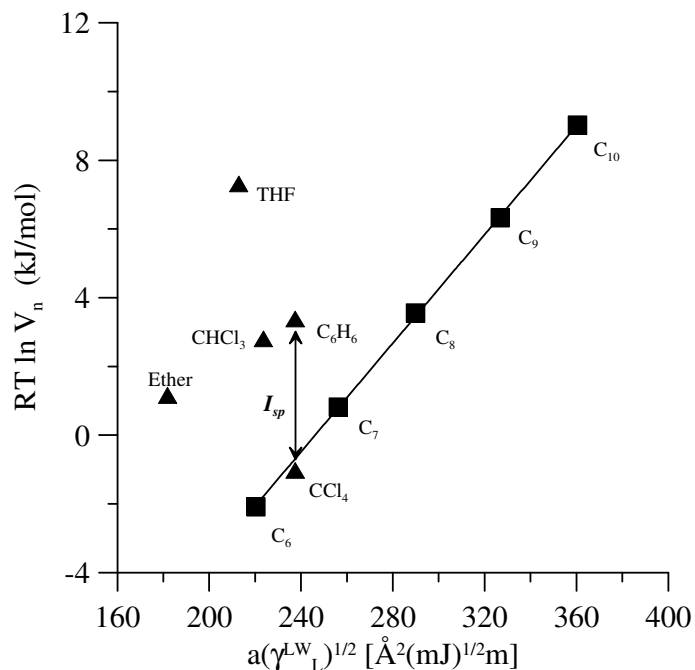


Fig. 1.  $RT \ln V_n$  versus  $a(\gamma_L^{LW})^{1/2}$ . Squares: alkane liquids. Triangles: other liquids. Slope of linear fit to alkane liquids gives  $\gamma_s^{LW}$  and vertical displacement of triangular points from linear fit gives  $I_{sp}$ .  $I_{sp}$  ( $\Delta G^{ab}$ ) is the free energy resulting from acid-base interactions.

### 4.3. XPS

XPS (ESCA) [42] employs the photoelectric effect to determine the energy of emitted electrons. The energy of the emitted electrons is specific to the element from which the electrons are emitted. Furthermore, the oxidation state of the element can be discerned.

XPS has been used extensively to understand the chemical composition of surfaces.

Shifts of the emitted electron energies (i.e. binding energies) have also formed the basis of an acid-base scale for metal oxides [13].

The scales are:

$$\Delta O = BE(O_{1s}) - 530 eV \quad (17)$$

and

$$\Delta M = BE(M_{2p}) - BE(M_{2p}^0) \quad (18)$$

where BE is the binding energy and  $O_{1s}$  refers to the oxygen 1s orbital and  $M_{2p}$  the metal 2p orbital. The superscript zero refers to the metallic state. No superscript refers to the oxidized state. The sum  $\Delta O + \Delta M$  has been found to correlate with isoelectric point measurements. XPS has been used with other chemical markers as well.

#### 4.4. SPM

The scanning probe microscopy [13] can be used to measure the adhesion force between the probe and a surface. The SPM probe may be chemically modified with specific chemical groups giving it specific acid-base or other chemical properties. The measured adhesion forces have been found to depend on pH, surface charge and acid-base properties in the expected way.

#### 4.5. Colloid Titration

The point of zero charge (pH units) or the isoelectric point (zeta potential equal to zero) can be determined and appear to be a measure of surface acidity [11,43]. Such values have been found to correlate with Gutmann donor numbers [43].

#### 4.6. Indicator Dye Adsorption

As discussed above, indicator dyes may be adsorbed on surfaces. The ionization state of the dye can be used as an indicator of surface acidity. The Hammett acidity function  $H_0$  defined above has been found to correlate with isoelectric points [11,43].

#### 4.7. Calorimetry

Heats of adsorption can be conveniently used with the models of Drago and Gutmann and have been exploited by Fowkes [19]. Heats of adsorption, however, do not always correlate with isoelectric points [43].

## 5. CURRENT ISSUES

### 5.1. What is the Best Scale for Determination of Acid-Base Character?

From the above discussion, it is clear that the concept of acids and bases arose early in the history of chemistry and has been extensively exploited by

chemists. The definition of acids and bases has also evolved over the past 250 years or so. Several quantitative scales for acidity and basicity have been suggested and many are discussed above. For about 100 years, the Sorensen pH scale based on Brønsted-Lowry theory has found particular usefulness for understanding the behavior of aqueous systems.

Acid-base scales in modern use are of a few types.

1. pH [6] based scales are of the first type. The scales are continuous with low numbers reflecting acids and high numbers bases. Isoelectric point and indicator dye adsorption measurements are of this type. The pH scale is most frequently used with dilute aqueous systems. It possible to construct other pH scales in other protic solvent systems but the measurements on one scale cannot be readily translated to results on another scale. pH scales are, therefore, not unique; many scales exist.

2. Drago's [7] model is based on HSAB theory. As in the case of pH measurements materials are characterized as being either acids or bases. Two parameters, E and C, are required to specify the acid or base properties of a material.

3. Various Lewis acid-base scales have been constructed. These include the scales proposed by Gutmann [8] and by van Oss, Chaudhury and Good (See van Oss [24]). The modifications to van Oss et al.'s scale proposed by Della Volpe are also included. For models based on Lewis acid-base theory, two independent scales – one for acidity and one for basicity - exist. A given compound can have amphoteric properties in that it can be assigned a value on each of the two scales. The idea of neutrality is more complex. Hydrocarbons are usually assigned a value of zero on each of the two scales and thus can be thought of as neutral. A material with equal non-zero values on the two scales is more difficult to understand in terms of neutrality. The values assigned for acidity and basicity on each scale are based on different criteria and thus the ratio of the acid value to base value can vary significantly. Both Morra [10] and Della Volpe [30] have discussed this point. At this time the "holiness" of one scale over another is unclear [44]. It is, however, clear that if the ranges of values of the two scales differs from one another other an apparent imbalance of acidity versus basicity could be perceived. The lengths of the two scales in the van Oss, Chaudhury and Good model do not appear to be equal (see for instance [13] ) leading some to conclude that the materials are most often more basic than acidic, sometimes in contradiction to usual chemical intuition.

4. The Chang-Chen [25] model is also based, perhaps somewhat more loosely, on Lewis acid-base theory. Like other such models, two parameters describe the acid-base character of a material. In this instance, however, the two parameters are each allowed to take on both positive and negative values. Bases are

considered to have negative parameter values. Uniquely, the Chang-Chen model allows for base-base and acid-acid repulsive contributions to  $W_a^{AB}$ .

At the present moment it is unclear which scale most accurately reflects nature.

## 5.2. Experimental Issues

The use of contact angles to determine the acid-base properties requires that the measured contact angles meet each of the required assumptions listed above. Earlier work by Kwok [45], Etzler [44] and Dalal [35] suggests that these assumptions may not always be met, leading to incorrect acid-base parameters. Della Volpe, furthermore, suggests that the set of probe liquids must be carefully chosen so that suitable condition numbers for curve fitting are obtained. IGC leads to high values of acid-base parameters presumably because data are taken at low surface coverage where only high energy sites are occupied.

A comprehensive discussion of various aspects of curve fitting and other statistical issues related to the determination of surface free energy components seems to be missing. Della Volpe [30] and Bialopiotrowicz [46,47], however, have discussed some issues in this regard.

Particular attention should be paid to the linearization of equations (transforming coordinates so that linear plots can be constructed) done to calculate slopes and intercepts. While determining slopes and intercepts by least squares is easy to perform and is good for illustration, linearization has unintended consequences on the resulting calculations because standard errors are often not constant for all y-axis (vertical axis on graph) values. Modern mathematical software makes such linearization unnecessary. It is statistically more robust not to perform such linearizations.

With particular regard to the van Oss, Chaudhury and Good model several calculation methods have been used.

As stated earlier by Gardner [48] the equation below,

$$W_a = \gamma_l [1 + \cos(\theta)] = 2(\gamma_l^{LW} \gamma_s^{LW})^{1/2} + 2(\gamma_l^+ \gamma_s^-)^{1/2} + 2(\gamma_l^- \gamma_s^+)^{1/2} \quad (19)$$

may be solved in several ways. Some methods allow for  $\gamma^+$  and  $\gamma^-$  to have negative values. Other methods require both these values to be positive as suggested by van Oss [24]. In a given paper, the author's choice of calculation method is frequently unclear to the reader. A non-linearized approach would only allow the acid and base parameters to be positive. Similarly for Gutmann's model  $\Delta H_{ads}^{AB} / DN$  vs.  $AN^* / DN$  will be linear with a slope equal to  $K_d$  and intercept of  $K_a$ . Here  $K_d$  is the solid base parameter and  $K_a$  the solid acid

parameter. Statistical errors may sometimes cause  $K_a$  to be negative. A non-linearized approach to fitting will always result in positive values for both  $K_d$  and  $K_a$ .

Standardized and statistically sound practices must be adopted by all future investigators.

### 5.3. Is the World Basic?

For purposes of investigating the acid-base character of solid surfaces, the van Oss, Chaudhury and Good approach has become popular. As pointed out by, for instance, Morra [10], the use of this model suggests that many materials are predominantly basic ( $\gamma^- > \gamma^+$ ). Is the van Oss, Chaudhury and Good model the best choice for the assessment of acid-base character of surfaces?

In this paper various scales for characterization of the acid-base character of materials have been discussed. It is clear that the van Oss, Chaudhury and Good model provides some good insights into the acid-base character of surfaces. It is equally clear that the acid-base scale chosen by these authors is not obviously more holy than others. Indeed, water is considered to be neutral, a choice necessary only for Sorensen's pH scale in aqueous media. Indeed the generally smaller values of  $\gamma^+$  for probe liquids may be significantly responsible for the apparent basic character of all materials.

van Oss [32][32] argues that the choice of numerical values for  $\gamma^-$  and  $\gamma^+$  for water is unimportant. In striking contrast, Della Volpe [30] and Lee [49-51] suggest that the choice is in fact important for both scientific and statistical reasons. These authors also propose alternate scales. Morra [10], in particular, suggests that acid-base scales must be consistent with chemical intuition and, furthermore, suggests that van Oss' scale appears to be inconsistent with chemical intuition.

With perhaps a few exceptions, a careful and consistent application of sound statistical principles to the fitting of various parameters does not appear to be the general practice. A consensus on sound scientific and statistical approaches must be reached.

It is clear that despite more than 250 years of investigation into the nature of acids and bases a quantitative description of this property of matter has not been fully or universally achieved. Both experimental and theoretical issues affect the application to surface and adhesion science. The authors encourage others to improve the state of the art through the design of critical experiments.

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