

Hasok Chang on the nature of acids

Abstract

For a period of several years the philosopher of science Hasok Chang has promoted various inter-related views including pluralism, pragmatism, and an associated view of natural kinds. He has also argued for what he calls the persistence of everyday terms in the scientific view. Chang claims that terms like phlogiston were never truly abandoned but became transformed into different concepts that remain useful. On the other hand, Chang argues that some scientific terms such as acidity have suffered a form of “rupture”, especially in the case of the modern Lewis definition of acids. Chang also complains that the degree of acidity of a Lewis acid cannot be measured using a pH meter and seems to regard this as a serious problem.

The present paper examines some of these views, especially what Chang claims to be a rupture in the definition of acidity. It is suggested that there has been no such rupture but a genuine generalization, on moving from the Bronsted-Lowry theory to the Lewis theory of acidity. It will be shown how the quantification and measurement of Lewis acidity can easily be realized through the use of equilibrium theory and the use of stability constants.

Introduction

Hasok Chang is without a doubt one of the finest historians and philosophers of science working today. He generally focuses on the scientific details rather than retreating into abstract metaphysics or analytical philosophy of science. He is also the author of several books including *Inventing Temperature*, for which he was awarded the prestigious Lakatos award as well as *Is Water H₂O?* among others (Chang, 2004, 2012).

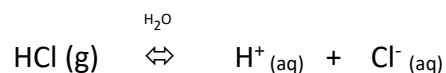
Chang is also the initiator of a brand of the history and philosophy of science that seeks to expand scientific knowledge itself, which he calls “complementary science”. This project aims to give a novel function to history and philosophy of science, without denying its traditional role. Although a philosopher of physics by training, Chang has made a number of ‘excursions’ into chemistry (Chang, 2016). The present article will focus on one of these chemical studies, namely his writings on acidity.

Chang generally shows a remarkable attention to the scientific details of fields such as thermometry, the scientific revolution and electrochemistry. But I believe that he may be imposing his philosophical view onto the science in some cases, and that he is perhaps being selective of the parts of science that support his philosophical and historiographical approach.

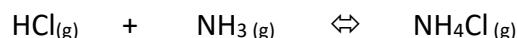
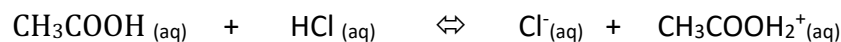
Chang on acids

Chang believes that there is what he calls a “rupture” between the way in which acids were conceived according to the Arrhenius and the Brønsted-Lowry theories, on one hand, and the Lewis theory of acidity on the other hand. Chang also rather strenuously rejects the notion that Lewis’ theory of acidity represents a generalization of the Brønsted-Lowry definition.

Let me begin by reviewing the three elementary definitions of acidity. According to Arrhenius’ theory, an acid is any substance that forms H⁺ ions in aqueous solution. HCl for example is regarded as an acid, because on reacting with water it forms H⁺ ions,



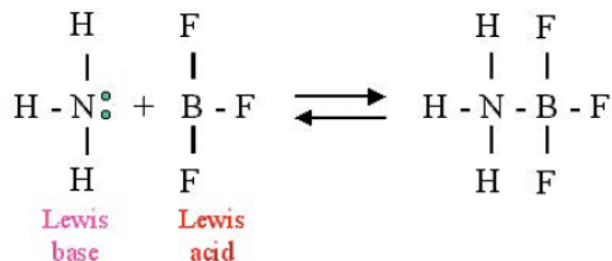
Brønsted and Lowry, both of whom worked on the physical chemistry of solutions, generalized this definition so that an acid is a substance that donates H^+ ions to any polar solvent and even in the absence of a solvent. The following are examples of each of these types of reactions.



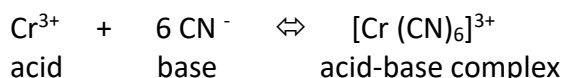
In the first of these two reactions, HCl acts as an acid while CH_3COOH , whose common name is acetic acid, is actually acting as a base. The notions of acidity and basicity are therefore seen to be relational, in that no single substance may be said to be an acid or a base in all circumstances.

The second example contains no solvent whatsoever. According to the Arrhenius definition, this example would not therefore be classified as an acid-base reaction, whereas according to the Brønsted-Lowry definition HCl is acting as an acid since it can donate protons, or H^+ ions, to ammonia.

Thirdly, there is a definition by G.N. Lewis, who had a broader vision of chemical phenomena than Brønsted and Lowry, and whose initial concern was the application of Gibbs' thermodynamics to non-ideal solutions. According to the Lewis' theory, an acid is an electron pair acceptor whereas a base is an electron pair donor as shown in the following example,



This reaction clearly does not fall within the earlier definitions of acidity since no transfer of H^+ ions takes place. Another example of a reaction that falls under the Lewis definition of an acid-base reaction, but not the two earlier definitions is,

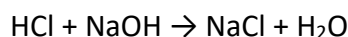


Neither the BF_3 molecule in the first example, or the Cr^{3+} ion in the second, are donating protons and yet are considered as acids in Lewis' definition since they each accept a pair of electrons.

But Chang strongly disagrees with the generally held view that the Lewis definition subsumes the earlier ones, or that it represents a true generalization of them. In addition, Chang sees a rupture between the Brønsted-Lowry and Lewis definitions. Here is what he has written,

I am almost inclined to say that the two concepts are incommensurable. It might be sufficient, for present purposes, to say that the Lewis and the Brønsted-Lowry definitions refer to two different sets of chemical substances; there is an overlap between the two sets, but one is not a subset of the other (Chang, 2012, 694).

Perhaps the most popular story told by good chemists is that the Lewis definition encompasses the Brønsted-Lowry definition, that it is a generalization of the latter, because a proton donor is also capable of accepting an electron pair. But I have my doubts about this. Consider the reaction of hydrochloric acid and sodium hydroxide...



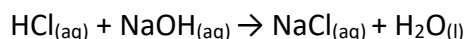
But how would the same reaction be understood from the Lewis point of view? Does HCl accept a pair of electrons from NaOH? That is not obvious since the HCl molecule does not have an empty orbital into which to accept an electron pair (Chang, 2012, 693-694)

I believe there are two errors in the second quotation. First of all, HCl accepts a pair of electrons from the OH⁻ ion, not simply from NaOH as Chang writes. Secondly, the author fails to mention that the H⁺ ion contains an empty 1s orbital which *does* allow it to readily accommodate a pair of electrons.

In the following passage Chang seems to partly acknowledge his earlier oversight when he says,

At any rate, nearly all of the HCl in an aqueous solution will be dissociated into H⁺ and Cl⁻ ions, so what must happen is that the H⁺ ion accepts the electron pair from the OH⁻ ion. But then what is acidic is the H⁺ ion, not HCl as a substance or a molecule, which is contrary to the Brønsted-Lowry concept (and to common parlance) (Chang, 2012, 694).

As a matter of fact, according to Brønsted-Lowry, HCl (g) or "HCl as a molecule", is *not* acidic. It is only acidic when it reacts with water). Matters would have been clearer if Chang had perhaps written,



Whereas the over-simplified equation that appears in the second of the quotations above may give the impression that HCl is incapable of acting as an acid, the more correct version, that includes the aqueous solvent, emphasizes that it is only HCl in water that is acidic. Chang may perhaps be unaware of the fact that HCl in gas form is not acidic. As every high school student

learns, HCl the gas is neutral whereas aqueous HCl is acidic, as can be demonstrated in the classic fountain experiment.

One cannot help wondering why Chang appears to show such nostalgia for acids that only form H^+ ? Chang also appears to hold a parallel nostalgic view regarding such entities as phlogiston in his book on water (Chang, 2012). If the motivation is an urge to highlight the continuity in scientific development, then I am in full agreement and in fact would wish to go a good deal further in emphasizing continuity and incremental steps in scientific development rather than any forms of Kuhnian revolutions or ruptures.

However, it would appear that Chang may also be siding with Kuhn in the case of acidity, in choosing to focus on rupture, whereas he has also frequently written about the virtue of retaining scientific terms (Chang, 2011).

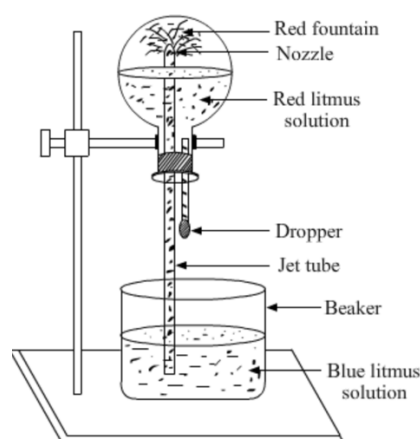


Figure 1. The fountain experiment in which water containing litmus indicator is made to enter the glass bulb filled with HCl gas.

The pH meter

One of the main reasons that Chang cites for his reluctance to accept that Lewis achieved a true generalization would appear to be that Lewis acidity cannot be quantified by means of a pH meter. In the same article he writes,

At this point there may be a strong temptation to get back to something more certain and sensible like measurement to anchor the meaning of acidity, rather than seeking security in ever-changing theories... We do have a widely used measure of acidity in the form of pH, but I will argue that it is not a measure entirely fit for grounding the concept of acidity in its theoretical or empirical aspect. (Chang, 2012, 695).

I believe this may be an example of putting one's philosophical views ahead of the science. Chang has a long-standing and well-known penchant for pragmatism, operationalism and experiments in general, and what would appear to be a certain disdain for theories in science.

Returning to his views of acids we also read,

... pH only measures Brønsted-Lowry acidity and has no clear connection to Lewis acidity. This is of course understandable, given that the definition and measurement of pH by Sørensen ... dates back to 1909, more than a decade before Lewis articulated his theory of acids." (Chang, 2012, 696).

However, this is not why pH does not apply to Lewis acids. The measure of pH obviously measures H^+ concentration and is consistent with how Brønsted and Lowry define acids in terms of the formation of H^+ ions. Since Lewis' definition does not involve H^+ ions, one would not expect his concept of acidity to be quantifiable through pH measurement ?

Chang, presses on by saying,

History aside, this situation raises a scientific and philosophical difficulty: even if we assume that all Brønsted-Lowry acids are Lewis acids, it is certainly not the case that all Lewis acids are Brønsted-Lowry acids; therefore, there are Lewis acids that lack any precise quantitative measure empirically (Chang, 2012, 696).

I believe this to be a non-sequitur. The fact that "not all Lewis acids are Brønsted-Lowry acids" does not immediately imply that Lewis acids "lack any precise quantitative measure". The fact that the acidity in the Cr^{3+} reaction, mentioned earlier, cannot be quantified by means of the pH meter does not imply that its acidity cannot be quantified *tout court*. This feature does not refute or threaten the Lewis definition of acidity in any way.

Equilibrium theory

There is a perfectly good approach to the quantification of Lewis acidity which Chang appears not to be aware of. Lewis acidity can be quantified through the well-known use of stability constants for any reaction, which is given by the expression below, in which square brackets denote the concentration of each chemical species.



$$K_{\text{stability}} = \frac{[Cr(CN)_6]^{3+}}{[Cr^{3+}][CN^-]^6}$$

The greater the value of the equilibrium constant K , the greater the acidity of the Cr^{3+} ion in this case. Said otherwise, the greater the magnitude of the equilibrium constant, the more the position of equilibrium is said to lie towards the right side. The individual values that contribute to this constant can very readily be measured, but as far as I am aware, Chang has never so much as ever mentioned stability constants in all of his writings on Lewis acids.

Moreover, the same general approach, of chemical equilibrium theory, can be applied to the earlier definitions of Arrhenius and Brønsted-Lowry. There are no Kuhn losses therefore on moving to quantifying acidity by appeal to the concept of equilibrium.¹

In the case of a strong acid such as aqueous HCl for example, one could quantify the degree of acidity or ionization in an analogous fashion to the way that the Cr³⁺ case was handled above. Consider the reaction below,

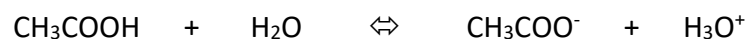


The equilibrium constant is given by the expression,

$$K = \frac{[\text{H}^+_{(\text{aq})}] [\text{Cl}^-_{(\text{aq})}]}{[\text{HCl}_{(\text{g})}]}$$

However, reactions of this kind involving strong acids proceed towards the right to such an extent that the equilibrium constant can be said to be effectively infinite. Equilibrium constants for strong acids are not therefore cited in the literature. Strong acids are simply fully ionized such that the denominator approaches zero and consequently the right-hand side of the above expression, and hence the equilibrium constant, approach infinity.

Matters are different for weak acids, such as Chang's favorite example of acetic acid, for which the reaction with water and the equilibrium constant are given by the following expressions,



$$K = \frac{[\text{CH}_3\text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}] [\text{H}_2\text{O}]}$$

Unlike aqueous HCl in the previous example, acetic acid is only weakly ionized and has a Ka value of approximately 10⁻⁵ at room temperature and pressure. In order to calculate the pH of a molar or 1.00 M solution of acetic acid one needs to perform a simple equilibrium calculation as shown below,

	CH_3COOH	+	H_2O	\rightleftharpoons	CH_3COO^-	+	H_3O^+
Initial concentrations	1.00 M				0		0
Equilibrium concentrations.	1.00 – x				x		x

$$\text{Since } K_a = \frac{[\text{CH}_3\text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{(1.00 - x)} = 1.8 \times 10^{-5}$$

One can obtain the value of x by solving a quadratic equation and consequently one obtains the pH by taking the negative logarithm to base 10 of the value of x . There is no need to use a pH meter in cases such as these, provided that the concentrations of the relative chemical species can be measured.² Sometimes a little theory can go a long way.

To summarize, the use of equilibrium theory allows one to quantify acidity in Arrhenius, Brønsted-Lowry and even Lewis acids, whereas the use of pH meters only applies to Arrhenius and Brønsted-Lowry acids. This feature supports the notion that Lewis acidity is indeed a generalization of the earlier definitions and certainly not a case of “rupture”.

In textbook presentations of this topic a Venn diagram is often produced to make precisely this point, and to illustrate the gain in generality on moving from the Arrhenius, to the Brønsted-Lowry theory and on to the Lewis theory. In fact, the increasing generality of definitions of acidity has now extended even further than Lewis’ definition such as is shown in the Venn diagram in figure 2.

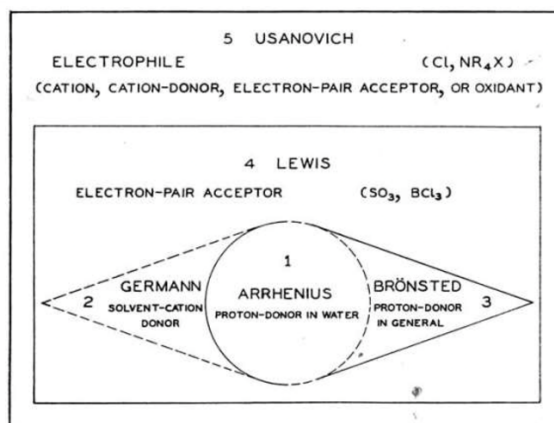


Figure 2. Venn diagram showing the relationship between various definitions of acidity. N.F. Hall, *Systems of Acids and Bases*, J. Chem. Ed. 1940, 124-128.

The author of the article from which figure 3 is reproduced clearly asserts that Lewis’ theory is a genuine generalization of that of Brønsted,

Readers will observe that this system [Lewis] includes all the acids and bases of the Brønsted system and no other bases, while it points out a host of new acids (including most cations) which the Brønsted system does not recognize as such (Hall, 1940, 127).

There is a striking analogy here with the changing definitions of oxidation and reduction that have arisen through the history of chemistry, a fact that was even recognized by Brønsted, about 100 years ago (Brønsted, 1923).

Initially oxidation meant the combination of oxygen with any particular element. The same term was later applied to mean the reaction of any given element with any highly electro-negative element, of which oxygen is just one particular example. Even later the modern definition of oxidation became expressed in terms of electrons, or the lingua franca of

chemistry. Whereas oxidation is any process which results in a loss of electrons, reduction represents the opposite trend, namely the gain in electrons. As in the case of Lewis acidity, nobody doubts that this development represents a gain in generality, rather than any form of rupture. In the words of Lewis,

To restrict the group of acids to those substances which contain hydrogen interferes as seriously with the systematic understanding of chemistry as would the restriction of the term oxidizing agent to substances containing oxygen (Lewis, 1938).

Non-ideality in solutions

Philosophers of science may well be familiar with the concept of an ideal gas and the accompanying ideal gas equation whereby $PV = nRT$. Such ideal gases have often featured in discussions of scientific models as have discussions of non-ideal gases and the use of the Van der Waals equation (Mizrahi, 2012 ; Woody, 2013).

However, philosophers of science are generally not aware of an equally well-developed subject of non-ideal solutions. Consider for example a solution of an ionic substance such as sodium chloride in water. Let us also assume that this solution is of concentration 0.10 molar (0.10 M). Solutions of ionic substances invariably behave non-ideally because their ions are not hard spheres that merely collide with each other. The fact that they have electrical charges immediately introduces forces of attraction, which are ignored in the case of ideal solutions just as they are for ideal gases. In the case of non-ideal solutions, the departure from ideality is actually more complicated. In addition to the forces of attraction between oppositely charged ions, some ions are also surrounded by those of the opposite charge, which tends to reduce the attraction between the original positive and negative ions. Furthermore, not all ions behave similarly since the attraction depends on the charges on the ions which typically have values of ± 1 , ± 2 or ± 3 .

Consider for example a situation in which 100 ions of Na^+ are present, of which 25 are hydrated, meaning they are surrounded or shielded by water molecules. As a result, not all Na^+ ions are said to be “active” and the nominal concentration of Na^+ ions becomes somewhat irrelevant. One must appeal to the effective concentration or, to use the technical term, to the activity of the solution instead of its concentration. The definitive treatment of this subject was published as long ago as 1907 by none other than G.N. Lewis. The topic is invariably treated in advanced courses in thermodynamics, physical chemistry and analytical chemistry (Atkins, Paula, Keeler, 2018; Harris, Lucy, 2019). Applications of the concept of activity range from electrochemistry to the behavior of biological cells in biophysics.

Returning to the subject of pH, this is of course very much an ionic process since it concerns H^+ ions that are produced by acids according to both the Arrhenius and the Brønsted-Lowry definitions. The more general expression for pH which is expressed in terms of activities is,

$$\text{pH} = -\log (\gamma_{\text{H}^+} [\text{H}^+])$$

rather than the more elementary expression of,

$\text{pH} = -\log [\text{H}^+]$ where the square brackets denote concentration.

In the case of very dilute solutions the two expressions lead to approximately the same numerical value for pH, but this is not so in cases of more concentrated solutions. Figure 3 shows a comparison between experimentally measured pH values, which depend on activity values, as opposed to values calculated on the basis of the concentration of various solutions of the typical strong acid HCl.

Molar concentration	pH calculated from concentration	Experimentally measured pH
0.00050	3.30	3.31
0.0100	2.00	2.04
0.100	1.00	1.10
0.400	0.40	0.52

Fig 3. Calculated and experimental values for various concentrations of HCl at 25°C. The increasing disparity that occurs between values calculated from concentrations and experimental values, that depend on activities, can clearly be seen, as concentration increases. Experimental values were obtained from McCarty, Vitz and Maynard (2006).

The authors McCarty et al. make the further important point regarding pH measurements, in an article entitled, “pH Paradoxes: Demonstrating That It Is Not True That $\text{pH} = -\log[\text{H}^+]$ ”,

This reaffirms our point that pH cannot be defined as $= -\log[\text{H}^+]$, because these operational definitions are based on cell potentials, which in turn are dependent on activities, not concentrations (McCarty, Vitz and Maynard, 2006).

Similarly, a recent website on the analytical chemistry of water states that,

The definition of pH first introduced by Sørensen (the concept that pH is determined by hydrogen concentration) was therefore partly amended as science advanced. However, his definition confers advantages in terms of practical usage, and the corresponding amendment does not downgrade its biological and chemical significance. Advances in thermodynamics and practical methods of pH measurement have played an important role in the process of this redefinition. For this reason, from the point of view of the engineers who use pH, it can still be said that “the Father of pH” is a title that Sørensen deserves. Sørensen’s first definition is still used in basic general chemistry courses, in order to make the concept easier to understand. Note that the theoretical definition of pH uses the extremely difficult concept of activity, as shown here (Horiba website).

The authors then proceed to give the rigorous version of what pH actually measures, in terms of activity rather than concentration.

Thermodynamic activity

Chang quotes Bates, an expert of pH measurement as saying,

With the perfection of chemical thermodynamics, it became evident that Sørensen's experimental method did not, in fact, yield hydrogen ion concentration....[The numbers obtained] were not an exact measure of the hydrogen ion *activity* ..." (Bates, 1930) [My italics].

to which he adds the further remark,

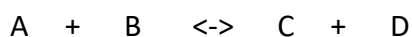
All in all, the correspondence between the theoretical notions of acidity and the methods of its measurement has been, and continue to be, less than tight (Chang, 2012, 697).

Thermodynamic *activity*, as mentioned in the previous section, is a technical term that Chang does not seem to be familiar with. This quantity is given the symbol upper case A and is expressed in the following formula in which the term in square brackets is the concentration of any substance and γ is its associated activity coefficient.

$$A = [A] \gamma$$

Thermodynamic activity does not just mean 'acting as an acid' as Chang seems to believe. It is a term that was introduced, by Lewis in 1907, in order to account for the rather specific phenomenon of the hydration of ions and their resulting ionic strengths.

In elementary treatments of chemical equilibrium such as in a typical reaction,



The equilibrium constant K is expressed by the formula,

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

A more general approach consists of replacing each of these concentrations by their thermodynamic activities to give,

$$K_{eq} = \frac{[C] \gamma_C [D] \gamma_D}{[A] \gamma_A [B] \gamma_B}$$

The various activity coefficients, or γ 's are calculated according to the Debye-Hückel equation of,

$$\log \gamma_i = \frac{-0.51 z_i^2 \sqrt{\mu}}{\dots} \quad \text{at } 25^\circ\text{C}$$

$$1 + \left\{ \alpha \left(\sqrt{\mu} / 305 \right) \right\}$$

where α is the size of the hydrated ion in picometers,
 μ is the ionic strength
 z is the charge of the ion.

Meanwhile, when Chang cites the term “activity” as used by Bates, he seems to assume its everyday meaning, in the sense of the way that acids act, rather than the technical thermodynamic sense that Bates is referring to. What Bates is discussing is that the more accurate definition of pH, that takes account of activities rather than concentrations, takes the form of,

$$\text{pH} = -\log (\gamma_{\text{H}^+} [\text{H}^+])$$

rather than the more familiar version of

$$\text{pH} = \log [\text{H}^+]$$

as mentioned in the previous section of the present article.

The more accurate treatment recognizes the difference between concentration of chemical species as compared with their activities. In the case of dilute solutions the difference is of little significance. For example, a 0.025 molar solution of HCl has a pH of 1.60 without any correction for activity coefficients, whereas it has a value of 1.66 if activity is taken into account. As mentioned in the previous section, this is not the case for concentrated solutions for which it is essential to utilize activities instead of values of concentration.

Chemical Bonding and Electron Pairs

Let me return to Lewis’ definition in order to explain why this is not only a genuine generalization of the previous definitions of acidity, but also part of a much greater development in the history of chemistry and a major unification that was initiated by Lewis. This too is an area that Chang does not broach, while taking Lewis acidity out of context, as I see it.

Lewis is responsible for introducing the view that chemical bonding, and chemical reactivity in general, are primarily concerned with pairs of electrons. His definition of acidity, which Chang objects to, should be seen in this wider context of the development of the central concepts of structure and bonding and not in isolation. (Lewis, 1923).

Lewis is famously remembered for having proposed the idea that a covalent bond consists of a shared pair of electrons. This has little to do with the very limited insight that the Arrhenius and Brønsted-Lowry theories of acidity have to offer and everything to do with Lewis’ theory of acidity. Moreover, Lewis is equally remembered for having stressed that covalent and ionic bonding lie at opposite ends of a continuum of bonding types. Ionic bonding represents a case of very unequal sharing of electron pairs rather than a categorically different species of bonding.

Furthermore, all the quantum theories of chemical bonding that were subsequently developed, including valence bond theory and molecular orbital theory, have maintained the

notion of electron pairs as being central to an understanding of chemical bonding. Here is how Robert Kohler expressed the importance of Lewis' work in his classic article on the history of Lewis' account of the chemical bond,

The first satisfactory picture of the chemical bond was proposed early in 1916 by Gilbert N. Lewis (1875-1946), the American physical chemist better known to some for his work on thermodynamics. His book, *Valence and the Structure of Atoms and Molecules* (1923), which elaborated the picture of the bond as a shared pair of electrons, was the textbook of the new generation of mechanistic chemists. Without Lewis's conception of the shared pair bond, the interpretation of reaction mechanisms already begun by the English school of A. Lapworth (1872-1941), T. M. Lowry (1874-1936), C. K. Ingold (b. 1893), and R. Robinson (b. 1886) would not have gotten very far. Likewise, without the idea of the shared pair bond, then being used with increasing confidence and success by organic chemists, the application of quantum mechanics to the chemical bond in the late 1920's by H. London, E. Schrödinger, and L. Pauling would have begun on far less certain ground (Kohler, 1971).

Now a pair of electrons should lead to the mutual repulsion of two particles of like charge. Lewis grappled with this notion from the beginning of his work. First, he proposed that perhaps Coulomb's law might break down in the microscopic realm.

Secondly, Lewis began to suggest that the opposite magnetic properties of a pair of electrons might be responsible for overcoming the mutual repulsion between them. Many of these ideas have been retained in some form or other, following the advent of quantum theories of bonding. Electrons were found to be characterized by two possible spin quantum numbers. Moreover, the notion of pairs of electrons is retained in the quantum notion of an atomic orbital containing just two electrons with opposite spin quantum numbers as dictated by the Pauli principle.

Needless to say, the quantum theoretical approach provides a quantitative account of chemical bonding through the mechanism of electron exchange energy, which serves to stabilize a molecule. Nevertheless, the iconic idea of pairs of electrons at the heart of chemistry retains its validity. Nor was Lewis' idea confined just to inorganic chemistry, since it also had a profound influence on the development of physical organic chemistry at the hands of Robinson, Ingold and a host of other chemists up to and including Roberts, Woodward and Hoffmann in more recent times (Laidler, 1995; Brock, 1993).

Lewis also developed a simple 'back of the envelope' method of discovering the number and nature of the bonds as well as lone pair electrons in any given molecule. These Lewis structures remain useful to the present day, and continue to form part of the general chemistry teaching curriculum and for good reason. Although there are cases in which this approach breaks down or gives incorrect predictions, it remains as part of the staple diet of working chemists as an immensely practical way of thinking about chemical bonding that requires absolutely no quantum mechanics or computation.

On the basis of the Lewis structure of any molecule and using the equally classical and non-quantum mechanical approach known as valence shell electron pair repulsion (VSEPR) method, chemists can also predict the 3-D shape of most molecules to a considerable degree of

accuracy. From the shape of the molecule one can go on to predict whether any particular molecule might have a net dipole or not, a fact that can serve to explain all manner of other properties of molecules. For example, the bent shape of the water molecule explains why it has a net dipole which in turn explains why it is capable of dissolving ionic salts, why it has an anomalous boiling point and so on.

Of course, these classical approaches to bonding which are the direct outcome of Lewis' notion of identifying bonding with electron pairs can sometimes fail, but they remain as very useful methods that can yield rationalizations and even predictions about any given molecule. Returning to Lewis' definition of acidity, it is not only a genuine generalization of the previous definitions of acidity, but also part of a much greater unification between various central ideas in chemistry including structure and bonding as well as chemical reactivity in general that was initiated by Lewis.

Some genuine philosophical issues concerning Lewis Acidity

One genuine concern with the Lewis definition, which has been known since the inception of his definition, is that acids have different relative strengths depending on the base with which they react, an issue that is not discussed by Chang incidentally.

As a result of this apparent disadvantage, no unique order of acid strengths can be formulated within the Lewis definition. This feature is due to the fact that acidity becomes a response function for Lewis. That is to say a substance is acidic or basic depending on what substance it is chemically related to.³

Nevertheless, many approaches have been devised including the use of the SbCl_5 affinity scale, the BF_3 affinity scale, various thermodynamic and spectroscopic scales and gas phase affinity scales (Laurence, Graton, Gal, 2011). Indeed, the existence of all of these additional approaches to quantifying acidity serve to further refute Chang's claim that Lewis acidity is not capable of being quantified.

Conclusions

I claim there is no rupture between the Brønsted-Lowry and Lewis conceptions of acidity contrary to what Chang believes. The fact that a pH meter cannot be used to measure the degree of acidity in the case of some Lewis acids does not imply an absence of possible means of measuring acidity. A simple appeal to the principles of chemical equilibrium provides us with the well-known concept of stability constants for the formation of acid-base complexes such as in the reactions of transition metal ions with a set of ligands.

Lewis' theory of acidity has the advantage of being centered on the concept of pairs of electrons which are also essential to the discussion of all chemical reactions and the formation of chemical bonds. Only by ignoring these other uses of the concept of electron pairs can Chang create the illusion that Lewis' definition of acidity is somehow inferior to the earlier more classical definitions in terms of the transfer of H^+ ions.

Moreover, the concept of electron pairs retains its central importance in the quantum theories of bonding, namely molecular orbital theory and valence bond theory. To downgrade Lewis' definition of acidity because it deals with electron pairs rather than protons amounts to

also downgrading huge swathes of modern chemistry, such as equilibrium thermodynamics as well as classical and quantum theories of chemical bonding.

Lewis unified our understanding of acids and bases, together with reactions that lead to covalent bond formation in general in that they all involve electron pairs. According to Lewis, an acid accepts both the electrons in a pair in the process of forming a dative bond. Meanwhile, a hydrogen atom reacting with a bromine atom, for example, do so by each providing one electron in the shared pair in a typical covalent bond. Dative bonds and typical covalent bonds are thereby regarded as variations on the same theme.

All these unifications achieved by Lewis, are indirectly undermined by Chang's sustained attack on Lewis acidity. Instead of looking at Lewis acids as 'failed acids', we should consider the situation the other way round. Lewis acids (dative covalent bonding formation) form a subset of covalent bonding in general. Like oxidation and reduction, the modern view of acids and bases transcends the layperson's view and it is puzzling to read about Chang's nostalgia for acids in the layperson's sense of the term?

As was emphasized above, HCl is not intrinsically acidic. It only becomes acidic on reacting with water or another polar solvent. It is perfectly consistent to consider H^+ as a Lewis acid and Lewis' definition is a genuine generalization of that of Brønsted & Lowry. As was argued earlier, and contrary to Chang's claims, there is no "rupture" or incommensurability. Our inability to measure Lewis acidity with a pH meter is neither here nor there given that Lewis acidity *can* be quantified, as can Arrhenius and B-L acidity, by appeal to equilibrium theory and stability constants.

Activity is a technical term used to characterize the non-ideal behavior of ions. This is a well-understood phenomenon and does not point to any aspect that is "less that tight", to cite Chang's words one again. Electron pairs, which lie at the heart of Lewis' theory of bonding as well as his definition of acids, rather than protons, are the key to understanding bonding both classically and quantum mechanically.

Acid-base behavior emerges as just one kind of chemical reaction among many other types that involve electron pairs and is thus placed into a wider context by means of Lewis' definition. As was suggested earlier, Lewis achieved the unification between acid-base reactions and reactions involved in bonding in general. Perhaps Chang should consider the advantages of this profound unification rather than claiming that there is dis-unity and rupture in our current knowledge of acids.

Finally, there is an important logical point. Any concept refers to a set of items and a definition of the concept intends to identify all the members of that set. In turn, generalizing a concept implies enlarging the set of the items referred to by the concept. Furthermore, a concept can be generalized in two ways. One is by adding a new property to the property which originally identified the set. Another way is by changing the property that identifies the members of the set.

The case of acidity corresponds to the second way, in that the property that identifies acid substances in Lewis' theory is different from the property that identifies acid substances in Brønsted-Lowry theory. Perhaps it is this fact that leads Chang to talk about "rupture." However, this does not mean that the two definitions are incommensurable. Since the set of acid substances identified by Brønsted-Lowry definition is a subset of the set of acid substances

identified by Lewis definition, as shown in figure 2, then Lewis' definition is a generalization of the Brønsted-Lowry definition.

In logical language, one can say that, strictly speaking, there are two concepts whose intensions are different, but whose extensions are related by inclusion. In simpler words, all substances that are acid according to Brønsted-Lowry definition are also acid according to Lewis definition, but not vice versa. But, if this is the case, Chang's claim, as cited earlier, that

... the Lewis and the Bronsted-Lowry definitions refer to two different sets of chemical substances; there is an overlap between the two sets, but one is not a subset of the other.

is simply incorrect. This comment does not depend on particular views about the real nature of acidity or about which of the two definitions is 'better', but is a logical remark, which I believe serves to strengthen the present critique.⁴

Notes

¹ The term Kuhn loss was first introduced by the late, Heinz Post, to mean something that was explained in the previous paradigm but that the successor paradigm fails to explain. Post believed that there were no such examples of Kuhn losses.

² This point will be discussed more rigorously in a later section of this article.

³ I thank a review of this article for urging me to emphasize this point.

⁴ I thank another reviewer of the present article for bringing this logical point to my attention.

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