

# Equilibrium and pH

Stewart Ian Wells  
PO Box 223, Truckee, CA 96160  
e-mail: [cywells@gmail.com](mailto:cywells@gmail.com)

An analysis of the development of equilibrium chemistry, particularly as applied to acid-base relations, reveals numerous inaccuracies and inconsistencies in the quantification procedures. The dimensionality of the equilibrium constant is distorted by the consistent failure to include the aqueous concentration of 55.5 moles per liter in the denominator of the equations. Other inaccuracies result from the neglect of the change in non-ionized solute concentration by the ionized portion, the neglect of the volume displacement of the solvent by the solute in aqueous solutions, and the neglect to factor in the pre-existent aqueous contribution to the hydrogen ion concentration in pH determinations. Corrections to the equilibrium equation and to the Henderson-Hasselbalch equation are proposed on this basis, along with a shift from a 'molar' context to a 'molal' context for solute concentrations. A new quantification scheme is developed in which 'neutral' is found at zero rather than at seven.

*"A chemist who is not a physicist is nothing." –Robert Bunsen*

## 1. Introduction

Chemistry and physics, often so intimately related as to seem indistinguishable, are nevertheless different enough in the scope of study, approach, and methodology to precipitate occasional confusion between their respective practitioners, chemists and physicists. The tendency toward higher mathematical expression in physics is contrasted by the meticulous empiricism of the chemist. But what distinguishes physics from chemistry more even than this is its insistent attention to *dimensionality* in all expression of natural law. The chemist's very empiricism, however, can lead to neglect of such a fundamental concern, which, in the case of the determination of "pH" and chemical equilibrium constants, has resulted in not only a dimensional misconception, but in an egregious quantitative error as well.

## 2. Equilibrium

The 'standard derivation' for equilibrium is customarily presented as follows:

From the simplest "law of mass action", when two substances (reactants),  $a$  and  $b$ , react to form two other substances (resultants),  $c$  and  $d$ , not all of reactants become

resultants, and remain so; rather, *some* of the resultants (from statistical considerations) tend to revert back into the original reactants. Hence the chemical equation:



which indicates the reaction is to some degree reversible. When the substances are in solution, the rate  $r$  of the reaction is proportional to the product of the mutual availabilities, or respective concentrations  $C$ , of the reacting substances, multiplied against one another. Thus the *algebraic product* of the respective concentrations determines the rate of reaction:  $r_1 \propto C_a \cdot C_b$ ;  $r_2 \propto C_c \cdot C_d$ . When the concentration  $C$  of each substance, in units of moles/liter, is denoted by the substance placed in brackets [ ], the reaction constants  $k_1$  and  $k_2$  may be inserted to form the more specific equations:

$$r_1 = k_1[a][b] \quad r_2 = k_2[c][d] \quad (2)$$

When the forward reaction and the reverse reaction reach the same rate, there is no further change in the respective concentrations of the substances, and the condition of *equilibrium* has been attained, whereby

$$k_1[a][b] = k_2[c][d] \quad (3)$$

Since  $k_1, k_2$  are constants, their ratio is also constant; this relation defines an overall "equilibrium constant" (a dimensionless number):

$$K_{eq} = \frac{k_1}{k_2} = \frac{[c][d]}{[a][b]} \quad (4)$$

This is claimed to be an accurately measurable quantity (directly or indirectly), whose precise value is specific to the type of reaction and the ambient conditions.

## 3. The Case of Water

Since water is observed to undergo a spontaneous, though slight, dissociation reaction:



it may be said to react with itself. With the concentration of "pure" water taken at 55.5 moles per liter, the equilibrium relation is presented as

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16} \quad (6)$$

Application of simple algebra to the above statements yields (approximately)

$$[H^+][OH^-] = K_{eq}[H_2O] = 55.5 \times 1.8 \times 10^{-16} = 1.0 \times 10^{-14} = K_w \quad (7)$$

which is known as the "ion product of water". Since the solution remains electrically neutral overall, the ions must exist in equal concentrations

$$10^{-14} = [H^+][OH^-] = 10^{-7} \cdot 10^{-7} \quad (8)$$

each concentration understood to be in moles/liter. Any solution in which the hydride and hydroxyl concentrations are equal is defined as *neutral*, and from this information a "pH" scale has been devised to quantify the acidity (predominance of  $H^+$ ) or alkalinity (predominance of  $OH^-$ ) of solutions of various substances in general. *Neutral* in this system is defined as

$$pH_{neutral} = \log_{10}\left(\frac{1}{1.0 \times 10^{-7}}\right) = -\log_{10} 10^{-7} = 7.0 \quad (9)$$

Simple inspection indicates that "acid" solutions, with  $H^+$  concentrations greater than  $10^{-7}$ , will have pH *less* than 7.0, and alkaline solutions will have pH *more* than 7.0.<sup>i</sup> It is noteworthy that this result may be obtained directly from the equilibrium equation:

$$[H^+] = K_{eq} \frac{[H_2O]}{[OH^-]} \quad (10)$$

where the equal concentrations  $[H^+] = [OH^-]$  yield  $[H^+] = (K_{eq}[H_2O])^{0.5}$ , whence

$$\begin{aligned} pH &= -\log[H^+] = -\log K_{eq} - \log \frac{[H_2O]}{[OH^-]} \\ &= -0.5(\log K_{eq} - \log[H_2O]) \end{aligned} \quad (11)$$

which is a precursor to the celebrated Henderson-Hasselbalch equation, **to be discussed in detail below**.

Although this derivation is quite the standard in the chemistry textbooks, from a physics perspective it is fraught with inaccuracies, inadequacies, and inconsistencies: in fact it leads to a quantification which, under general application, is *demonstrably erroneous*.

## 4. Importance of Dimensionality

As stated at the outset, of paramount importance to physicists, but frequently neglected by chemists, is attention to a precise system of dimensions, or 'units', for all physical (or chemical) quantities. Without expression in definite and consistent dimensions, an equation is scientifically meaningless; this is the principal inadequacy in the 'standard derivation' of pH. Specific units for the concentration  $C$ , rate  $r$ , and reaction constant  $k$  are often merely implied, or inconsistent if specified at all. In the general equilibrium equation,  $K_{eq}$  must be a dimensionless constant, yet for the dissociation of water, it is evidently in units of moles/liter. But with concentration  $C$  also in moles/liter,  $r$  could be in units of moles/second, or in grams/second, or in something else per second— whence the reaction constant  $k$  could be in units of  $\frac{mol/sec}{mol^2/lit^2} = \frac{lit^2}{mol \cdot sec}$ , or in  $\frac{gm \cdot lit^2}{mol^2 \cdot sec}$ , or in something else. In any case, without squaring the concentration

<sup>i</sup> In reality, 'neutral pH' has been accurately determined at 6.997 (Handbook of Chemistry).

$C_{H_2O}$  in the denominator of the dissociation equilibrium equation,  $K_{eq}$  comes out persistently in moles/liter. But squaring the concentration term (55.5 moles/liter) in order to render  $K_{eq}$  dimensionless results in a numerical value  $K_{eq} = \frac{C_{H^+} \cdot C_{OH^-}}{(C_{H_2O})^2} = 3.24 \times 10^{-18}$ , a figure which is entirely **incompatible** with the textbook standard.

The confusion is in fact initiated in the selection of moles/liter as the unit for molecular concentration. Suppose, instead of the arbitrary volume of liter, a unit volume of 1 'lom', which shall be defined as 18cc, is introduced, and that the concentration is expressed in units of moles/lom. Then the denominator becomes numerical unity (and remains so whether squared or not), and the numerator terms are consequently divided by 55.5 (the number of loms in a liter). This will indeed yield

$$K_{eq} = \frac{(1.8 \times 10^{-9} mol/lom)(1.8 \times 10^{-9} mol/lom)}{(1 mol/lom)^2} = 3.24 \times 10^{-18} \quad (12)$$

When the option of squaring {2} the denominator is now taken,  $K_{eq}$  comes out as a dimensionless constant; the numerical value  $3.24 \times 10^{-18}$  emerges in either case.

Original determination of pH was evidently an indirect procedure. From such statements as: "The primary standard for measurement of  $H^+$  ion concentration (and thus of pH) is the hydrogen electrode." And "The electromotive force at the electrode responds to the equilibrium  $H_2 \leftrightarrow 2H^+ + 2e^-$  and can be used to calculate the  $H^+$  ion concentration."<sup>[1]</sup> It can be surmised that  $[H^+]$  is actually measured, and from this the ion product, the equilibrium constant, and then pH are determined.

(However, another text <sup>[2]</sup> seems to indicate that it is the equilibrium constant for the dissociation reaction which is the measured quantity, with the statement: "The equilibrium constant for this reaction has been accurately measured and at 25° has the value  $1.8 \times 10^{-16}$ ." Then from this the ion product, the ion concentrations, and pH are derived.)

In any case, the values obtained for  $K_{eq}$  (water) in the standard derivation obviously do not comport with the empirical values for the respective  $H^+$  and  $OH^-$  concentrations when proper attention is given to the physical dimensions of the relevant quantities.

The consequence for the pH scale is as obvious: With  $K_{eq}$  correctly determined at  $3.24 \times 10^{-18}$ , and the respective ion concentrations at  $1.8 \times 10^{-9}$  (essentially in moles/mole), a pH of 'neutral' should not be assigned the value of "7"; rather the value for neutral of

$$pH_{neutral} = -\log(1.8 \times 10^{-9}) = 9 - .2553 = 8.7447 \quad (13)$$

would be the more appropriate figure (though the odd number 8.7447 for neutral strongly suggests the need to adjust the scaling of pH itself). Expression of the ion concentrations in the implied dimensionless moles/mole also has the advantage of rendering a pure number for this quantity, rather than the traditional concentrations of moles/liter --as logarithms of dimensioned quantities,

strictly speaking, do not exist. That confusion with the numbers persists even among professional chemists may be evidenced in their own texts: In at least one edition of a standard textbook in widespread use [3] in whose section on acids and bases, the statement is made that a  $pH = 7.0$  (neutral) for water signifies that "one in ten million" molecules have dissociated into  $H^+; OH^-$  ions. This figure neglects division by the number of moles in a liter, which means that *one in 555 million* molecules have dissociated. Even the august and authoritative Harper's Biochemistry, after rightly stating that the actual probability of a hydrogen atom in pure water existing as a hydrogen ion is " $1.8 \times 10^{-9}$ ", proceeds with the sentence: "Stated another way, for every hydrogen ion and hydroxyl ion in pure water, there are 1.8 billion or  $1.8 \times 10^9$  water molecules." [4]. In fact,  $1.8 \times 10^{-9}$  means that for every hydrogen ion, the number of water molecules is *555 million*. Thus both references are off (though in opposite directions) by the same factor. Further evidence of confusion in ionization quantities may be found in...

Thus far, the consequences of this re-evaluation should not have any great immediate practical impact in the laboratory (chemistry relying heavily on empiricism), although for the purely scientific understanding of the underlying physics it should be worthy of consideration. In fact, if it were all merely a matter of scaling, this would not be a very strong argument for changing the convention –once instituted, any practicable system, even though awkward or cumbersome, is best kept in its original working order. However, several potentially serious calculative inaccuracies can be discovered in the determination of  $pH$  and related quantities, which together merit reformulation of the basic equilibrium equations.

## 5. Calculative Inaccuracies

In addition to the confusion over units and dimensions of chemical quantities, three specific and immediate numerical inaccuracies occur in the equilibrium calculations. These may be identified respectively as:

1. "The Displacement Disaster"
2. "The Concentration Catastrophe"
3. "The Alkaline Calamity"

The 'Displacement Disaster' is a direct consequence of the neglect to include the concentration of water [ $HOH$ ] in the denominator of the ionization equation. Not only are the aforementioned physical objections pertinent, but also [ $HOH$ ] cannot remain at its 'pure' value  $c = 55.5 \text{ moles/liter}$ . Rather, some of its volume must be displaced by the presence of solute in the liter of solution. This reduces the number of moles of water remaining to  $c' < c$ . This in turn must alter the value of the ion concentrations if the equilibrium constant is to maintain its integrity. **For example, the ionization constant for acetic acid is found to be**  $K_a = 1.754 \times 10^{-5}; 1.8 \times 10^{-5}$  (from  $pK_a = 4.756$ ).<sup>5</sup>

A 10% solution (by weight) of this substance is 1.685 molar, and the specific gravity is 1.0121. Therefore one liter of this solution will weigh 1,012.1 grams, and the remaining 90% mass of water will be 910.89 grams, which will comprise 50.6 moles

$HOH$ . If the equation  $K_a = \frac{[H^+][A^-]}{[HA][HOH]}$  incorporates this figure, [ $HOH$ ]' =  $50.6 \text{ mol/lit}$ , into the denominator, the result will deviate somewhat from that obtained with the standard [ $HOH$ ] =  $55.5 \text{ mol/lit}$  in the denominator. Reverting for the moment to the traditional expression of  $pH$ , when these quantities are rationed into the customary dissociation equation (where 55.5 moles/liter is taken as 'unit'  $HOH$  concentration) the ratio of the difference may be found from:

$$K_a = \frac{[H^+][A^-]}{[HA] \cdot (50.6/55.5)} \quad ()$$

The [ $H^+$ ] ion concentration for this solution will be found to be  $5.19 \times 10^{-3} \text{ mol/lit}$ , which will compute to  $pH = 2.2847$ . By contrast, the customary 'unit' concentration of  $HOH$  in the denominator will yield [ $H^+$ ] at  $5.43 \times 10^{-3} \text{ mol/liter}$  and  $pH = 2.2647$  -- a small but not insignificant difference. As the concentration of acetic acid is increased, this difference becomes ever more pronounced, such that for extremely high concentrations, the two computations bear no semblance to one another, owing to the great displacement of water out of the liter of solution. Although this degree of 'disaster' does not occur for dilute solutions, there is nevertheless a definite inaccuracy involved for any concentration; the physics of the chemistry is not adequately represented.

Another inaccuracy involving  $pH$  results from the 'Concentration Catastrophe':

In that the equilibrium constant for ionization reactions is calculated from the respective concentrations of solute and ions in aqueous solution, the various ion concentrations may conversely be calculated from the ionization constant and concentration of solute. When a representative weak electrolyte,  $HA$  (hydrogen and conjugate base), forms an aqueous solution of a given concentration, the value for the ionization constant  $K_a$  is customarily stated by the general equation:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ()$$

where the brackets [ ] denote concentrations in moles per liter (and the constant concentration of  $H_2O$  in itself is omitted from the denominator). Since in the case of simple solutions, overall electrical neutrality is maintained by *equal* concentrations of cation  $H^+$  and anion  $A^-$ , (ignoring, for the moment, the minute ion contributions from water) the individual concentrations of either ion may be found from:

$$[H^+] = \sqrt{K_a[HA]} = [A^-] \quad ()$$

If this equation is taken literally, a calculative catastrophe will result for very low concentrations of  $HA$ . For example, when  $[HA] = K_a$  numerically,  $[H^+], [A^-]$  will each become equal to  $[HA]$ , meaning that the solute must be completely dissociated at this concentration. If the concentration were then reduced by the addition of more solvent ( $HOH$ ), the ion concentrations

would calculate to a value greater than the solute  $[HA]$  concentration: e.g., for  $[HA] = K_a/4$ , the individual ion concentrations,

$$[H^+] = [A^-] = K_a/2 = 2[HA] \quad (0)$$

constitute a quantity of solute greater than that originally dissolved! Obviously, the equilibrium equation is incorrect; its presented form in fact demands either that:

- the ionization 'constant' varies directly with the concentration of solute, or
- ion concentration is dependent upon the square of the solute concentration in the denominator.

But since there is no experimental support for either contention, the error in fact results from the failure to subtract the concentration of the ionized portion of the solute  $[H^+]$ , (or  $[A^-]$ ), from the original non-ionized concentration  $[HA]_0$  in the denominator—thus the remaining non-ionized solute concentration  $[HA]' = [HA]_0 - [H^+]$  will quantitatively alter the customary equilibrium relation to read:

$$K_a = \frac{[H^+][A^-]}{[HA]_0 - [H^+]} \quad (0)$$

which will produce a quadratic solution to the ion equation:

$$[H^+] = \sqrt{K_a[HA]_0 + \frac{K_a^2}{4}} - \frac{K_a}{2} \quad (0)$$

Again, a small but non-trivial difference is rendered by this adjustment; a 0.001 molar solution of acetic acid will now calculate to  $[H^+] = 1.25 \times 10^{-4} \text{ mol/lit}$ , whereas the unadjusted value would calculate to  $[H^+] = 1.34 \times 10^{-4} \text{ mol/lit}$  -- a discrepancy which however increases drastically with greater dilution. (In truth, the above correction may be applied to the dissociation equation for pure water, whereby

$$K_{eq} = \frac{[H^+][OH^-]}{[HOH] - [H^+]} \quad (0)$$

whose solution for  $[H^+], [OH^-]$  will differ minutely from that of eq. (?); this correction, however, will not herein be regarded as significant.)

A third inaccuracy in  $pH$  determination is found to occur also in very dilute solutions, or very weak electrolytes: when the solution is acidic, the 'Alkaline Calamity' results (and when the solution is basic, an 'acidity calamity' would result).

For example, if a weak electrolyte such as Boric Acid, ( $K_a = 6.4 \times 10^{-10}$ ) is diluted to a concentration of  $\frac{1}{6.4} \times 10^{-4}$  molar, the solution should have  $[H^+] = \sqrt{K_a[HA]} = 10^{-7}$ ; with  $pH = 7$ , the solution should be neutral. Thus when the concentration is less than  $\frac{1}{6.4} \times 10^{-4}$  molar, the  $pH$  will calculate to a number greater than 7, and the acid solution will be assessed as alkaline! The inaccuracy is due to neglect to include the concen-

tration of  $[H^+]$  from water alone (already  $10^{-7} \text{ mol/liter}$ ) in the calculation. Though the discrepancy is small for moderate concentrations, it becomes a calamity for sufficiently low concentrations; **Therefore, it is necessary to include the 'water term' in the conventional ionization equation:**

$$[H^+] = \sqrt{K_a[HA]} + 10^{-7} \text{ mol/liter}$$

from which the corresponding logarithm may be taken to find the actual  $pH$ . (In the process, the  $[OH^-]$  concentration will be reduced to satisfy the equilibrium of water, i.e.  $[OH^-] = \frac{K_{eq}}{[H^+]}$ .)

These inaccuracies are ordinarily very slight numerically, and may even be ignored in some situations. Nevertheless, they could lead to a serious error in other situations. Furthermore, their omission in the elucidation of the chemical relations severely distorts the underlying physics—without which the chemist is reputedly "nothing".

Therefore, it shall be most prudent to the interests of science to re-formulate the equilibrium relations with these points in mind, and to include such in future textbook expositions of the subject, if not for need of complete accuracy of the chemistry, certainly for the full understanding of the physics.

## 6. Corrected Equilibrium Equation

To compose the fully adjusted equilibrium equation, first the concentration of solvent  $[HOH]$  must be included in the denominator. This quantity can only be determined experimentally, due to unknown factors in the volume displacement by the solute. As in the acetic acid example employed above, the specific gravity of a solution of known molarity must be measured, along with the precise quantity of solvent added to produce a liter of solution. Once this is accomplished, the concentration of solvent (now distinguished with primed notation  $[HOH]'$ ) can be determined.

Second, the quantity of dissociated solute must be subtracted from the original solute concentration to render the concentration of undissociated solute:  $[HA]' = [HA]_0 - [H^+]$ , so that  $[HA]'$  can now be placed in the denominator.

Third, the "water factor" must be included in the equation, to render an accurate assessment of the total hydrogen (or hydroxyl) ion concentration in the solution.

When these adjustments are included, the ionization equation will take the form:

$$K_a = \frac{[H^+][A^-]}{[HA]'[HOH]'} \quad (0)$$

where  $K_a$  is now a dimensionless constant, and from which, with the inclusion of the 'water factor', the actual ion concentration may be accurately determined:

$$[H^+] = \sqrt{K_a[HA]_0[HOH]' + \frac{(K_a[HOH]')^2}{4}} - \frac{K_a[HOH]'}{2} + (10^{-7} \text{ mol/liter}) \quad (0)$$

A reformed  $pH$  value may hence be obtained by taking the common logarithm of the above result. This value would differ from that previously suggested (eq. ( )) by only a small amount under ordinary circumstances, since the revised concentration of water is only slightly altered by low to moderate concentrations of solute (one molar or less). However, for very high concentrations of solute, the water factor becomes critical; and for very low initial concentrations of solute, the remaining solute concentration becomes critical, as does the added ion concentration from the water itself. Thus, only for moderate solute concentrations, do the inaccuracies fortuitously tend to cancel.

{The above equation may be 'rationalized' into the customary quantification by division of the  $[HOH]'$  term by the ordinary concentration of water (55.5 moles per liter) throughout; the result will differ proportionately from the traditional calculated ion concentration.}

In either case, the reformed expression is considerably more complex, such that its use might be found unnecessary in many ordinary applications; nonetheless, all chemists should at least be introduced to the reforms, and the physics underlying them.<sup>ii</sup>

Titration, Buffers and the Henderson-Hasselbalch equation.

The inaccuracies, which have been documented thus far for simple solutions of a single solute (acid or base) in water, persist in cases of complex solutions—those which have been created by titration of a simple solution with a respective base or acid, or by the equivalent addition of a salt. For these types of solutions, a general form of eq. (11) is employed. In the case of an acid solution the hydrogen ion concentration is calculated from the final acid concentration and the total anion concentration:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \quad ( )$$

This results in the Henderson-Hasselbalch equation for  $pH$ :

$$pH = -\log[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]} = pK_a + \log \frac{[A^-]}{[HA]} \quad ( )$$

Although reasonably accurate for solutions in which the total additional anion concentration (from a salt) is much larger than the original acid anion concentration, an inaccuracy is introduced by the neglect to include this factor, along with the failure to adjust for the change in acid concentration, water concentration, and the contribution of water to the total hydrogen ion content. When eq. ( ) is employed in constructing a precise form of the Henderson-Hasselbalch equation, in which  $[A^-]_a$  refers to the acid source anion concentration, and  $[A^-]_s$  refers to the salt source anion concentration, the result will take the form:

$$pH = -\log K_a - \log \frac{[HA]}{[A^-]_s} - \log \frac{[HA]}{[A^-]_a} \quad ( )$$

where  $[A^-]_a$  is numerically equal to the original non-buffered  $[H^+]$  concentration as rendered by eq. ( ).

<sup>ii</sup> Subtraction of  $H^+$  ion from  $HOH$  in denominator of water equilibrium?

$$[A^-]_a = [H^+] = \sqrt{K_a[HA]_0[HOH]' + \frac{(K_a[HOH]')^2}{4}} - \frac{K_a[HOH]'}{2} + (10^{-7} \text{ mol/liter}) \quad ( )$$

from which the actual  $pH$  is found by taking the common logarithm.

A graphic textbook example of compounded inaccuracy resulting from the 'standard' equations may be found in (Conn & Stumpf, p. 21):

The practical problem of preparing 1 liter of 0.1M acetate buffer, with a prescribed  $pH$  of precisely 5.22 is proposed. The ratio of total acetate ion to conjugate base is first calculated from the H-H equation, where

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} \quad 5.22 = 4.74 + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \text{anti log}(5.22 - 4.74) = \text{anti log} 0.48 = 3$$

Thus, the molar ratio of acetate ion to acetic acid in this solution should be 3 to 1, or 75% to 25%. "Since 1 liter of 0.1M acetate buffer will contain 0.1 g mole of acetate (ion) and acetic acid combined, 0.75 X 0.1 or 0.075 mole of acetate ion will be present."

"This amount of acetate ion is contained in 6.15 g of sodium acetate. The acidic component will, of course, be 0.25 X 0.1 or 0.025 mole of acetic acid, which amounts to 1.5 g of acetic acid. When mixed with sodium acetate in final volume of 1 liter, this amount of acetic acid will give a liter of buffer of the desired  $pH$  and concentration."

But then the text somewhat remarkably declares:

"It is an experimental fact that when such a solution is carefully prepared and its  $pH$  is measured accurately with a  $pH$  meter the observed value will not be 5.22." (italics added)

The discrepancy is then attributed to the *activity coefficients* of the components of the solution, which differ from their actual concentrations. Such calculative errors are thus generally accounted for; but might not the mysterious 'activity coefficients' really be the result of wrongly formulated equations? If the various quantitative corrections are employed in composing a reformed H-H equation, a slight, but significant, difference in the calculated  $pH$  would result in the above example—(etc.)

Another distortion of the actual physical relations occurs in the assessment of the 'maximum buffering action' of a given buffer in solution. The standard titration curve {figure 1} seems to indicate that the greatest resistance to alkalization of an acid solution occurs somewhere mid-range in the relative concentrations of remaining acid and buffering salt, as a result of titration with a strong base. This is claimed to be an obvious conclusion from the general shape of the titration curve itself: its slope appears indeed the most gradual in the mid-range of the respective concentrations. But this particular slope is merely an artifact of the *logarithmic* scaling of the actual hydrogen ion concentration. Without this artifice, the titration curve of the  $H^+$  itself concentration would appear in the general form of {figure 2}. Here it is evident that the resistance to alkalization is greatest at the very beginning of the titration process, when the acid concentration is

greatest. (But it is also to be noticed that the resistance to acidification by addition of a strong acid would be greatest when the original acid concentration is least, i.e., near the end of the titration with the base.) In support of this observation, it is merely necessary to point out that the scaling convention, though useful, is entirely arbitrary: instead of taking  $\log H^+$ , for example, one could instead impose a function such as *hyperbolic arctan*  $H^+$ . This would result in a different form for the resulting titration curve. By selecting any function of choice by which to scale the "pH", the 'maximum buffering action' (least slope) could be located anywhere along the titration process.

## 7. Conclusion

All of the foregoing argues for a thorough reformulation of the equilibrium relations, and a reformation of the 'pH' scaling system. The dimension error resulting from the failure to represent properly the concentration of solute in the denominator of the equilibrium and H-H equations, constitutes a most serious conceptual inadequacy, and misrepresents the physics behind the chemistry. The three enumerated 'calculative inaccuracies' conspire to yield faulty quantitative results, which are particularly serious for extremely dilute and extremely concentrated solutions of electrolytes. Although for many practical purposes, the results are sufficiently accurate for general laboratory application, in certain circumstances the discrepancies could have critical consequences—especially in biomedical applications. In any case, the student of equilibrium chemistry will emerge from study with a faulty conception of how things actually work in acid-alkaline relations, if measures are not taken to correct the presentation of the subject matter. Hence it is urgent that a new quantification scheme be considered to this end. Such is offered in the Appendix.

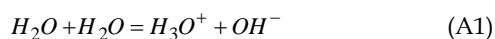
## 8. Appendix

### 8.1. Reformulated Quantification Schedule for Equilibrium Relations

In that error has been discovered in the traditional equilibrium relations (corrected by reforms of the type previously suggested), an opportunity for thorough overhaul of the scaling of "pH" and related quantities presents itself on this occasion. That is, since the numbers are generally incorrect already, a new quantification schedule is in order: one that is not only numerically accurate, but chemically sensible as well as physically sound.

### 8.2. Physics of the Chemistry

To begin with, the basic chemical equation must be completed to describe the actual physics of dissociation accurately. In the basic case for pure water:



[In reality, ions form with multiple  $H_2O$  complexes—but the physics is essentially the same as eq. (A1); subsequent appearance of  $H^+$  in the equations will be understood to represent  $H_3O^+$  etc.] The second  $H_2O$  quantity on the left is necessary to signify that water reacts with itself; its role in the equilibrium

equation changes the value of the equilibrium constant (now ' $K_{eq}$ ') and ensures that it is dimensionless:

$$'K_{eq}' = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]} = 3.24 \times 10^{-18} \quad (A2)$$

### 8.3. Reform Schedule

A simple, if tentative, reform of the 'pH' system for solutions in general may then be based upon two adjustments:

1. Inclusion of  $[H_2O]$  in the denominator of all ionization equations.
2. Correction for the 'egregious error' in the quantification of non-unimolar solutions.

The first adjustment is based upon the concentration of water in itself as a truly universal constant,  $[H_2O] = 55.5 \text{ mol/lit} = c$ ; all dissociation equations must carry this term in the denominator to indicate that the solute *reacts* with the solvent. The second adjustment factors in the proper molarity-specific value ' $K_a$ ' for the ionization constant, as obtained in the preceding paper. These adjustments produce a reformed ionization equation:

$$('K_a')_n = \frac{[H^+]_n[A^-]_n}{[HA]_n[H_2O]} = n(K_a)_1 \quad (A3)$$

where  $n$  is the number of moles per liter and  $(K_a)_1$  is the traditional value for the ionization constant, valid for unimolar solutions only.

### 8.4. A Molal Standard

In the formative part of this paper, a special unit of volume, the "lom", was introduced to elucidate the confusion arising from the capricious appearance and disappearance of the 55.5 moles/liter in the course of the standard calculations. The "lom" is special in that it contains precisely 1 mole of  $H_2O$ , hence a system may be devised incorporating this unit, which, by unambiguously accommodating the troublesome 55.5 into the equations, eliminates the need for recurrent division and multiplication by this term. This procedure will also confirm a proper value for ' $K_{eq}$ ' at the dimensionless  $3.24 \times 10^{-18} \text{ moles/mole}$ , since this constant is the molar ion product of water divided by  $(55.5 \text{ loms/liter})^2$ , in turn divided by the square of the unit  $1.0 \text{ mol/lom}$  concentration of water. [The equilibrium constant, and ion product, for water (or for any other solvent) are truly universal constants, since the concentration of any substance *in itself* is necessarily unchangeable.]

With this background, a new "isomolal" system may be devised, based upon the concept of *molality* of solutions and concentrations rather than *molarity*:

First, let the concentrations of all substances be expressed in dimensionless units of moles solute/mole solvent, and let this new convention be distinguished by the enclosure of the concentrated substance in the marks  $\langle \rangle$ . When 1 mole of solute  $S$  is dissolved in 1 mole solvent, it shall be designated as a "one isomolal" solution, identified by the symbol  $\mu$ ; e.g., 1 mole  $S$  dissolved in 1 mole  $H_2O$  shall be written  $\langle S \rangle = 1.0\mu$ , signifying

that the concentration of solute  $S$  is *one isomolal*. This convention is advanced for its purely *theoretical* utility: such high concentrations are generally not practicable in the laboratory, but it is a very convenient basis for representation of the physical reality of solution dynamics. In practice, chemists might commonly speak of concentrations in “*millimolal*” terms; e.g.,  $0.017\mu = 17m\mu$ .

Second, whereas acidity (or alkalinity) is traditionally reckoned from the molar concentration of  $H^+$  (or  $OH^-$ ) ions (the square root of the ion product for dilute solutions of weak electrolytes), in the reformed system it shall be reckoned instead from the *ratio* of *molal*  $H^+$  to  $OH^-$  ion concentrations in solution. This defines the “ion quotient”  $Q_i$  of the ionized solution:

$$Q_i = \frac{\langle H^+ \rangle}{\langle OH^- \rangle} \quad (A4)$$

Third, the scaling, or “ $qH$ ” (which shall replace the traditional “ $pH$ ”) of the solution shall be accomplished by taking the *positive natural logarithm* of the ion quotient:

$$qH = \ln \frac{\langle H^+ \rangle}{\langle OH^- \rangle} = \ln Q_i \quad (A5)$$

Then, the acidity, or  $qH$ , of pure water (or any neutral solution) now becomes

$$qH_{neutral} = \ln \frac{1.8 \times 10^{-9}}{1.8 \times 10^{-9}} = \ln 1 = 0 \quad (A6)$$

The advantage here should be obvious: the number “7” (which is after all only approximate) conveys no sense of neutral, whereas the number “0” (which is here axiomatically exact) communicates a natural sense of neutrality.<sup>iii</sup> A schedule for assessment of the new quantities, and their relations to the old, may hence be developed: (etc.)

## References

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<sup>iii</sup> The common logarithm function might, however, prove more practicable to chemists in this situation.