

Errata (2020 Dissertation)

Michael J. Braus, Ph.D.

2021-05-01

*My doctoral dissertation, completed at the UW-Madison from 2016-2020, was heavily negatively influenced by the interfering SARS-CoV-2 pandemic **response** from approximately March 2019 to June 2020. What resulted during that period were the oversight—on the part of both myself and my doctoral committee—of a number of typos in that document, which was archived for public use in August 2020. These irritating errors were wholly benign and collectively posed zero threat to the findings of the research, but, in the interest of completeness, accuracy, and precision, I have listed below their respective errata. Each item reports the page number according to the pagination of the original dissertation document, followed by the correction.*

All figures and tables required no corrections. However, because Appendix A was not proof-read to the same level of rigor as the body of the dissertation, that appendix has been revised and reprinted here in full, then the list of errata continues for Appendices B and C.

~ M.J.B.

Title Page & Table of Contents

NO ERRATA

0.1 Abstract & Acknowledgements

NO ERRATA

1 Introduction (Errata, 2021)

Pagination 2: The word 'bewteen' should be written 'between'.

Pagination 5: The first sentence of section 1.4 that reads, 'A model is only as applicable as its assumption allow,' should read instead, 'A model is only as applicable as its assumptions allow.'

2 Standard and Non-Standard Measurement of Acidity in Wisconsin's Soils. I. Is 'Soil pH' a Dilution or a Delusion? (Errata, 2021)

Pagination 8: To agree with the remainder of the paragraph it begins, the sentence, "The techniques for measuring 'pH' are by definition applied to solutions of ionic strength (I_s) greater than 0.1 molar..." should read "The techniques for measuring 'pH' are by definition applied to solutions of ionic strength (I_s) less than 0.1 molar..."

Pagination 9: The phrase term "assistantcs" in the sentence containing the phrase "coined the term 'pH' in 1909..." should be spelled "assistants".

Pagination 18: The word "sampels" should be spelled "samples".

Pagination 29: The sentence ending, "... much in the same manner as a titration curve will reach an infelction point," ought to read, "... much in the same manner as a titration curve will reach an inflection point."

Pagination 32: The paragraph ending, "... and the pH of these extracts would greatly complement or even replace standards soil pH values," ought to read, "... and the pH of these extracts would greatly complement or even replace standard soil pH values."

Pagination 34: At the top of the page, the term "astiobiology" ought to be spelled "astrobiology".

Pagination 37-40: The "three other ratios" referring to "water:soil" in these captions ought to be reversed (e.g. "1 : 2" in place of "2 : 1") to accurately reflect what is correctly depicted in the vertical axes of these supplemental figures.

3 Standard and Non-Standard Measurement of Acidity in Wisconsin's Soils. II. Do Bacterial Communities Correspond with Soil pH or Not? (Errata, 2021)

Pagination 43: The sentence continuing at the top of the page ending, "... and 4 : 1 water:soil ratio," ought to read, "... and 1 : 4 water:soil ratio."

Pagination 46: The second sentence of the Results section uses the phrase, "but to a lesser degrees ..." but this ought to read, "but to a lesser degree ..."

Pagination 50: Akin to the error on pagination 43, the sentence beginning, "However, the further concentration of analyte beyond a 4-to-1 water-to-soil ratio ..." ought to read, "However, the further concentration of analyte beyond a 1-to-4 water-to-soil ratio ..."

4 Acidity as Proticity in Soils, Blood, and Brines with Theory and Evidence for Temporal Bond State Dynamics (Errata, 2021)

Pagination 56: The parenthetical '(see Appendix C)' should read '(see Appendix B and C)'. Appendix B provides the translation, whereas Appendix C provides a guide to that work's notation.

Pagination 58: The sentence reading, 'What if we considering water a reactant with other reactants in the mixture, with no "solvent" or "solutes" whatsoever?' ought to read, 'What if we consider water to be a reactant along with other reactants in the mixture, with no "solvent" or "solutes" whatsoever?'

Additionally, the question and sentence reading 'Would not the net charge travel as current through the mildly conductive solvent and reach far more rapidly than even on of the diffusing chloride ions? Such questions—be they for research or teaching—require an new and more apt mental model to embrace physical reality' ought to read, 'Would not the net charge travel as current through the mildly conductive solvent and reach me far more rapidly than even one of the diffusing chloride ions? Such questions—be they for research or teaching—require a new and more apt mental model to embrace physical reality.'

Pagination 60-61: The sentence, 'I believe that most the questions above are scientific questions wrapped in a pedagogical questions, so one must answer both questions to answer either' should instead read, 'I believe that each of the questions above is a scientific question wrapped in a pedagogical question, so one must answer both questions to answer either.'

Pagination 61: The reference reading, 'Silverstein, from his works spanning almost two decades from (2000, 849–50) to (2014, 608–10), appraised the "quarterback" model, ...' should instead read, 'Silverstein, from his works spanning almost two decades from 2000 (pgs. 849–50) to 2014 (pgs. 608–10), appraised the "quarterback" model, ...'

Pagination 62: The sentence ending, '... for logarithmic transformation to calculate pKA' ought to end, 'for logarithmic transformation to calculate pK_a .' Though extremely similar in typeset form, the remaining instances of the variable 'Ka' ought to have rendered more correctly as ' K_a '.

Pagination 63: The sentence beginning, 'This model does not adapt to the situation wherebe a reactant is the same as the solvent ...' should begin, 'This model does not adapt to the situation whereby a reactant is the same as the solvent ...'

Pagination 66: The sentence beginning, 'In other words, postive charge density flows ...' should read 'In other words, positive charge density flows ...'

Pagination 70: Where the text reads, 'Every molecule would then have a lifetime in the solution composed of dynamic protic bond states as they interact, which together emerge as acidity,' the text ought to read, 'Every molecule would then have a lifetime in the solution composed of dynamic protic bond states as they interact, which together emerge as acidity.' On the last paragraph of this page, the word 'extrenal' ought to be 'external'.

Pagination 71: The term 'equilibrated' ought to have been spelled correctly as 'equilibrated'.

Pagination 72: The parenthetical expression ' $(V_M/2)$ ' ought to read ' $(V_m/2)$ ', where V_m represents the maximum rate of protonation in the system.

Pagination 74: The term 'borwn' ought to be 'brown'.

Pagination 77: The description reading, 'Acidity, as detected simultaneously by both an acidity-sensitive and two glass microprobes ...' ought to read, 'Acidity, as detected simultaneously by both an acidity-sensitive dye (thymol blue) and two glass microprobes ...'

5 The Iplate Suite: Affordable and Customizable Implementations of Ichip Technology (Errata, 2021)

NO ERRATA

6 Concluding Remarks (Errata, 2021)

NO ERRATA

7 Appendices

7.1 Appendix A (Revised April 2021)

This appendix is intended to convey the seriousness with which it must be communicated that the metric for acidity called "pH" does not apply to many of the systems where it is measured. pH values cannot be measured among solutions of ionic strength greater than 0.10 moles per liter (100 millimolar) or otherwise exhibit ionic activities diverging from ionic concentrations, and I have listed below the many references throughout the 20th century that define the adherence of "pH" to this dilute solution assumption. Each of the following subsections is a direct quotation, and the subheading provides each passage's citation, all of which are listed in the list of references. ~ MJB

7.1.1 Bjerrum and Gjaldbæk (1919, 17), translated by J. K. Rundo at the Atomic Energy Research Establishment (Harwell Laboratory, Oxfordshire, 1956)

It is now required to use the values of pH in Table 4 to calculate K . We shall first show how one can obtain an approximately correct result by using equation (5) and putting $\text{pH} = -\log C_{\text{H}^+}$. Taking logarithms in equation (5) and putting in pH we obtain

$$-\log K = \text{pH} + \frac{1}{2} \log C_{\text{Ca}^{++}} + \frac{1}{2} \log p_{\text{CO}_2} \dots \quad (14)$$

The calculation of $\log p_{\text{CO}_2}$ does not present any difficulties. On the other hand by calculating the calcium ion concentration we cannot just set this equal to the concentration of the calcium chloride since, as known, calcium carbonate in the presence of carbon dioxide dissolves slightly as bicarbonate. It is however easy to calculate the amount of the dissolved calcium carbonate from Schlösing's measurements of the solubility of calcium carbonate in water at different carbon dioxide pressures. Bodlander has given the theory for Schlösing's measurements. In the following we give a new calculation of Schlösing's measurements since this has become necessary by our altered views in recent times of the activity conditions of ions.

In a solution which is saturated with calcium carbonate at a definite carbon dioxide pressure there must be equilibrium between the bicarbonate ions on the one side and the carbon dioxide and the solid calcium carbonate on the other side according to the equation:



Where we ignore the change in the activity of the water, which is very small in the dilute solutions under consideration here, the law of mass action gives

$$\frac{a_{\text{Ca}^{++}} \cdot a_{\text{HCO}_3^-}^2}{p_{\text{CO}_2}} = K' \dots \quad (15)$$

* * *

7.1.2 Debye and Hückel (1923, 197), translated by Michael J. Braus (2020)

Theorem 1.

For all electrolytes, in the limit for low concentrations, the percentage deviation of the freezing point depression from the classical value is proportional to the square root of the concentration.

It is possible to state this law as a general law because all the electrolytes for large dilutions can be considered as completely dissociated into ions. Of course, only the strong electrolytes practically reach that area of complete dissociation.

Secondly, equation (39) makes a statement about the influence of ion valence, which can be formulated as follows:

Theorem 2.

If the dissolved molecule dissociates into $\nu_1, \dots, \nu_i, \dots, \nu_s$ different ions of types 1, \dots, i, \dots, s with the valences $z_1, \dots, z_i, \dots, z_s$, then, for low concentrations, the percentage deviation of the freezing point depression from the classical value is proportional to a valence factor w , which is calculated from

$$w = \left(\frac{\sum \nu_i z_i^2}{\nu_i} \right)^{3/2}.$$

As an example for the calculation of this valence factor, Table 2 is presented, where in the left column an example of the type of salt is given, and in the right column the value of w is given:

The influence of the ions therefore increases considerably with increasing valence, which also corresponds to the qualitative findings.

Thirdly, the solvent has an influence, in the sense of Nernst's well-known suggestion for explaining the ionizing force of solvents with a high dielectric constant. Following equation (40), one finds

Theorem 3.

For low concentrations, the percent deviation of the freezing point depression from the classical value is inversely proportional to the 3/2th power of the dielectric constant of the solvent.

* * *

7.1.3 MacInnes (1939, 148)

General Remarks Concerning the Debye-Hückel Theory. Experimental studies concerning the validity of the Debye-Hückel theory have been made using freezing-point data, measurements of the solubilities of electrolytes, and the results of determinations of the potentials of concentration cells. The discussion in this book will be limited to the last of these methods since the interpretation of the first two types of data will be considered, somewhat arbitrarily, to be outside the field of electrochemistry. Although the interionic attractions postulated in the theory would be expected to exist at all concentrations in solutions of ions, and to be even more effective in determining the properties of such solutions at high concentrations than in dilute solutions, the validity of the theory as developed in the preceding pages is limited to dilute solutions. At higher concentrations various complicating effects must be considered. For instance there is probably a change of the dielectric constant of the solvent, due to the presence of the charged ions. Also the mathematical approximations that were made in the derivation as given must be considered in connection with the range of applicability of the theory to actual solutions.

There is no detail of the derivation of the equations of the Debye-Hückel theory that has not been criticized. Its incompleteness mathematically is evident, since only the first term of the expansion of equations (3) and (29) is used. The extensions of the theory to overcome this deficiency are, however, briefly considered below. A possibly more serious deficiency of the theory as given is that it does not take account of "fluctuation terms." This amounts to the statement that the Boltzmann equation does not yield a correct average potential if, this being subject to wide variations for which allowance should be made in the theory.

* * *

7.1.4 Ashcraft (1947, 29)

DISCUSSION

Mr. Martin Kilpatrick – There are four things that I should like to point out:

1. Assigning a value to f_{H^+} on the basis that $f_{\text{K}^+} = f_{\text{ce}^-}$ is reasonable when the solvent salt is largely potassium chloride. When the solvent salt is largely sodium chloride or sodium acetate or other solvent salt the assumption is no longer correct.
2. The Lewis rule that a given ion has the same activity coefficient in all solutions at the same ionic strength is only true as a limiting law, that is, as one approaches infinite dilution.
3. In 1926 it was shown that measurements of cells with or without liquid junction do not yield any information on ionic free energies. For references and discussion see Mary Kilpatrick and Martin Kilpatrick.
4. A quantity cannot be measured more accurately than it can be defined, and it is useless to talk about pH in terms of thousandths of a unit.

...

Mr. D. S. McKinney. – ... The points mentioned by Mr. Kilpatrick are, we believe, adequately discussed in the paper. It is obvious that such terms as pH or individual ion activities cannot be defined on thermodynamic grounds, without resort to some solution theory. Since our present theories are in the nature of limiting laws, exact agreement cannot be expected at finite concentrations. However, this should not prevent us from making pH measurements at higher concentrations, if such measurements serve a useful purpose.

* * *

7.1.5 Feldman (1956, 1865)

COLLOIDS AND SUSPENSIONS

The existence of the “suspension effect” on the pH of clays, soils, and ion exchange resins has been known for some time. In general, the pH of suspensions and pastes appears to be lower than the pH of their supernatant liquids.

For instance, Jenny and associates reported that a pH of 9.2 was obtained for a 10% potassium bentonite suspension, whereas a 1 to 1 potassium bentonite-water paste gave a pH of 5.8. They attributed the suspension effect to the liquid junction potential at the point of contact between the potassium chloride bridge and the suspension. As evidence, they presented the following results. For an ion exchange resin sediment in contact with its supernatant liquid, a pH of 6.0 was measured when both the glass and calomel electrodes were immersed in the supernatant, but a pH of 2.0 was indicated when the electrodes were immersed in the sediment. The e.m.f. equivalent of this pH difference, 240 mv., was obtained between two calomel electrodes when one was suspended in each phase, but when a glass electrode was suspended in each phase no potential difference existed between the two glass electrodes.

Although there is disagreement ([many references listed]) as to whether the suspension effect is due to the liquid junction potential or is a true membrane potential at a Donnan system, there is no question that the effect exists and that, as a result, pH measurements on suspensions of highly charged particles are meaningless. The effect is not significant, however, for solutions containing mobile colloidal ions or proteins of high equivalent weight because of the efficiency of the potassium chloride bridge. For instance, the author detected no difference between the pH of whole blood, the sedimented cells obtained on centrifugation, and the supernatant plasma. The meaning of the pH near cell surfaces or of dental plaques, however, may be questionable.

* * *

7.1.6 Ashcraft (1957, 3)

These fundamental applications of measured pH values are permissible for many rather dilute aqueous systems. However, there is always the temptation to extend the interpretation beyond the limited range of its validity, to systems that are not dilute or not aqueous. It must always be borne in mind that the experimental (that is, operational) pH value in such media as 50 per cent alcohol, molasses, and glacial acetic acid cannot be interpreted in terms of hydrogen ion concentration or the conventional hydrogen ion activity.

—ROGER G. BATES

* * *

7.1.7 Sena (1972), Appendix 3

pH Index

The activity of electrolyte solutions depends on the concentration of ions in them. This relationship, however, is not quite single-valued owing to the interaction between ions. For this reason concentration can serve to describe the activity of a solution only when it is greatly diluted. At high concentrations the concept of equivalent concentration is introduced, which is the product of the actual concentration and an activity factor less than unity. Since both the actual and the equivalent concentrations of ions can change within very broad limits, a logarithmic scale is used. The index measured in this scale (designated pH) is equal to the common logarithm, with sign reversed, of the activity or equivalent concentration of hydrogen ions measured in gram-equivalents per litre. Since the concentration of hydrogen ions in water (and chemically neutral solutions) is 10^{-7} , then for water $\text{pH} = 7$. In acid solutions the hydrogen ion concentration is higher, and, accordingly $\text{pH} < 7$, and in alkaline solutions, on the contrary, $\text{pH} > 7$.

* * *

7.1.8 Pourbaix (1974, 14)

When the metal forms soluble complexes of great stability with other substances (such as cyanides or ammonia), the equilibrium diagrams for the binary system metal-water must be modified: one must then take into account the equilibrium conditions of these two complexes, for example by plotting equilibrium diagrams for a ternary system. This may modify appreciably the domains of relative predominance of the dissolved species and the domains of thermodynamic stability. In these cases one must therefore be very careful, particularly because only when a dissolved species is greatly predominant, in the case of dilute solutions at least, can one assume, as has been in this Atlas, that the activities are virtually the same as the molarities.

Use of the diagrams therefore renders necessary corrections of activities with respect to molarities (or molalities): these corrections, which may be important for all the diagrams when one considers concentrated solutions, may also be important when one envisages the use of binary diagrams for studying ternary systems which involve stable complexes.

* * *

7.1.9 Volk and Rozen (1977, 1569)

Eqn. (4) allows us to calculate the analytical concentration of hydrogen ions at any point of the isotherm from the known values of $\Delta_1\text{pH}$ and $\Delta_2\text{pH}$. We can see from this equation that in the presence of the salting-out agent the conventional assumption that $[\text{H}^+] = 10^{-\text{pH}}$ is quite incorrect, the error increasing with $\Delta_1\text{pH}$, i.e. with the concentration and with the degree of hydration of the salting-out agent (see Fig, 2 of Ref . 1). For example, for a $2m$ solution of $\text{Ca}(\text{NO}_3)_2$ at pH 5 we find that $[\text{H}^+] = 3.05 \times 10^{-5}\text{M} \neq 10^{-5}\text{M}$ (300% error).

* * *

7.1.10 Butler (1998, 462–63)

pH in Brines: Limitations and Ambiguities

pH measurements are less certain in brines than in dilute solutions for several reasons.

- The usual pH electrode-calomel reference electrode combination does not measure hydrogen ion activity (i.e., pH) alone, but rather measures a combination of hydrogen ion activity, counter-ion activity, membrane potentials, and liquid junction potentials.
- In the standard two-electrode or combination-electrode pH setup, liquid junction potentials arise between the calibration or test solution and the salt bridge leading to the reference electrode. When the calibration and test solutions are similar in composition, the liquid junction potentials are close in value, and errors are small. If the calibration and test solutions are very different in composition, however, the difference in liquid junction potentials can also be large—introducing an error equivalent to one or more pH units.
- The standard buffers developed by the National Bureau of Standards, and widely available commercially, have much lower ionic strength (< 0.1 M) than brines (4 – 6 m), and standard buffers of composition similar to the brines are not available.
- Liquid junction potentials have traditionally been eliminated by using the a “Harned cell,” a hydrogen gas/platinum electrode with a silver/silver chloride electrode (see Chapter 2, p. 53). The Harned cell has been used to measure the activity of HCl in a wide variety of multi-component solutions, and is still the method of choice for the most accurate potentiometric measurements on acid-base systems. A variant on this theme, using a glass electrode and a chloride ion-selective electrode, has been investigated, and some of the results are described below.
- However, even a cell without liquid junction measures the combination of hydrogen and chloride activities, not the hydrogen ion activity alone. To establish a pH scale, some theoretical assumptions must be made to evaluate the activity coefficient of at least one of the ions. For the NBS scale, the Bates-Guggenheim convention 8 for the activity coefficient of chloride ion was chosen:

$$\log(\gamma_{\text{Cl}}) = -\frac{A\sqrt{I}}{1 + 1.5\sqrt{I}}$$

but this convention was not intended to apply at ionic strengths greater than 0.1. Other possibilities for calculating activity coefficients theoretically include Guggenheim’s and Pitzer’s equations, which are extensions of the Debye-Hückel theory.

* * *

7.1.11 Galster (1991, 16)

1.5.7 Activities in Concentrated Solutions

Electrolyte solutions having concentrations greater than 1.0 mol/L no longer conform to the Debye-Hückel theory, because none of the simplifying assumptions in Section 1.5.3 for dilute solutions is applicable any longer. Glueckauf and Stokes and Robinson attribute the large variations in the activity coefficients in concentrated solutions to the fact that there is no longer sufficient water present for all ions to form complete hydration sheaths. At higher concentrations further difficulties are often encountered as a result of the formation of complex compounds with differing charge numbers, so that smaller ionic concentrations are often measured than would be expected from the amounts of substance dissolved in the solution.

The increase in the activity coefficients in acid solutions corresponds to an increase in acid strengths. According to Schwabe the addition of neutral salt in the range between $b = 0.5$ mol/kg and saturation causes the pH to fall almost linearly and can be expressed by the empirical formula

$$\text{pH} = \text{pH}_0 - 5,55bz\left(\frac{h_+}{r_+} - \frac{h_-}{r_-}\right).$$

Here pH_0 is the pH with no added salt, b the concentration of added neutral salt and z the electrochemical charge number of the added salt, h the hydration numbers of the added ions and r the radius of the ions in pm plus the radius of the water molecule ($r_{\text{H}_2\text{O}} = 138$ pm). The number 5.55 is a theoretically based constant.

The factor

$$K = 5,55z\left(\frac{h_+}{r_+} - \frac{h_-}{r_-}\right)$$

represents the increase in the acidity and is characteristic of the neutral salt added.

* * *

7.1.12 Anderegg and Kholeif (1994, 1521)

CONCLUSIONS

If enough values for the examined equilibrium constants are known for a given system ($N \geq 10$), and are well distributed on the I [ionic strength] scale particularly at low I values near 0.01 to 0.1, then the problems discussed here can be treated without difficulty. When N is reduced to 5 with three points at $Z < 0.1$, the accompanying increase in error is not dramatic as far as the constants are not affected by large errors. This is the case for acetic acid but probably not for NTA. These last inconsistencies can be because of the large Δz^2 that makes ${}^*\beta_{1,0,1}$ more dependent on the I values. If the values of the constants are only known for $I \geq 0.5$, the error of ${}^*\beta_{n,p,m}^0$ can be very large but the values of the constants can be well extrapolated if they are properly distributed on the I scale.

* * *

7.1.13 Sparks (1998, 112)

Some confusion exists regarding the term “extended Debye-Hückel equation” since the more detailed equation:

$$\log \gamma_{\pm} = -Az^2 \frac{I^{0.5}}{1 + BaI^{0.5}}$$

is sometimes called the Debye-Hückel equation²⁶ in contrast to the Debye-Hückel limiting law... This equation is considered to give acceptable results to about $I = 0.1$.

The extended form of this equation:

$$\log \gamma_{\pm} = -\frac{Az^2 I^{0.5}}{1 + BaI^{0.5}} + bI$$

is considered the extended Debye-Hückel equation by Robinson and Stokes... usable to about $I = 1.0$, but this is very dependent on the mixed electrolyte under consideration.

* * *

7.1.14 Baucke (2002, 774)

The incorporation of pH values into the SI system necessitates one to state a numerical value of the uncertainty of the Bates-Guggenheim convention. This is accomplished by estimating the possible range of the conventional product $aB = 1.5$ in Eq. (6). The recommended estimate is $1.0 \leq aB \leq 2.0$ corresponding to varying the ion size parameter a from 0.3 to 0.6 nm, which yields a range from ± 0.012 (at $I = 0.1 \text{ mol kg}^{-1}$) to ± 0.007 (at $I = 0.05 \text{ mol kg}^{-1}$) for $\lg \gamma_{\text{Cl}}^0$. The 0.01 uncertainty of $\lg \gamma_{\text{Cl}}^0$ thus covers this variation Cl and must be included in the uncertainty of pH values if they are to be regarded as traceable to SI. pH values stated without this contribution to their uncertainty are conventional pH values without a numerical link to the SI system, which, however, will suffice in most cases.

* * *

7.1.15 Wright (2007, 382)

10.8 Shortcomings of the Debye-Hückel model

When the Debye-Hückel equation is tested against experimental results it is very successful in accounting for behaviour at low concentrations, and it is believed that the theory is basically correct for low concentrations (see Section 10.10). Having to test the theory rigorously at very low concentrations proved a great stimulus in developing precision techniques for deriving experimental values of γ_{\pm} . At moderate and higher concentrations deviations from theoretical behaviour become apparent, and ways of dealing with these problems are described later in the chapter.

It is constructive to look again at the physical basis of the simple Debye-Hückel model and its mathematical development to see where both could be modified, and to consider whether this would be mathematically possible. What has been written in Chapter 1 on ions and solvent structure shows that the Debye-Hückel model is painfully naïve and cannot even approach physical reality. A brief reassessment of the features 1–7 of the simple Debye-Hückel model is given below, along with indications as to how these problems have been tackled.

10.8.1 Strong electrolytes are completely dissociated

...

10.8.2 Random motion is not attained

...

10.8.3 Non-ideality results from coulombic interactions between ions

...

10.8.4 Ions are spherically symmetrical and are unpolarisable

...

10.8.5 The solvent is a structureless dielectric

...

10.8.6 Electrostriction is ignored

...

10.8.7 Concept of a smeared out spherically symmetrical charge density...

This is an absolutely crucial part of the model and has been dealt with by statistical mechanical averaging procedures. But only spherical symmetry has been assumed. And so for large non-spherical ions a modification to the smearing out procedure is needed, but see Sections 10.17.3 and 10.19.

Any one given distribution of ions around a spherically symmetrical central j-ion need not necessarily be spherically symmetrical, but on average all possible arrangements will correspond to

spherical symmetry. A charge density necessarily corresponds to an average distribution of ions, so conversion of the Poisson-Boltzmann equation to spherical symmetry is purely formal.

But as has been hinted at above, there is one important limitation to this when considering large complex electrolytes such as are found in aqueous solutions of biological materials. Here the central ion is non-spherical. An ion which is not spherically symmetrical may impose a non-spherically symmetrical distribution of charge around it, and this ought to be taken care of, but is not, in the theory. The Debye-Hückel theory can thus only be approximate for non-spherical ions.

* * *

7.1.16 de Levie (2010)

Where do those limits originate? A pH meter with an indicator electrode, plus an external reference electrode (i.e., separated from the sample solution by a liquid junction), and calibrated with the usual reference or standard buffer solutions, can only yield an approximation for $-\log(a\text{H}^+)$ as currently defined by IUPAC, for the following reasons.

- The ionic activity coefficient is, admittedly, an immeasurable quantity and therefore needs an approximation. Well beyond the estimated range of validity of the chosen Bates-Guggenheim approximation, which IUPAC set at $I = 0.1 \text{ mol kg}^{-1}$, the method becomes powerless. At $I = 0.1 \text{ mol kg}^{-1}$, it already has an estimated uncertainty of at least $\pm 10\%$.
- The measurement specifically includes a liquid junction to make the measured response maximally independent of the anions in the sample. Unfortunately, the resulting liquid junction potential is also immeasurable and can only be estimated by approximate models that neglect the difference between ionic concentration and activity.

...

Using Popper's criterion (36), the hydrogen ion activity as defined by IUPAC is not falsifiable and therefore falls outside the demarcation that separates science from non-science. That is why the problem lies with IUPAC rather than with the original Sørensen definition.

* * *

7.1.17 Spitzer and Pratt (2011, 75)

The work on the traceability and dissemination of pH is not yet complete. The Bates–Guggenheim convention is only valid at ionic strengths up to 0.1 mol kg^{-1} . For applications in clinical chemistry and in environmental samples (e.g., rainwater, seawater), pH reference buffer solutions with ionic strengths more similar to these samples are expected to improve the comparability of measurement results in these matrices. Further investigations into solution theory and into the concept of single ion activity are necessary to overcome present limitations for the primary procedure for measurement of pH.

* * *

7.1.18 de Levie (2014, 615)

To summarize, within the constraints that all measurements are restricted to samples with $I \leq 0.1$ mol kg⁻¹, $2 \leq \text{pH} \leq 12$, and $5 \leq t \leq 50$ C, the assumptions currently adopted by IUPAC are:

1. Ionic activity coefficients are fully and solely determined by the absolute ionic valency $|z_i|$ of the ions considered, and by the ionic strength $I = 1/2 \sum z_j^2 c_j$ of the solution.
2. The activity coefficient of chloride ions is given by the Bates-Guggenheim approximation with $Ba = 1.5$ kg^{1/2} in the Debye-Hückel expression, which then reads (in 10-based logarithmic format) as $\log \gamma_{\text{Cl}} = -(A\sqrt{I})/(1 + 1.5\sqrt{I})$, regardless of the nature of the counterion(s), where $A \approx 0.5108$ kg^{1/2} mol^{1/2} at 25 C.
3. Moreover, for actual pH measurements, the liquid junction potential is assumed to be constant for the cell in contact with either the sample or the two bracketing pH standards.

* * *

7.1.19 Covert and Hore (2016, 235–38)

Several models exist to describe charge distribution and electric fields at solid–liquid interfaces. One of the earliest models was proposed by Gouy in 1910 and Chapman in 1913. This model describes the distribution of charged species in the region adjacent to a surface by an exponential decay function. As an example, let us consider a negatively charged surface in contact with a dilute NaCl solution. With respect to the bulk ionic concentrations of this solution, there are, immediately adjacent to the surface, a net depletion of Cl and a net accumulation of Na . The interfacial concentrations are determined by the surface potential, Ψ_0 , that decays exponentially with distance from the surface. The characteristic thickness of this layer, termed the Debye length, is roughly given (in dilute solutions) by

$$\kappa^{-1} \approx \sqrt{(0.09\text{nm}^2\text{mol L}^{-1}I^{-1})}$$

where I is the ionic strength of the bulk electrolyte. Notice that the Debye length decreases with increasing ionic strength. This is a result of a screening of the surface charge by the mobile charges in solution, thereby decreasing the penetration of Ψ_0 . This description of the interface is appropriate for dilute electrolyte solutions ($< 0.1 \text{ mol L}^{-1}$) but is not applicable at higher concentrations. At higher electrolyte concentrations, the Stern model of the interface is more appropriate. This model considers the interface as two layers. The inner layer is characterized by contact adsorption to the charged surface of counterions in solution, and the outer layer is described by the exponential decay function of the Gouy–Chapman model. The physical size of the ions sets a lower limit on the proximity to the surface that the screening charges can inhabit. At this limit, the surface may be modeled as a capacitor—two charged plates separated by a finite distance.

* * *

7.1.20 Dobrovolskii et al. (2018, 87)

$$\text{pH} = -\log(a_{\text{H}}\gamma_{\text{Cl}})_{m_{\text{Cl}\rightarrow 0}} + \log(\gamma_{\text{Cl}})_{m_{\text{Cl}\rightarrow 0}},$$

where the component $(a_{\text{H}}\gamma_{\text{Cl}})_{m_{\text{Cl}\rightarrow 0}}$ is called the acidity function and is denoted by pa_0 .

The coefficient γ_{Cl} (see (2)) was calculated according to the Bates–Guggenheim convention:

$$\log \gamma_{\text{Cl}} = -A\sqrt{I/m^0} / \left(1 + 1.5\sqrt{I/m^0}\right)$$

where I is the ionic strength of the solution; A is the Debye–Hückel constant. Equation (3) is justified when $I < 0.1$ mol/kg.

7.2 Appendix B: Original Translation of Debye and Hückel (1923)

Pagination 107: The sentence reading, 'Please refer to Appendix B for a guide to better understanding the many symbols the authors used, some of which were endemic to Germany in the beginning of the 20th century' ought to read instead, 'Please refer to Appendix C for a guide to better understanding the many symbols the authors used, some of which were endemic to Germany in the beginning of the 20th century.'

7.3 Appendix C: Mathematical Symbols Used by Debye & Hückel (1923) (Errata, 2021)

NO ERRATA

8 References

For Appendix A (Revised, 2021)

- Anderegg, G, and S Kholeif. 1994. "The Extrapolation of Experimental Equilibrium Constant Data to Zero Ionic Strength: Critical Review and New Approach." *Talanta* 41 (9): 1507–22.
- Ashcraft, E B, ed. 1947. *Symposium on pH Measurement: Forty-Ninth Annual Meeting (1946)*. Philadelphia: American Society for Testing Materials.
- , ed. 1957. *Symposium on pH Measurement: Fifty-Ninth Annual Meeting (1956)*. Philadelphia: American Society for Testing Materials.
- Baucke, Friedrich G. 2002. "New Iupac Recommendations on the Measurement of pH—Background and Essentials." *Analytical and Bioanalytical Chemistry* 374 (5): 772–77.
- Bjerrum, N J, and J K Gjaldbæk. 1919. "Undersøgelser over de Faktorer Som Bestemmer Jordbundens Reaktion." *Den Kongelige Veterinær-Og Landbohøjskole Aarskrift*, 48–91.
- Butler, J N. 1998. *Ionic Equilibrium: Solubility and pH Calculations*. Wiley.
- Covert, Paul A, and Dennis K Hore. 2016. "Geochemical Insight from Nonlinear Optical Studies of Mineral–Water Interfaces." *Annual Review of Physical Chemistry* 67. Annual Reviews: 233–57.
- de Levie, Robert. 2010. "Potentiometric pH Measurements of Acidity Are Approximations, Some More Useful Than Others." *Journal of Chemical Education* 87 (11): 1188–94.
- . 2014. "A pH Centenary." *Electrochimica Acta* 135. Elsevier: 604–39.
- Debye, Peter, and Erich Hückel. 1923. "Zur Theorie Der Elektrolyte. I. Gefrierpunktserniedrigung Und Verwandte Erscheinungen." *Physikalische Zeitschrift* 24 (9): 185–206.
- Dobrovolskii, VI, VA Zvezdina, SV Prokunin, and AN Shchipunov. 2018. "Investigation of Metrological Characteristics of Buffer Solutions in pH Measurements." *Measurement Techniques* 61 (1). Springer: 85–89.
- Feldman, Isaac. 1956. "Use and Abuse of pH Measurements." *Analytical Chemistry* 28 (12). ACS Publications: 1859–66.
- Galster, H. 1991. *pH Measurement: Fundamentals, Methods, Applications, Instrumentation*. VCH.
- MacInnes, Duncan A. 1939. *The Principles of Electrochemistry*. Reinhold Publishing Corporation.
- Pourbaix, M. 1974. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. National Association of Corrosion Engineers.
- Sena, Lev Aronovich. 1972. *Units of Physical Quantities and Their Dimensions*. Moscow: Mir Publishers.
- Sparks, D L. 1998. *Soil Physical Chemistry, Second Edition*. Taylor & Francis.
- Spitzer, Petra, and Kenneth W Pratt. 2011. "The History and Development of a Rigorous Metrological Basis for pH Measurements." *Journal of Solid State Electrochemistry* 15 (1): 69–76.
- Volk, V I, and A M Rozen. 1977. "Interpretation of pH Measurements in Salt Solutions. I. The Influence of the Salting-Out Agent on the Determination of the Activity of Hydrogen Ions from pH Measurements (Parts I, li, and lii)." *Russian Journal of Physical Chemistry* 51 (12).
- Wright, Margaret Robson. 2007. *An Introduction to Aqueous Electrolyte Solutions*. John Wiley & Sons.