JCE DigiDemos: Tested Demonstrations

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pH Paradoxes: Demonstrating That It Is Not True That pH ≡ -log[H⁺]

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When equal volumes of 5 M lithium chloride solution and hydrochloric acid solution with pH = 1 are mixed, the hydrogen ion concentration decreases and we might presume that the solution becomes “less acidic”. But the pH actually decreases! The acidity, as measured correctly by indicators or a pH meter, increases!

This is one of several related paradoxes that exist because an alarming number of textbooks perpetuate the false claim that pH is *defined* in terms of the hydrogen ion concentration, $[H^+]$:

$$\mathrm{pH} \equiv -\log\left[\mathrm{H}^+\right] \qquad (1)$$

It is the purpose of these demonstrations to show that this equation often gives paradoxical results that are far from correct. We suggest that eq 2,

$$\mathrm{pH} \equiv -\log a_{\mathrm{H}^+} \qquad (2)$$

where a_{H^+} is the activity of the hydrogen ion, should be presented in general chemistry courses when pH is introduced, because it is consistent with the accepted definition[1] of pH in terms of the response of a hydrogen-sensitive electrode *(1).* Memorable, *concrete* examples where eq 1 fails, like the ones that follow, should be presented to show why eq 2 is necessary. Although the ionic strength of solutions and concentrations of acid used in these demonstrations are often outside of the range where IUPAC defines pH with eq 2, our goal is to produce a dramatic effect that is easily demonstrated in a classroom and demonstrates a principle that is true at *all* concentrations; that is, pH is not $-\log[H^+]$. It is true that other, operational definitions of pH are used for solutions of higher concentration. This reaffirms our point that pH cannot be defined as $-\log[H^+]$, because these operational definitions are based on cell potentials, which in turn are dependent on activities, not concentrations.

We do not advocate extensive use of activities in general chemistry courses, but we do suggest that students be aware of the errors involved when they do not use them. There are several reasons for using the correct definition of pH as opportunity to demonstrate the need for activities: (i) the definition usually comes early in the study of solution equilibrium so activities can be introduced before more approximate methods; (ii) pH is a fundamental concept that is central to acid–base chemistry; and (iii) most importantly, it is easily demonstrated that pH depends on solution properties other than hydrogen ion concentration. These properties are included in the activity, a, in eq 2. The activity is an “effective concentration” calculated by multiplying the concentration of a solute by an “activity coefficient”, usually symbolized γ, to give a quantity that more accurately represents the intensity of the chemical properties of the solute than the concentration itself does:

$$a = \gamma C$$

The name “activity” is aptly chosen for this parameter; indeed, it is difficult to define without circularity, because “activity” expresses the idea of “intensity of the chemical properties” of the species so well. Hydrogen ion activities are much better than concentrations for describing chemical reactivity of acid solutions, and these demonstrations show that rates of reaction and “equilibrium shifts” are related to activities, not concentrations. Clearly, using activities is not an esoteric, purely theoretical issue related to pH measurement. Ten or fifteen minutes spent in a general chemistry course on demonstration 1, possibly combined with demonstration 5, should provide a dramatic introduction to the concept of activity. The concept can then be mentioned during *all* subsequent equilibrium calculations where it applies. Demonstration 4 also provides surprising results without requiring great care in execution, while demonstrations 2 and 3 require more time and care and may be better suited to an upper-level analytical or physical chemistry course where the definition of activity is stressed. We suggest that exam questions like the multiple-choice question shown in Text Box 1 are appropriate in general chemistry. Students can be reminded of these concrete demonstrations throughout the semester as topics in equilibrium are discussed, and we recommend that the “≈” sign be used whenever concentration based equilibrium equations are displayed, for example, $\mathrm{pH} \approx -\log[\mathrm{H_3O^+}]$, or $K_a \approx [\mathrm{H_3O^+}][\mathrm{A^-}]/[\mathrm{HA}]$. The “≈” symbol reminds students that this is not a rigorous definition, but just an approxima-

The activity of the hydrogen ion is

a. not as good as an accurate concentration for calculating pH.
b. close to the concentration of $[H^+]$ if the concentration of all species are 0.001 or less.
c. not affected by other ions.
d. a theoretical concept not related to the chemical reactivity of an acid solution.
e. never more than 10% different from the concentration.

Text Box 1. Possible mulitple-choice exam question.

tion. Students should *first* be taught the stark truth, that chemical thermodynamics and kinetics depend on activities, not concentrations, so they do not have to "unlearn" the incorrect idea that concentrations are more fundamental than activities. We could tolerate an approach that sacrificed reasonable practical answers for a sound theoretical foundation (or vice versa) but our current pedagogy seems to provide neither!

These demonstrations can lead to a more realistic understanding of solution chemistry and were inspired by the earlier work of Hawkes *(2)*.

The Paradoxes

Willard Van Orman Quine *(3)* said that because a paradox may "expose the absurdity of a buried premise…Catastrophe may lurk, therefore, in the most innocent-seeming paradox." The catastrophe in this case is the large error in many concentration-based calculations, and the loss of information about the nature of solutions that results from ignoring activities. Quine pointed out that paradoxes may be "veridical"; that is, they need not be illogical or false. The paradoxes below are veridical ones. The paradoxes arise only if the false premise that pH is defined in terms of the concentration, not the activity, is accepted.

Paradox I

The measured pH may *decrease* while $[H^+]$ decreases, even though the pH is supposed to *increase* as acidity decreases if eq (1) is applied.

Demonstration 1: With a meter, measure the pH of 25 to 50 mL of 0.1 or 0.01 M HCl or $KH(IO_3)_2$, then gradually adding an equal volume of 5 M LiCl, $CaCl_2$, or 4 M $MgCl_2$. The pH meter reading shows that the solution is getting more acidic as the acid is diluted. The pH meter need not be calibrated precisely for this demonstration, and the acid solution can be of any concentration that gives a pH reading around 2. In a typical experiment, the pH of 25 mL of approximately 0.015 M HCl solution is 1.79 before adding 22 mL of 5 M $CaCl_2$ and 0.91 afterwards.

A plot of the pH as 5 M LiCl or $CaCl_2$ are added to an HCl solution initially at pH ≅ 1 is shown in Figure 1, along with calculated values for $-\log[H^+]$ for comparison, which is plotted against a second vertical scale on the right to emphasize that it is not the same as pH. The exact initial concentration of acid was not determined precisely, but if it were exactly 0.100 M, for example, the pH would be about 1.1 (not $-\log 0.100 = 1.0$, as discussed below). We chose $KH(IO_3)_2$ for several of our demonstrations because it is a primary standard that is also a strong acid; that makes it possible to calculate the concentration of hydronium ion from the directly observable mass of acid. Other common primary standards (potassium hydrogen phthalate, benzoic acid, etc.) are weak acids or solutions (HCl azeotropes, for example) with indirectly determined concentrations.

Paradox II

The concentration calculated from the pH according to eq 1 is not the concentration measured by titration, even in 0.01 M acid! Paradox I is not a trick: the pH is not related to the concentration even with no foreign species present. This is one instance of a more general principle: it is impossible to calculate the concentration of any species directly from the response of an ion-selective electrode of *any* kind (unless activity coefficients are used).

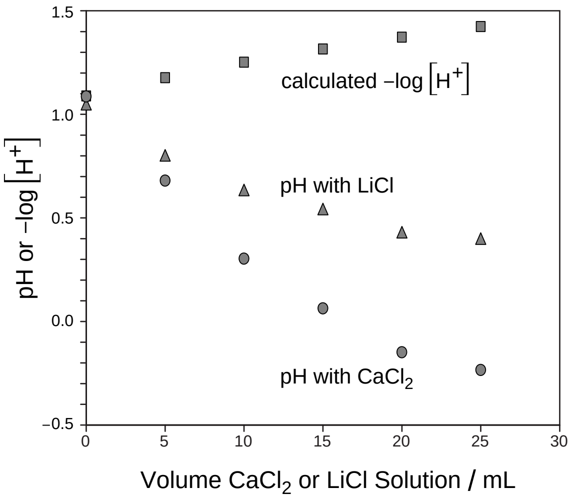

Figure 1. The measured pH as increasing volumes of 5 M calcium chloride or 5 M lithium chloride solutions were added to 25 mL of 0.1 M HCl is plotted. The value of $-\log[H^+]$ was calculated from the $[H^+]$ in the solutions and is also plotted.

Demonstration 2: Weigh about 6 g of $KH(IO_3)_2$ in a weighing dish on an analytical balance. Add about 0.5 g of the $KH(IO_3)_2$ to about 100 mL of water in a 250-mL beaker with a magnetic stirrer. Measure the pH of the solution with a pH meter calibrated at pH 1.68 (see the experimental section). Add solid $KH(IO_3)_2$ until the pH is 1.68, then determine the total mass added by reweighing the weighing dish and $KH(IO_3)_2$. A typical added mass will be 1.152 g. The volume of the solution (typically 101.0 mL) is determined from the density, 1.0066 g/mL, and the total mass. The concentration can be calculated (1.152 g)/[(389.92 g/mol)(0.1010 L)] = 0.0293 M. Clearly, we cannot calculate the concentration from the pH with eq 1, because we paradoxically obtain 10^(−1.68) = 0.0208 (which is the activity!), representing a 40% difference. The concentration can be corroborated by titrating 25.0 mL of the solution with standardized (~0.1 M) sodium hydroxide solution to a phenolphthalein endpoint. We also determined the equivalence point potentiometrically as described below.

Demonstration 3: Prepare ~0.050 M HCl by delivering 10.0 mL of ~1.0 M HCl from a pipet into a 200-mL volumetric flask and diluting to volume. Measure the pH. Confirm $[H_3O^+]$ by titrating 25.0 mL of the solution with standardized 0.1 M NaOH potentiometrically or to a phenolphthalein endpoint as described herein. Now we can show that the concentration erroneously calculated by eq 1 does not match the concentration determined by titration. For three trials, the average pH was 1.33, so a_{H^+} = antilog (−1.33) = 0.047, while the concentration was 0.051 M, so the activity coefficient was 0.92, significantly different than the accepted value of 0.83. For concentrations much above ~0.05 M, activity coefficients determined by this procedure are not significantly different than 1, apparently because of meter drift and difficulty of calibration in the strong acid region. If acid is added to adjust the pH to a given value, as in demonstration 2, even larger errors arise, probably because of meter drift during the longer time required by that procedure.

Demonstration 4: Dispense two 50-mL samples of hydrochloric acid with a pH close to 1.68 (chosen because it is the standardization point for the pH meter). The solution was prepared by adding 1 M HCl from a buret to distilled water until the pH reached 1.68. Add 25 mL of 5 M $CaCl_2$ solution to one of the samples to obtain a solution with pH ≈ 0.8. Now ask observers which will take a larger volume of standardized 0.1 M NaOH solution to titrate, the pH = 1.68 solution or the pH = 0.8 solution. According to most texts, the answer would (erroneously) be the "more acidic" solution with pH = 0.8! In truth, they require the same volume. The paradox arises if $[H^+]$ = antilog (−pH), because $[H^+]$ calculated (erroneously with eq 1) for the first solution is antilog(−1.68) = 0.021 M, and that for the second is 0.16 M. If these values were correct, then the first solution should require ~10 mL of 0.1 M titrant, and the second ~120 mL. Typical volumes of 0.080 M NaOH titrant were 11.0 and 11.1 mL. The amount of HCl is the same in both (0.00089 mol). The second solution has $[H^+]$ typically 0.012 M (0.000890 mol/0.075 L). The experimental molar activity coefficient is $\gamma = a_{H^+}/[H^+] = (0.16/0.012) \approx 13$.

Paradox III

The chemical reactivity of an acid solution may increase as the concentration of hydrogen ion decreases. Paradoxically, the equilibrium,

$$HIn + H_2O \Leftrightarrow In^- + H_3O^+$$

where HIn and In^- represent an acid indicator and its conjugate base, may shift *left* as $[H_3O^+]$ decreases! The pH meter, reflecting a_{H^+}, provides a much better measure of chemical reactivity than the calculated concentration. Activities are not just esoteric corrections to concentration required to understand pH meters; they reflect chemical reactivity. To be accurate, calculations involving equilibria like the one above must be done with activities.

Furthermore, the rate of a reaction of species A with hydrogen ion may paradoxically decrease as $[H_3O^+]$ increases, even though the rate law is usually written as

$$R = k\big[A\big]\big[H_3O^+\big]$$

Demonstration 5: Repeat Demonstration 1, but add 3–6 drops of methyl green indicator (or other suitable indicators) solution to the acid solution instead of using the pH meter. The indicator changes from the green basic form to the yellow acidic form as the acid is diluted with salt solution. Add a few drops of indicator to 0.01 M NaOH and 1 M HCl in separate beakers for color comparison. The change to yellow (the HIn form) indicates that the solution is getting more acidic. The indicator is responding to the *activity* of hydrogen ion, which is increasing as the *concentration* decreases, so at lower acid concentrations the acid form of the indicator, HIn, predominates. This demonstration can be conveniently and impressively done with 25 mL of pH 1.0 buffer solution (see below) with crystal violet indicator, which gives a teal blue color. Addition of 25 mL of 5 M $CaCl_2$ in 5-mL increments changes the color through green to yellow as the pH changes from 1 to −0.2. This cannot be done with pH = 1.68 buffer because a precipitate forms, but (less impressively) 25 mL of 5 M LiCl can be added to 25 mL of pH 1.68 buffer with methyl green indicator, changing the color from teal to yellow green at pH = ~1.1. Dilution with 25 mL of water in place of the 5 M LiCl increases the pH to about 1.8.

Demonstration 6: Add 10 mL of 1.0 M HCl to each of two 50-mL beakers, and to one add 9 g of $MgCl_2{\cdot}6H_2O$ (the final volume will be almost 20 mL). Provide 20 mL of bromine water in a third 50-mL beaker, and 20 mL of acetone in a fourth beaker. Use 3-mL syringes to deliver 3 mL of acetone and 2 mL of bromine water to each of two 24 × 200 mm test tubes. To one add 3 mL of 1.0 M HCl, and to the other add 3 mL of 1.0 M HCl with $MgCl_2{\cdot}6H_2O$. The rate of the reaction

$$C_3H_6O + Br_2 \rightarrow C_3H_5OBr + HBr$$

is catalyzed by H_3O^+ and has a rate law *(4)* usually written as

$$R = k\big[C_3H_6O\big]\big[H_3O^+\big]$$

But paradoxically, the demonstration shows that the rate is greater when the concentration of H_3O^+ is lower! The paradox is resolved when we realize that rates are dependent on the activities, not concentrations, of reacting species. The rate law should be written

$$R = k a_{C_3H_6O} a_{H_3O^+}$$

Since $a_{H_3O^+} = \gamma_{H^+}[H_3O^+]$, the rate will depend on the activity coefficient γ, which in turn depends on the ionic strength. An increase in rate due to an increase in the activity due to increased ionic strength is called the secondary salt effect *(5)* in chemical kinetics. In this case, the activities of all species are changed by the addition of the salt, so the enhanced rate is not solely due to the increased activity of hydrogen ion.

Discussion

The pH allows the calculation of activities, while the titrations provide concentrations. The molar activity coefficients (γ_M) can be calculated from the data from demonstration 2. For example if a $KH(IO_3)_2$ solution with pH = 1.68 is used:

$$a_M = \gamma_M C_M$$

$$\gamma_M = \frac{0.0208\,\frac{mol}{L}}{0.0286\,\frac{mol}{L}} = 0.73$$

An average of three determinations gives γ = 0.76 (σ = 0.056) by the direct weighing method and 0.78 (σ = 0.036) by the titration method. While activities can be defined in terms of any concentration scale *(6),* the most common convention is to define them in molal units:

$$a_m = \gamma_m C_m$$

The molarity-based activity coefficient is related to the molal activity coefficient by $\gamma_M = \gamma_m C_m D/C_M$ where D is the density of the solvent.

The extended Debye–Huckel equation[2] gives an activity coefficient of 0.85, while the Davies equation[3] gives 0.81 for $KH(IO_3)_2$ with pH = 1.68, using the constants $A = 0.509$, $B = 0.33$, $a = 9$, $z = 1$, and $I = 0.057$ $\{[KH(IO_3)_2] \cong 0.0286$ M, $I = 0.5\Sigma_i z_i^2 C_{M_i} = 0.5[(1^2)(0.0286) + (1^2)(0.028)6 + (1^2)(0.0572)]$

Table 1. Variation of the Activity Coefficients of Hydrogen Ion and HCl with Concentration

Parameter	Data								
m	0.000500	0.0100	0.100	0.40	0.70	1.0	4.0	9.0	16
M	0.000500	0.0100	0.100	0.40	0.69	0.98	3.7	7.6	11.9
$\gamma_\pm$	0.975	0.904	0.796	0.755	0.772	0.809	1.762	7.94	42.4
a_{H^+}	0.000488	0.00904	0.0796	0.302	0.540	0.809	7.048	71.46	678
a_{HCl}	2.4×10^{-7}	8.2×10^{-5}	0.0063	0.091	0.292	0.655	49.68	5106	4.6×10^{5}

NOTE: Data from ref *7*.

In HCl, the activity coefficient for hydrogen ion is generally assumed to be the same as that of the chloride ion, and it is called the mean activity coefficient, designated $\gamma_\pm$. For H^+ in HCl solutions, $\gamma_\pm$ has the values given in Table 1 *(7),* passing through a minimum at about 0.4 m. Less extensive tables of activity coefficients are given in the *Handbook of Chemistry and Physics*, and they can be estimated at low concentrations by the Debye–Hückel law or Davies equation. At concentrations above 0.5 M only newly developed special methods are useful. The extended Debye–Huckel law and Davies equation predict the increase in the activity coefficient after the initial decrease with increasing ionic strength.

Thus the pH of 0.01 M HCl is $-\log(0.00904) = 2.04$ (not 2.00), and the pH of 7.6 M HCl is about −1.85 (not −0.88). This large negative pH value will not be measurable with a pH meter and glass electrode calibrated in the standard way by the use of ordinary buffers because of the extreme curvature of the calibration curve at low pH and other technical complications. Nonetheless, large negative pH values have been measured when special calibration procedures are employed *(8).* The misconception that pH is limited to the range 2–14 may arise from the NIST or IUPAC definition, which is applicable only over that range. Operational definitions make pH a useful parameter over a much wider range. Interestingly, the activity of HCl itself ranges from 2.4×10^{-7} to 4.6×10^{5} over the common concentration range of HCl solutions. Although the effect is not directly related to the present study of pH, it is noteworthy that the extraordinary increase in the activity of undissociated HCl with concentration correlates with the intense odor of concentrated HCl solutions, which would be absent in solutions of completely dissociated HCl.

Demonstration 3 is susceptible to pH meter errors. A procedure that we thought would be superior gave activity coefficients of ~1.06, apparently because of pH meter drift. In that procedure, we added about 100 mL of distilled water to a 250-mL beaker, then added about 0.5 mL of 1 M HCl and measured the pH with a meter calibrated at pH 1.0, 1.68, or 2.0 (vide infra). Then 1 M HCl was added dropwise until the pH is very close to the pH of the buffer used to calibrate the meter, for example 1.68. This procedure gave inferior results compared to the procedure in which the pH of ~0.1 M HCl is measured just once, immediately after calibrating the meter at pH =1 and 1.68.

Many ionic compounds are appropriate for altering the activity of the acid solutions in these demonstrations. The ratio $\Delta pH/\Delta C_m$, which quantifies the change in pH that results with changes in the molal (m) concentration of salts, has been determined for several salts *(9)* and selected results are given in Table 2. Although calcium chloride is commonly available, innocuous, and inexpensive, it forms slightly soluble $Ca(IO_3)_2$ when added to the $KH(IO_3)_2$ solutions, so $MgCl_2$ may be preferable, even though it is deliquescent and only ~4 M solutions can be prepared. The demonstration will often work when an equal volume of $CaCl_2$ is added to an acid solution, because supersaturated solutions of $Ca(IO_3)_2$ may be stable for minutes before a precipitate appears and the pH begins to rise.

Added ionic compounds may affect the pH reading as a result of (i) their native acidity or basicity, (ii) direct interaction with the glass electrode, or (iii) activity effects, and the three should be distinguished and understood individually:

i. Although all of these added ionic compounds are acids or bases, none is of significant strength under the conditions of this experiment *(10).*

ii. Direct interaction of salts with the pH electrode probably will not explain the effects observed at the low pH readings of interest here, although the alkali metals and to a lesser extent, the alkaline earths interfere with the measurement of pH at high values. The "acid error" *(11),* leads to measured pH values higher than the true values, usually at acid concentrations greater than 1 m, but also in strong salt solutions. This would tend to make the lowest pH values reported here higher than they should be, so if the error is involved it reduces the effect we demonstrate, if anything. The acid error is often time-dependent, increasing linearly for several hours, then disappearing only after several days of electrode immersion in buffers of higher pH (this is the

Table 2. Change in pH with Concentration of Added Salt

Salt	$\Delta pH/\Delta C_m$
KCl	−0.10
NaCl	−0.20
LiCl	−0.248
KBr	−0.12
NaBr	−0.21
LiBr	−0.25
KNO_3	−0.04
$NaNO_3$	−0.08
$LiNO_3$	−0.12
$CaCl_2$	−0.46
$MgCl_2$	−0.48
$BaCl_2$	−0.36
$CaBr_2$	−0.50
$Ca(NO_3)_2$	−0.21

NOTE: Data from ref *8*.

reason why immersion of electrodes in concentrated acids is to be avoided). The chemical basis for the error may involve negative ion penetration into the glass of the electrode, reduction in the thickness of the swollen layer of hydrous silica in the surface of the glass membrane or other effects *(12)*. One explanation suggests that highly solvated hydrogen ions may somehow be involved in the interaction with the glass electrode, so the effect results from reduction of the activity of water *(13)*.

iii. Activity effects arise from interactions that do not occur in infinitely dilute solutions. They include both electrostatic and coordinate-covalent associations of ions (the former is exemplified by the formation of “counterion clouds” around the ion of interest and the latter is exemplified by weak acid association or formation of complex ions). Activity effects also arise from disturbance of the intermolecular structure of pure water, which leads to changes in its dielectric strength and other parameters, as well as reduction in the quantity of free solvent available to dissolve the solute. Added positive ions are highly hydrated, so fewer free water molecules are available to solvate the hydrogen ion, and its structure must change from the already complex structure that exists in pure water. Higher concentrations of counterions, whether from the acid itself or an added salt, create a “cloud” around the hydronium ion that differs from the environment in pure water. It has been said that concentrated solutions of calcium chloride have solvent properties more like molten salt than like water *(14)*. Clearly these effects are so great that to ignore them is to distort chemical understanding.

Asymmetry potentials may also be significant in the concentrated salt solution we measured, but they are probably not large. Details of the measurement of pH are exceedingly complex and beyond the scope of this article, but are described in many monographs *(11)*.

Schwabe *(9, 15)* found that the pH dependence on salt concentration follows the equation

$$\mathrm{pH} = \mathrm{pH}_0 - 5.55\,bz\left(\frac{h_+}{r_+} - \frac{h_-}{r_-}\right)$$

where h_+ and h_- are the hydration numbers of the added ions and r^+, r^- are their radii, z is the charge number, b is the molal concentration, and 5.55 is a constant based on theory. Neutral salt solutions may increase the acidity by a factor of one thousand, but large ions (like Cs^+) may actually decrease the acidity.

It is interesting that a NIST-traceable standard “buffer” for pH = 1.00 is actually 0.05 M HCl/KCl, which must be made so that $a_{\mathrm{H}^+} = 0.10$, even though $[\mathrm{H_3O^+}]$ is 0.05!

Experimental

Measurements of pH were done with glass electrodes measured with a Fisher Scientific AR20 pH–conductivity meter, or with the Vernier LoggerPro system. In general, two-point calibrations were used, with the second buffer at a pH equal to the pH to be measured, so that the electrode was transferred immediately to the test solution from a standard buffer of similar pH.

Materials

Potassium hydrogen iodate, $\mathrm{KH(IO_3)_2}$ is a primary standard *(16)* that also happens to be a strong acid. We used the pure solid[4] after drying at 105 °C for 1 hour, or a 0.100 N standard solution.[4] The standard solution is actually 0.00833 M, since the equivalent weight used by the supplier to calculate the 0.100 N concentration is based on the redox standardization in which it undergoes a 12 electron reduction to $2\ \mathrm{I}^-$. If the standard solution is purchased, it is convenient for standardization of sodium hydroxide solutions. $\mathrm{KH(IO_3)_2}$ has a maximum solubility of about 1.3 g/100 mL (~0.03 M) so it is difficult to prepare solutions below pH 1.5.

Sodium hydroxide (~0.1 M) was standardized using phenolphthalein indicator, by titrating either the commercial 0.100 N $\mathrm{KH(IO_3)_2}$ solution or solid potassium hydrogen phthalate.

Deionized water finished to <18 MW/cm by a Barnstead EASYpure UF water system. Prepared buffer solutions for pH = 1.0 and 1.68 were purchased[5] and pH = 2.00 and 3.00 buffer were prepared from buffer tablets.[6]

Methyl green indicator solution was prepared by dissolving 0.036 g of the solid[7] in 40 mL of water. Other indicators that change dramatically in color from pH 0 to pH 2 are malachite green, which is very similar to methyl green, crystal violet (violet to yellow), and methyl violet, which is similar to crystal violet. All these may be used interchangeably.

Calcium chloride dihydrate,[8] magnesium chloride hexahydrate,[9] and lithium chloride[10] were used as supplied. Although the solubility of $\mathrm{MgCl_2{\cdot}6H_2O}$ is 167 g in 100 mL of cold water, it is difficult to prepare solutions over 4 M because of the volume increase of the water as the salt is added.

Hazards

Potassium hydrogen iodate, $\mathrm{KH(IO_3)_2}$ is irritating to mucous membranes in the mouth, pharynx, esophagus and gastrointestinal tract, may cause coughing and shortness of breath if inhaled; it is irritating to eyes and skin. It should be handled in the hood, with gloves and safety goggles. Methyl green may be a skin, eye, or throat irritant, so gloves, eye protection, and appropriate ventilation are necessary.

Conclusion

We have demonstrated that the pH may decrease as the hydrogen ion decreases, and solutions that are 0.1 M in HCl can have pH values varying at least from 1.09 to -0.5 depending on the nature of the solution. Equilibrium calculations and rate laws expressed in terms of concentrations may lead to predictions that are the opposite to what is actually observed. It is clear that $\mathrm{pH} \neq -\log[\mathrm{H}^+]$ and that useful calculations of concentrations from electrochemical measurements like pH may be the exception rather than the rule. We suggest that demonstrations like these during the first-year general chemistry course will prepare students for upper-level courses, while the current denial of the fundamental importance of activity actually impedes their learning in upper-division courses. Much of analytical chemistry depends on accurate determinations of concentrations of analytes from methods that yield activities. General chemistry textbooks should include only accepted *definitions* of pH, while giving students concrete examples, like those above, of the unacceptably large errors that pH = $-\log[H^+]$ often engenders. That equation should certainly not be presented as the *definition* of pH, as is frequently done, but only as an approximation of true pH. Definitions should be sacrosanct in science.

The equation pH ≈ $-\log[H^+]$ is of limited practical use. It may also preclude fundamental understanding of a good deal of important contemporary chemistry that involves noncovalent bonds, by denying activity its central role. Activity coefficients reveal interesting and important interactions in solutions. As shown by the change in indicator color as a result of hydrogen ion activity (not concentration), nonideality often is needed to explain chemical reactivity. An understanding of the behavior of macromolecules, from protein folding to enzyme activity, and interactions of polynucleotides requires an understanding of the sensitivity of their molecular structure to ionic strength, dielectric constant, and solvation effects, all revealed by the activity coefficient. Teaching pH = $-\log a_{H^+}$ is an easy entree into a lot of fundamental and interesting chemistry.

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Notes

1. The definition for pH in the IUPAC Compendium of Chemical Terminology at *http://www.iupac.org/goldbook/P04524.pdf* (accessed Jan 2005) reads: "In the restricted range of dilute aqueous solutions having amount concentrations less than 0.1 mol dm^{-3} and being neither strongly acidic nor strongly alkaline (2 < pH < 12), pH = $-\log\{\gamma_{\pm}c(H^+)/\text{mol dm}^{-3}\} \pm 0.02$ where $\gamma_{\pm}$ is the mean ionic activity coefficient of a typical univalent electrolyte on a concentration basis. The operational definition is based on the electromotive force measurement of the galvanic cell: reference electrode |KCl(aq) || solution X|H_2(g) |Pt where the KCl solution has a molality greater than 3.5 mol kg^{-1} relative to a standard solution S, replacing X in the scheme above [usually KH_2PO_4(aq) of molality 0.05 mol kg^{-1} which has a pH = 4.005: pH(X) = pH(S) + $(E_S - E_X)F/(RT\ln 10)$."

2. The extended Debye–Huckel equation is

$$\log\gamma = -Az^2\left(\frac{\sqrt{I}}{1 + Ba\sqrt{I}}\right)$$

where I is the ionic strength, z is the ionic charge, A is a constant (0.5085 for water at 25 °C) that depends on the dielectric constant and other properties of the solvent, B is a constant that depends on P and T, and a is the radius of the hydrated ion (determined empirically). These constants can be found in standard reference texts.

3. The Davies equation is

$$\log\gamma = -Az^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I\right)$$

Symbols are defined as in Footnote 2.

4. $KH(IO_3)_2$, CAS 13455-24-8, Solid: Fisher P190-100, \$81.64/100g ; 0.100 N Solution: (#101923, Lab Safety Supply, PO Box 1368, Janesville, WI 53547-1368, 800-356-0783, *http://www.labsafety.com* (accessed Jan 2006).

5. For prepared buffer solution, pH = 1, we used Fisher SB140-500, \$21.10. For prepared buffer solution, pH = 1.68, we used Fisher LC12210-1, \$17.80, but it may be prepared by dissolving 12.70 g of $KH_3(C_2O_4)_2 \cdot 2\,H_2O$ in water and diluting to 1 L.

6. pHydrion sulfamic acid and potassium biphthalate buffer pH 2 ±0.02 or potassium biphthalate–sulphamic acid buffer pH 3.00 ±0.02, #270-3.00, were purchased from NISTStandards, Micro Essential Laboratory, Brooklyn, NY11210.

7. Methyl green indicator was purchased from Harleco, CAS 7114-03-6, #270, Lot 30301, Hartman-Leddon Co., Philadelphia, PA.

8. Calcium chloride dihydrate was purchased from Fisher $CaCl_2 \cdot 2H_2O$, CAS 10035-04-8, #C-79

9. Magnesium chloride hexahydrate was purchased from Acros Organics, Somerville, NJ, CAS 7791-18-6, #41341-5000.

10. Lithium chloride was purchased from Fisher LiCl, CAS 7447-41-8, #L121-100.

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