pH

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In chemistry, **pH** (/piː eɪtʃ/ or /piː heɪtʃ/) is a measure of the acidity or basicity of an aqueous solution. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline. Pure water has a pH very close to 7.

The sour taste of lemon juice is a result of it being composed of about 5% to 6% citric acid, an acid with a pH of roughly 2.2.

The pH scale is traceable to a set of standard solutions whose pH is established by international agreement.[1] Primary pH standard values are determined using a concentration cell with transference, by measuring the potential difference between a hydrogen electrode and a standard electrode such as the silver chloride electrode. Measurement of pH for aqueous solutions can be done with a glass electrode and a pH meter, or using indicators.

pH measurements are important in medicine, biology, chemistry, agriculture, forestry, food science, environmental science, oceanography, civil engineering, chemical engineering, nutrition, water treatment & water purification, and many other applications.

Mathematically, pH is the negative logarithm of the activity of the (solvated) hydronium ion, more often expressed as the measure of the hydronium ion concentration.[2]

Contents

History

The concept of p[H] was first introduced by Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory in 1909[3] and revised to the modern pH in 1924 to accommodate definitions and measurements in terms of electrochemical cells. In the first papers, the notation had the "H" as a subscript to the lowercase "p", as so: p_H.

The exact meaning of the "p" in "pH" is disputed, but according to the Carlsberg Foundation pH stands for "power of hydrogen".[4] It has also been suggested that the "p" stands for the German *Potenz* (meaning "power"), others refer to French *puissance* (also meaning "power", based on the fact that the Carlsberg Laboratory was French-speaking). Another suggestion is that the "p" stands for the Latin terms *pondus hydrogenii*, *potentia hydrogenii*, or potential hydrogen. It is also suggested that Sørensen used the letters "p" and "q" (commonly paired letters in mathematics) simply to label the test solution (p) and the reference solution (q).[5] Current usage in chemistry is that p stands for "decimal cologarithm of", as also in the term pK_a, used for acid dissociation constants.[6]

Definition and measurement

pH

pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity, a_{H^+}, in a solution.[1]

$$\mathrm{pH} = -\log_{10}(a_{\mathrm{H}^+}) = \log_{10}\left(\frac{1}{a_{\mathrm{H}^+}}\right)$$

This definition was adopted because ion-selective electrodes, which are used to measure pH, respond to activity. Ideally, electrode potential, E, follows the Nernst equation, which, for the hydrogen ion can be written as

$$E = E^0 + \frac{RT}{F}\ln(a_{\mathrm{H}^+}) = E^0 - \frac{2.303RT}{F}\mathrm{pH}$$

where E is a measured potential, E^0 is the standard electrode potential, R is the gas constant, T is the temperature in kelvin, F is the Faraday constant. For H^+ number of electrons transferred is one. It follows that electrode potential is proportional to pH when pH is defined in terms of activity. Precise measurement of pH is presented in International Standard ISO 31-8 as follows:[7] A galvanic cell is set up to measure the electromotive force (e.m.f.) between a reference electrode and an electrode sensitive to the hydrogen ion activity when they are both immersed in the same aqueous solution. The reference electrode may be a silver chloride electrode or a calomel electrode. The hydrogen-ion selective electrode is a standard hydrogen electrode.

Reference electrode | concentrated solution of KCl || test solution | H_2 | Pt

Firstly, the cell is filled with a solution of known hydrogen ion activity and the emf, E_S, is measured. Then the emf, E_X, of the same cell containing the solution of unknown pH is measured.

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{E_\mathrm{S} - E_\mathrm{X}}{z}$$

The difference between the two measured emf values is proportional to pH. This method of calibration avoids the need to know the standard electrode potential. The proportionality constant, *1/z* is ideally equal to $\frac{1}{2.303RT/F}$ the "Nerstian slope".

To apply this process in practice, a glass electrode is used rather than the cumbersome hydrogen electrode. A combined glass electrode has an in-built reference electrode. It is calibrated against buffer solutions of known hydrogen ion activity. IUPAC has proposed the use of a set of buffer solutions of known H^+ activity.[1] Two or more buffer solutions are used in order to accommodate the fact that the "slope" may differ slightly from ideal. To implement this approach to calibration, the electrode is first immersed in a standard solution and the reading on a pH meter is adjusted to be equal to the standard buffer's value. The reading from a second standard buffer solution is then adjusted, using the "slope" control, to be equal to the pH for that solution. Further details, are given in the IUPAC recommendations.[1] When more than two buffer solutions are used the electrode is calibrated by fitting observed pH values to a straight line with respect to standard buffer values. Commercial standard buffer solutions usually come with information on the value at 25 °C and a correction factor to be applied for other temperatures.

The pH scale is logarithmic and therefore pH is a dimensionless quantity.

p[H]

This was the original definition of Sørensen,[4] which was superseded in favor of pH in 1924. However, it is possible to measure the concentration of hydrogen ions directly, if the electrode is calibrated in terms of hydrogen ion concentrations. One way to do this, which has been used extensively, is to titrate a solution of known concentration of a strong acid with a solution of known concentration of strong alkali in the presence of a relatively high concentration of background electrolyte. Since the concentrations of acid and alkali are known, it is easy to calculate the concentration of hydrogen ions so that the measured potential can be correlated with concentrations. The calibration is usually carried out using a Gran plot.[8] The calibration yields a value for the standard electrode potential, E^0, and a slope factor, *f*, so that the Nernst equation in the form

$$E = E^0 + f\frac{2.303RT}{F}\log[\mathrm{H}^+]$$

can be used to derive hydrogen ion concentrations from experimental measurements of *E*. The slope factor, *f*, is usually slightly less than one. A slope factor of less than 0.95 indicates that the electrode is not functioning correctly. The presence of background electrolyte ensures that the hydrogen ion activity coefficient is effectively constant during the titration. As it is constant, its value can be set to one by defining the standard state as being the solution containing the background electrolyte. Thus, the effect of using this procedure is to make activity equal to the numerical value of concentration.

The glass electrode (and other ion selective electrodes) should be calibrated in a medium similar to the one being investigated. For instance, if one wishes to measure the pH of a seawater sample, the electrode should be calibrated in a solution resembling seawater in its chemical composition, as detailed below.

The difference between p[H] and pH is quite small. It has been stated[9] that pH = p[H] + 0.04. It is common practice to use the term "pH" for both types of measurement.

pH indicators

Main article: pH indicator

Indicators may be used to measure pH, by making use of the fact that their color changes with pH. Visual comparison of the color of a test solution with a standard color chart provides a means to measure pH accurate to the nearest whole number. More precise measurements are possible if the color is measured spectrophotometrically, using a colorimeter of spectrophotometer. Universal indicator consists of a mixture of indicators such that there is a continuous color change from about pH 2 to pH 10. Universal indicator paper is made from absorbent paper that has been impregnated with universal indicator.

Chart showing the variation of color of universal indicator paper with pH

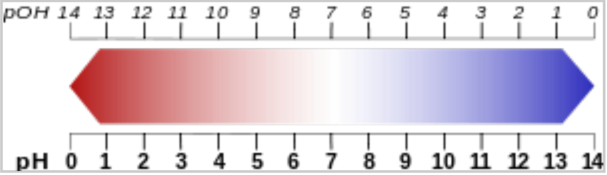
Universal indicator components

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue (first transition)	Red	1.2 – 2.8	Yellow
Methyl red	Red	4.4 – 6.2	Yellow
Bromothymol blue	Yellow	6.0 – 7.6	Blue
Thymol blue (second transition)	Yellow	8.0 – 9.6	Blue
Phenolphthalein	Colorless	8.3 – 10.0	Fuchsia

pOH

pOH is sometimes used as a measure of the concentration of hydroxide ions, OH^-, or alkalinity. pOH values are derived from pH measurements. The concentration of hydroxide ions in water is related to the concentration of hydrogen ions by

$$[\mathrm{OH}^-] = \frac{K_W}{[\mathrm{H}^+]}$$



Relation between p[OH] and p[H] (red = acid region, blue = basic region)

where K_W is the self-ionisation constant of water. Taking logarithms

$$\mathrm{pOH} = \mathrm{pK_W} - \mathrm{pH}$$

So, at room temperature pOH ≈ 14 – pH. However this relationship is not strictly valid in other circumstances, such as in measurements of soil alkalinity.

Extremes of pH

Measurement of pH below about 2.5 (ca. 0.003 mol dm^{-3} acid) and above about 10.5 (ca. 0.0003 mol dm^{-3} alkali) requires special procedures because, when using the glass electrode, the Nernst law breaks down under those conditions. Various factors contribute to this. It cannot be assumed that liquid junction potentials are independent of pH.[10] Also, extreme pH implies that the solution is concentrated, so electrode potentials are affected by ionic strength variation. At high pH the glass electrode may be affected by "alkaline error", because the electrode becomes sensitive to the concentration of cations such as Na^+ and K^+ in the solution.[11] Specially constructed electrodes are available which partly overcome these problems.

Runoff from mines or mine tailings can produce some very low pH values.[12]

Non-aqueous solutions

Hydrogen ion concentrations (activities) can be measured in non-aqueous solvents. pH values based on these measurements belong to a different scale from aqueous pH values, because activities relate to different standard states. Hydrogen ion activity, a_{H^+}, can be defined[13][14] as:

$$a_{H+} = \exp\left(\frac{\mu_{H+} - \mu^{\ominus}_{H+}}{RT}\right)$$

where μ_{H^+} is the chemical potential of the hydrogen ion, $\mu^{\ominus}_{H^+}$ is its chemical potential in the chosen standard state, R is the gas constant and T is the thermodynamic temperature. Therefore pH values on the different scales cannot be compared directly, requiring an intersolvent scale which involves the transfer activity coefficient of hydrolyonium ion.

pH is an example of an acidity function. Other acidity functions can be defined. For example, the Hammett acidity function, H_0, has been developed in connection with Superacids.

The concept of "Unified pH scale" has been developed on the basis of the absolute chemical potential of the proton. This scale applies to liquids, gases and even solids.[15]

Applications

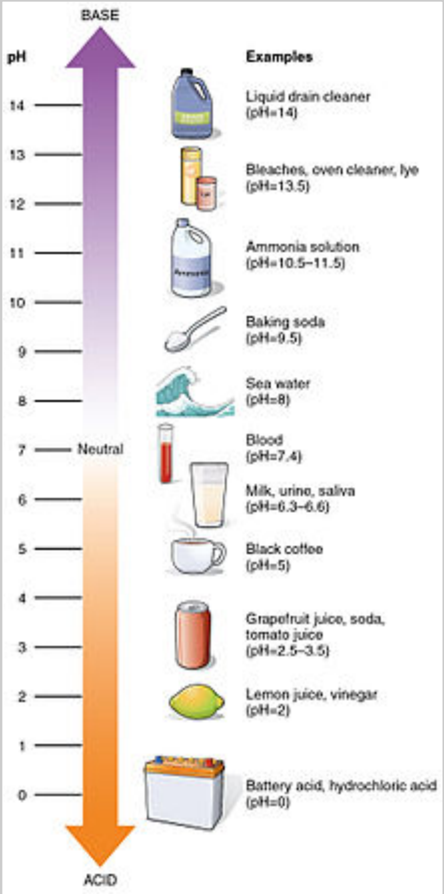
Water has a pH of $pK_w/2$, so the pH of pure water is about 7 at 25 °C; this value varies with temperature. When an acid is dissolved in water, the pH will be less than that of pure water. When a base, or alkali, is dissolved in water, the pH will be greater than that of pure water. A solution of a strong acid, such as hydrochloric acid, at concentration 1 mol dm^{-3} has a pH of 0. A solution of a strong alkali, such as sodium hydroxide, at concentration 1 mol dm^{-3}, has a pH of 14. Thus, measured pH values will lie mostly in the range 0 to 14. Since pH is a logarithmic scale, a difference of one pH unit is equivalent to a tenfold difference in hydrogen ion concentration. The pH of an aqueous solution of a salt such as sodium chloride is slightly different from that of pure water, even though the salt is neither acidic nor basic. This is because the hydrogen and hydroxide ions' activity is dependent on ionic strength, so K_w varies with ionic strength.

The pH of pure water decreases with increasing temperatures. For example, the pH of pure water at 50 °C is 6.55. Note, however, that water that has been exposed to air is mildly acidic. This is because water absorbs carbon dioxide from the air, which is then slowly converted into bicarbonate and hydrogen ions (essentially creating carbonic acid).

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

pH in nature

pH-dependent plant pigments that can be used as pH indicators occur in many plants, including hibiscus, red cabbage (anthocyanin) and red wine. The juice of citrus fruits is acidic mainly because it contains citric acid. Other carboxylic acids occur in many living systems. For example, lactic acid is produced by muscle activity. The state of protonation of phosphate derivatives, such as ATP, is pH-dependent. The functioning of the oxygen-transport enzyme hemoglobin is affected by pH in a process known as the Root effect.



pH values of some common substances

Seawater

The pH of seawater plays an important role in the ocean's carbon cycle, and there is evidence of ongoing ocean acidification caused by carbon dioxide emissions.[16] However, pH measurement is complicated by the chemical properties of seawater, and several distinct pH scales exist in chemical oceanography.[17]

As part of its operational definition of the pH scale, the IUPAC defines a series of buffer solutions across a range of pH values (often denoted with NBS or NIST designation). These solutions have a relatively low ionic strength (~0.1) compared to that of seawater (~0.7), and, as a consequence, are not recommended for use in characterizing the pH of seawater, since the ionic strength differences cause changes in electrode potential. To resolve this problem, an alternative series of buffers based on artificial seawater was developed.[18] This new series resolves the problem of ionic strength differences between samples and the buffers, and the new pH scale is referred to as the **total scale**, often denoted as **pH_T**.

The total scale was defined using a medium containing sulfate ions. These ions experience protonation, $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$, such that the total scale includes the effect of both protons (free hydrogen ions) and hydrogen sulfate ions:

$$[H^+]_T = [H^+]_F + [HSO_4^-]$$

An alternative scale, the **free scale**, often denoted **pH_F**, omits this consideration and focuses solely on $[H^+]_F$, in principle making it a simpler representation of hydrogen ion concentration. Only $[H^+]_T$ can be determined,[19] therefore $[H^+]_F$ must be estimated using the $[SO_4^{2-}]$ and the stability constant of HSO_4^-, K_S^*:

$$[H^+]_F = [H^+]_T - [HSO_4^-] = [H^+]_T \left(1 + [SO_4^{2-}] / K_S^* \right)^{-1}$$

However, it is difficult to estimate K_S^* in seawater, limiting the utility of the otherwise more straightforward free scale.

Another scale, known as the **seawater scale**, often denoted **pH_{SWS}**, takes account of a further protonation relationship between hydrogen ions and fluoride ions, $H^+ + F^- \rightleftharpoons HF$. Resulting in the following expression for $[H^+]_{SWS}$:

$$[H^+]_{SWS} = [H^+]_F + [HSO_4^-] + [HF]$$

However, the advantage of considering this additional complexity is dependent upon the abundance of fluoride in the medium. In seawater, for instance, sulfate ions occur at much greater concentrations (> 400 times) than those of fluoride. As a consequence, for most practical purposes, the difference between the total and seawater scales is very small.

The following three equations summaries the three scales of pH:

$$pH_F = -\log [H^+]_F$$
$$pH_T = -\log ([H^+]_F + [HSO_4^-]) = -\log [H^+]_T$$
$$pH_{SWS} = -\log ([H^+]_F + [HSO_4^-] + [HF]) = -\log [H^+]_{SWS}$$

In practical terms, the three seawater pH scales differ in their values by up to 0.12 pH units, differences that are much larger than the accuracy of pH measurements typically required, in particular, in relation to the ocean's carbonate system.[17] Since it omits consideration of sulfate and fluoride ions, the free scale is significantly different from both the total and seawater scales. Because of the relative unimportance of the fluoride ion, the total and seawater scales differ only very slightly.

Living systems

pH in living systems[20]

Compartment	pH
Gastric acid	1
Lysosomes	4.5
Granules of chromaffin cells	5.5
Human skin	5.5
Urine	6.0
Pure H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal fluid (CSF)	7.5
Blood	7.34–7.45
Mitochondrial matrix	7.5
Pancreas secretions	8.1

The pH of different cellular compartments, body fluids, and organs is usually tightly regulated in a process called acid-base homeostasis. The most common disorder in acid-base homeostasis is acidosis, which means an acid overload in the body, generally defined by pH falling below 7.35.* Alkalosis is the opposite condition, with blood pH being excessively high.

The pH of blood is usually slightly basic with a value of pH 7.365. This value is often referred to as physiological pH in biology and medicine. Plaque can create a local acidic environment that can result in tooth decay by demineralization. Enzymes and other proteins have an optimum pH range and can become inactivated or denatured outside this range.

Calculations of pH

The calculation of the pH of a solution containing acids and/or bases is an example of a chemical speciation calculation, that is, a mathematical procedure for calculating the concentrations of all chemical species that are present in the solution. The complexity of the procedure depends on the nature of the solution. For strong acids and bases no calculations are necessary except in extreme situations. The pH of a solution containing a weak acid requires the solution of a quadratic equation. The pH of a solution containing a weak base may require the solution of a cubic equation. The general case requires the solution of a set of non-linear simultaneous equations.

A complicating factor is that water itself is a weak acid and a weak base. It dissociates according to the equilibrium

$$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

with a dissociation constant, K_w defined as

$$K_w = [H^+][OH^-]$$

where $[H^+]$ stands for the concentration of the aquated hydronium ion and $[OH^-]$ represents the concentration of the hydroxide ion. K_w has a value of about 10^{-14} at 25 °C, so pure water has a pH of about 7. This equilibrium needs to be taken into account at high pH and when the solute concentration is extremely low.

Strong acids and bases

Strong acids and bases are compounds that, for practical purposes, are completely dissociated in water. Under normal circumstances this means that the concentration of hydrogen ions in acidic solution can be taken to be equal to the concentration of the acid. The pH is then equal to minus the logarithm of the concentration value. Hydrochloric acid (HCl) is an example of a strong acid. The pH of a 0.01M solution of HCl is equal to $-\log_{10}(0.01)$, that is, pH = 2. Sodium hydroxide, NaOH, is an example of a strong base. The p[OH] value of a 0.01M solution of NaOH is equal to $-\log_{10}(0.01)$, that is, p[OH] = 2. From the definition of p[OH] above, this means that the pH is equal to about 12. For solutions of sodium hydroxide at higher concentrations the self-ionization equilibrium must be taken into account.

Self-ionization must also be considered when concentrations are extremely low. Consider, for example, a solution of hydrochloric acid at a concentration of 5×10^{-8}M. The simple procedure given above would suggest that it has a pH of 7.3. This is clearly wrong as an acid solution should have a pH of less than 7. Treating the system as a mixture of hydrochloric acid and the amphoteric substance water, a pH of 6.89 results.[21]

Weak acids and bases

A weak acid or the conjugate acid of a weak base can be treated using the same formalism.

Acid: $HA \rightleftharpoons H^+ + A^-$
Base: $HA^+ \rightleftharpoons H^+ + A$

First, an acid dissociation constant is defined as follows. Electrical charges are omitted from subsequent equations for the sake of generality

$$K_a = \frac{[H][A]}{[HA]}$$

and its value is assumed to have been determined by experiment. This being so, there are three unknown concentrations, [HA], $[H^+]$ and $[A^-]$ to determine by calculation. Two additional equations are needed. One way to provide them is to apply the law of mass conservation in terms of the two "reagents" H and A.

$$C_A = [A] + [HA]$$
$$C_H = [H] + [HA]$$

C stands for analytical concentration. In some texts one mass balance equation is replaced by an equation of charge balance. This is satisfactory for simple cases like this one, but is more difficult to apply to more complicated cases as those below. Together with the equation defining K_a, there are now three equations in three unknowns. When an acid is dissolved in water $C_A = C_H = C_a$, the concentration of the acid, so [A] = [H]. After some further algebraic manipulation an equation in the hydrogen ion concentration may be obtained.

$$[H]^2 + K_a[H] - K_aC_a = 0$$

Solution of this quadratic equation gives the hydrogen ion concentration and hence p[H] or, more loosely, pH. This procedure is illustrated in an ICE table which can also be used to calculate the pH when some additional (strong) acid or alkali has been added to the system, that is, when $C_A \neq C_H$.

For example, what is the pH of a 0.01M solution of benzoic acid, $pK_a = 4.19$?

Step 1: $\mathrm{K_a} = 10^{-4.19} = 6.46 \times 10^{-5}$

Step 2: Set up the quadratic equation. $[\mathrm{H}]^2 + 6.46 \times 10^{-5}[\mathrm{H}] - 6.46 \times 10^{-7} = 0$

Step 3: Solve the quadratic equation. $[\mathrm{H}^+] = 7.74 \times 10^{-4}$; pH = 3.11

For alkaline solutions an additional term is added to the mass-balance equation for hydrogen. Since addition of hydroxide reduces the hydrogen ion concentration, and the hydroxide ion concentration is constrained by the self-ionization equilibrium to be equal to $\frac{K_w}{[H^+]}$

$$C_H = \frac{[H] + [HA] - K_w}{[H]}$$

In this case the resulting equation in [H] is a cubic equation.

General method

Some systems, such as with polyprotic acids, are amenable to spreadsheet calculations.[22] With three or more reagents or when many complexes are formed with general formulae such as $A_pB_qH_r$ the following general method can be used to calculate the pH of a solution. For example, with three reagents, each equilibrium is characterized by and equilibrium constant, β.

$$[\mathrm{A_pB_qH_r}] = \beta_{\mathrm{pqr}}[\mathrm{A}]^{\mathrm{p}}[\mathrm{B}]^{\mathrm{q}}[\mathrm{H}]^{\mathrm{r}}$$

Next, write down the mass-balance equations for each reagent

$$\begin{aligned}
\mathrm{C_A} &= [\mathrm{A}] + \Sigma \mathrm{p}\beta_{\mathrm{pqr}}[\mathrm{A}]^{\mathrm{p}}[\mathrm{B}]^{\mathrm{q}}[\mathrm{H}]^{\mathrm{r}} \\
\mathrm{C_B} &= [\mathrm{B}] + \Sigma \mathrm{q}\beta_{\mathrm{pqr}}[\mathrm{A}]^{\mathrm{p}}[\mathrm{B}]^{\mathrm{q}}[\mathrm{H}]^{\mathrm{r}} \\
\mathrm{C_H} &= [\mathrm{H}] + \Sigma \mathrm{r}\beta_{\mathrm{pqr}}[\mathrm{A}]^{\mathrm{p}}[\mathrm{B}]^{\mathrm{q}}[\mathrm{H}]^{\mathrm{r}} - \mathrm{K_w}[\mathrm{H}]^{-1}
\end{aligned}$$

Note that there are no approximations involved in these equations, except that each stability constant is defined as a quotient of concentrations, not activities. Much more complicated expressions are required if activities are to be used.

There are 3 non-linear simultaneous equations in the three unknowns, [A], [B] and [H]. Because the equations are non-linear, and because concentrations may range over many powers of 10, the solution of these equations is not straightforward. However, many computer programs are available which can be used to perform these calculations; for details see chemical equilibrium#Computer programs. There may be more than three reagents. The calculation of hydrogen ion concentrations, using this formalism, is a key element in the determination of equilibrium constants by potentiometric titration.

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External links

- The pH Scale (http://www.science.uwaterloo.ca/~cchieh/cact/c123/ph.html)
- Chem1 Virtual Textbook, Acid-base Equilibria and Calculations (http://www.chem1.com/acad/webtext/pdf/c1xacid2.pdf)
- Red Cabbage pH Indicator (http://chemistry.about.com/library/weekly/aa012803a.htm)
- Food and Foodstuff - pH Values (http://www.engineeringtoolbox.com/food-ph-d_403.html)

Retrieved from "http://en.wikipedia.org/w/index.php?title=PH&oldid=592488670"
Categories: Acid-base chemistry | Equilibrium chemistry | Units of measurement | Water quality indicators

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