Chemical Analysis

THE WORKING TOOLS

Volume II

CHEMICAL ANALYSIS

THE WORKING TOOLS

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VOLUME II

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INTRODUCTION

THE pH SCALE

In a given quantity of water, a certain number of the molecules are split up into hydrogen ions and hydroxyl ions, one molecule giving one ion of each kind. If a molecule of water is represented by H_2O, the hydrogen ion by H^+, and the hydroxyl ion by OH^-, the dissociation of water is represented by the equation

$$H_2O \rightleftharpoons H^+ + OH^-.$$

The resulting equilibrium is expressed mathematically by the equation

$$(H^+) \times (OH^-) = K_w,$$

K_w being known as the dissociation constant of water.

In pure water, the hydrogen and hydroxyl ions are present in equal and very small amounts, the concentration at 22° C being 0·0000001 (10^{-7}) gram ions per litre of each. In dilute aqueous solutions, the splitting up of a chemical compound influences the proportion of (H^+) to (OH^-), but the product of the concentration always remains a constant at 10^{-14} gram ions per litre at 22° C. Thus, as a first approximation, a normal solution of a strong acid at room temperature contains 1 gram ion of hydrogen per litre of water, pure water 10^{-7} gram ions, and a normal solution of a strong base 10^{-14} gram ions of hydrogen per litre.

Sörensen [1], who was responsible for the original concept of hydrogen ion concentration, suggested that a convenient scale would result from the use of the negative logarithm of the hydrogen ion concentration (H^+) rather than the inconvenient concentration itself, and introduced the symbol Ph^+ (later to be written as pH) to represent this function.

Thus
$$pH = \log_{10} \frac{1}{(H^+)} = -\log_{10}(H^+).$$

At one time, it was thought that the hydrogen ion concentration (H^+) could be determined by conductivity measurements; later, it was realized that these measurements did not give true values for the hydrogen ion concentration, and it became the practice to measure pH by means of a cell containing a hydrogen electrode; it was supposed that the quantity that was so measured was not the concentration of hydrogen ion, but its thermodynamic activity, usually written $[H^+]$.

Translated, therefore, into the modern concept of thermodynamic activity $[H^+]$, the Sörensen function becomes

$$pH = \log_{10}\frac{1}{[H^+]} = -\log_{10}[H^+],$$

so that for dilute solutions the pH scale ranges from 0 to 14.

The relationship that exists between pH and hydrogen ion activity is as given in Table 1.

TABLE 1

pH values, hydrogen ion activities, and approximate solution strengths

$[H^+]$	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}
$[OH^-]$	$10^0(=1)$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
pH	14	13	12	11	10	9	8
Approximate solution strength	1·0N alkali	0·1N alkali	0·01N alkali	0·001N alkali	0·0001N alkali	0·00001N alkali	0·000001N alkali

$[H^+]$	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	$10^0(=1)$
$[OH^-]$	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	7	6	5	4	3	2	1	0
Approximate solution strength	neutral	0·000001N acid	0·00001N acid	0·0001N acid	0·001N acid	0·01N acid	0·1N acid	1·0N acid

Unfortunately a difficulty arises with the definition

$$pH = -\log_{10}[H^+],$$

in that the activities of the individual ions are thermodynamically undefined, and have no exact simple fundamental significance; this has been pointed out in a comprehensive review by Bates [2]. In view of this difficulty, pH numbers are now simply defined in practice directly in terms of the measurements that can actually be made.

In order to ensure that, when different workers refer to a stated measured value of pH, they mean the same thing within $\pm 0{\cdot}005$ pH units, the British Standards Institution has adopted an operational and, to some extent, an arbitrary definition of pH [3], which applies strictly to *aqueous* solutions at temperatures between 0° C and 95° C.

The *difference* in pH between two solutions X and S at the same temperature is *defined* as follows:

The electromotive force E_x of the cell

Pt, H_2/Solution X/3·5M KCl/Reference electrode

and the electromotive force E_s of the cell

Pt, H_2/Solution S/3·5M KCl/Reference electrode

are measured, both cells being at the same temperature throughout, and the reference electrodes being identical in the two cells.

The pH of the solution X, denoted by pH (X), is then related to the pH of the solution S, denoted by pH (S), by the definition:

$$\text{pH}(X) - \text{pH}(S) = \frac{E_x - E_s}{2{\cdot}3026RT/F},$$

where R denotes the gas constant, T the absolute temperature, and F the Faraday.

In this equation, the numerator and denominator must be expressed in the same units, so that the pH difference as here defined is a *pure number*.

(The above definition, extracted, with minor alterations, from *B.S. No. 1647 : 1961, pH Scale*, is reproduced by permission of the British Standards Institution, 2 Park Street, London, W.1, from whom official copies of the complete standard may be obtained, price 4*s*. 6*d*.)

Numerical values of the factor $2{\cdot}3026RT/F$ at several temperatures are given in Table 2.

TABLE 2

Values of 2·3026 RT/F and its reciprocal

Temp. ° *C*	*2·3026 RT/F millivolt*	*F/2·3026 RT volt*$^{-1}$	*Temp.* ° *C*	*2·3026 RT/F millivolt*	*F/2·3026 RT volt*$^{-1}$
0	54·20	18·45	50	64·12	15·60
5	55·19	18·12	55	65·11	15·36
10	56·18	17·80	60	66·10	15·13
15	57·17	17·49	65	67·09	14·90
20	58·17	17·19	70	68·08	14·69
25	59·16	16·90	75	69·08	14·48
30	60·15	16·63	80	70·07	14·27
35	61·14	16·36	85	71·06	14·07
40	62·13	16·09	90	72·06	13·88
45	63·13	15·84	95	73·04	13·69

(The above table, extracted from *B.S. No. 1647 : 1961, pH Scale*, is reproduced by permission of the British Standards Institution, 2 Park Street, London, W.1, from whom official copies of the complete standard may be obtained, price 4*s*. 6*d*.)

THE PRIMARY STANDARD

The difference between the pH of two solutions having been thus defined, the definition of pH is completed by assigning a value of pH at each temperature to one chosen solution called the *primary standard*, in this case a one-twentieth molar solution of pure potassium hydrogen phthalate.

The pH of this solution is *defined* as having the value 4 exactly at 15° C. At any other temperature t° C between 0° C and 55° C its pH is defined by the formula:

$$\text{pH} = 4{\cdot}000 + \tfrac{1}{2}\left(\frac{t-15}{100}\right)^2;$$

between 55° C and 95° C the formula becomes

$$\text{pH} = 4{\cdot}000 + \tfrac{1}{2}\left(\frac{t-15}{100}\right)^2 - \frac{t-55}{500}$$

PRECAUTIONS FOR THE PREPARATION AND USE OF THE PRIMARY STANDARD

It is important that the potassium hydrogen phthalate should be of high purity and, in particular, free from excess of phthalic acid and from any sodium salt.

To prepare the primary standard, dissolve 10·21 g of pure dry potassium hydrogen phthalate in freshly distilled water (or distilled water recently boiled and cooled out of contact with atmospheric carbon dioxide) and dilute the solution to one litre. The pH values of this primary standard at temperatures up to 95° C are given in Table 3.

TABLE 3

Values of pH of primary standard—potassium hydrogen phthalate

Temp. °C	*pH*	*Temp.* °C	*pH*	*Temp.* °C	*pH*
0	4·011	35	4·020	70	4·121
5	4·005	40	4·031	75	4·140
10	4·001	45	4·045	80	4·161
15	4·000	50	4·061	85	4·185
20	4·001	55	4·080	90	4·211
25	4·005	60	4·091	95	4·240
30	4·011	65	4·105		

Note. The third decimal figure is not significant, but is included merely to facilitate smooth interpolation.

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The quantity pH thus specified has no precise simple fundamental meaning, and the definition adopted as standard is a practical one. However, in the restricted range of dilute aqueous solutions that do not exceed one-tenth molar, and are neither strongly alkaline nor strongly acid, i.e. between pH 2 and 12, the definition is such that

$$\text{pH} = -\log_{10} C_H f_1 \pm 0{\cdot}02,$$

where C_H denotes the concentration of hydrogen ion in gram ions/litre, and f_1 denotes the mean activity coefficient of a typical uni-univalent electrolyte in the solution.

THE ELECTRICAL DETERMINATION OF pH

ELECTRODES

Indicator electrodes

The hydrogen electrode

When a noble metal, coated with an adherent layer of a noble metal in finely divided form to increase its surface, is saturated with hydrogen gas it behaves like an electrode of 'metallic' hydrogen. Many forms of hydrogen electrode and of the vessel containing the electrode have been devised; most of these have been used for the measurement of pH and, from a survey of the literature, it is evident that to make a satisfactory hydrogen electrode is a matter of some difficulty. For information on types other than that described below the extensive literature may be consulted [4, 5, 6, 7].

A simple form of hydrogen electrode, due to Hildebrand [8], is shown in Fig. 1. The electrode itself consists of a piece of platinum foil, having a total area of about 2 sq. cm, spot-welded to a platinum wire and fused into a soft glass tube B in such a way that a little of the glass flows over the foil to give it mechanical strength. Connexion between the electrode and the rest of the circuit is made by means of a copper wire dipping into mercury in tube B, which has a wider tube A sealed on to it at its upper end. When required, the electrode is first prepared in the way described below. A current of hydrogen is then passed through the side tube C while the lower, expanded end of A is dipped into the test liquid.

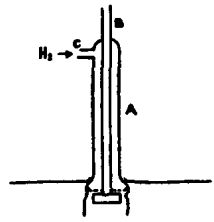

FIG. 1. Hydrogen electrode.

It is essential for the electrode to have a good coat of platinum black on the metal. The electrode is well cleaned in a cleaning solution of 10% potassium dichromate in sulphuric acid, and thoroughly washed with water, after which it is electroplated with a film of platinum black. It is of advantage to plate the electrode first for ten minutes with a solution containing 1% of gold chloride and 1·25% of potassium cyanide, at a current of 50 mA, the electrode being made negative [9]. Two gold-plated electrodes are suspended in a platinizing solution containing 3 g of platinum chloride and 0·02–0·03 g of lead acetate in 100 ml of water, and are joined through a 4-volt accumulator and a reversing switch. The current is adjusted so that there is only a moderate evolution of gas, and is allowed to pass for ten to fifteen minutes, its direction being

reversed every half-minute. The coating should be black and velvety in appearance; a moderately thick coat is preferable to a very thin one. The electrode is washed thoroughly with water, placed in approximately N/2 sulphuric acid, and connected to the negative pole of a 4-volt battery. Another platinum electrode is connected to the positive pole and a current is passed through the solution. The hydrogen formed at the electrode reduces any chlorine that has been absorbed from the platinizing liquid. After a vigorous evolution of gas for about ten minutes the current is stopped; the electrode is washed repeatedly with water and is then ready for use; when the electrode is not in use it should be kept in water. The electrode becomes rather sluggish in attaining its constant potential after it has been used for some time; when this happens, it should be cleaned and replated. The coating of black may be stripped from the electrode by immersing it in an 18% (approximately 5M) solution of hydrochloric acid, connecting it to the positive pole of a 4-volt battery, and passing a current through the solution for a short time.

The most convenient source of hydrogen is the compressed gas obtainable in cylinders. If it is not sufficiently pure, it should be passed over solid potassium hydroxide, and then through a tube of platinized asbestos heated to 200° C. This process removes the carbon dioxide and oxygen, which are the most likely impurities.

Advantages

1. The electrode is capable of giving very accurate results. Standard pH values accurate to $\pm 0{\cdot}01$ pH unit are obtained.
2. Its range is unlimited, and it gives accurately reproducible results from pH 0–14.
3. It is entirely free from salt errors, i.e. apparent shifts of pH caused by variation in the salt content of a solution.
4. The hydrogen electrode has low electrical resistance and thus may be used with an ordinary potentiometer calibrated to match the accuracy of the electrode.

Disadvantages

1. The electrode cannot be used in the presence of air or oxygen.
2. It cannot be used in the presence of oxidizing or reducing agents.
3. Difficulties arise when the solution contains any other gas than hydrogen, e.g. carbon dioxide in bicarbonates.
4. The catalytic platinum black deteriorates and must be renewed frequently.
5. Certain substances, such as alkaloids, hydrogen cyanide, arsenic, and antimony compounds poison the platinized surface; colloids are also absorbed on the surface and influence the e.m.f.

The antimony/antimony oxide electrode

The antimony electrode may be used for pH determinations; it consists of the pure metal dipping into the solution under test. An oxide skin is rapidly formed on the electrode and this oxide is in equilibrium with the antimony ion according to the equation

$$Sb_2O_3 + 3H_2O \rightleftharpoons 2Sb^{+++} + 6OH^-;$$

the activity of H_2O and solid Sb_2O_3 being taken as unity,

$$[Sb^{+++}]^2[OH^-]^6 = K, \quad \text{or} \quad K' = [Sb^{+++}][OH^-]^3.$$

The potential of the antimony metal is then influenced by $[Sb^{+++}]$, which in turn is influenced by $[H^+]$; thus

$$[Sb^{+++}] = \frac{K'}{[OH^-]^3} \quad \text{and} \quad OH^- = \frac{Kw}{[H^+]},$$

so that

$$[Sb^{+++}] = K''[H^+]^3.$$

To prepare an antimony electrode solder 4–5 in. of stout copper wire to one end of a cylinder of pure antimony 1–2 in. long. Slide the whole into a glass tube of slightly larger diameter so that the antimony protrudes beyond the tube. Use sealing wax or some other suitable material to fix the electrode in position in such a way that the copper/antimony junction cannot come into contact with the liquid to be tested. Polish the antimony with fine emery before use, and keep it in water when not in use.

Advantages

1. The electrode is extremely rugged and, within the limits of its applicability, is especially suited to industrial recording and pH control.
2. It functions well in the alkaline region up to pH 12.
3. It does not contaminate the test solution.
4. As it has low electrical resistance, it can be used with simple potentiometer circuits.
5. The electrode can be used in sludges, pastes, and viscous solutions.

Disadvantages

The stability and limits of error of the electrode depend upon many conditions, e.g.

1. The nature and condition of the electrode surface.
2. The concentration of dissolved air or oxygen in the solution; the electrode cannot be used in the presence of oxidizing agents.
3. The degree of agitation prevailing at the electrode surface.
4. The nature and concentration of dissolved salts.
5. Temperature changes. With the antimony/saturated calomel