

# Calcium Hydroxide as a Highly Alkaline $pH$ Standard

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The National Bureau of Standards conventional activity scale of  $pH$  is defined by a series of standard buffer solutions prepared from certified materials issued as NBS Standard Samples. The five standards thus far established cover the  $pH$  range 1.68 to 9.18 at 25° C. In order to increase the accuracy of measurements at high  $pH$ , a highly alkaline standard is needed.

A solution of calcium hydroxide saturated at 25° C is recommended as the sixth  $pH$  standard. No weighing is necessary, for the solution is easily prepared by shaking finely granular calcium hydroxide with water. The material must not be contaminated with soluble alkalies, but the presence of insoluble carbonate is of no concern. The filtered solution supersaturates readily and can usually be used from 0° to 60° C without the separation of solid phase.

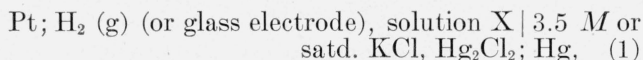
Electromotive-force measurements of 29 cells containing mixtures of calcium hydroxide and potassium chloride were made in the range 0° to 60° C, and standard  $pH$  values were assigned to 0.0203-, 0.02-, 0.019-, 0.0175-, and 0.015- $M$  solutions of calcium hydroxide without added chloride. The saturated solution is about 0.0203  $M$  and has a  $pH$  of 12.45 at 25° C. The buffer capacity is high (0.09 mole/ $pH$ ). Like most other alkaline solutions, however, this standard has a rather large dilution value ( $-0.28$   $pH$  unit) and a large temperature coefficient of  $pH$  ( $-0.033$   $pH$  unit/deg C).

## 1. Introduction

The National Bureau of Standards standard  $pH$  scale is defined in terms of several fixed points in much the same manner as the International Temperature Scale. The primary standards are solutions whose  $pH$  values are only slightly affected by dilution or by accidental contamination of the solution with traces of acid or alkali from the walls of the container or from the atmosphere. The substances from which the standards are prepared are, in turn, stable materials; they are obtainable in the form of certified samples from the Bureau. The five standards thus far established cover the  $pH$  range 1.68 to 9.18 at 25° C.<sup>1</sup> It is the purpose of this paper to describe the establishment of a sixth standard, a solution of calcium hydroxide saturated at 25° C, which will extend the standard scale to  $pH$  12.45 at 25° C.

## 2. Need for an Alkaline $pH$ Standard

In practice, most  $pH$  values are derived either directly or indirectly from the emf of the cell



where the vertical line marks a boundary between two liquid phases. The transfer of positive and negative ions at different rates across this liquid junction gives rise to a potential difference. Inasmuch as the transference numbers of the ions vary through the boundary, as do the concentration gradients, the net charge transferred is rarely zero. Furthermore, the sign of the potential difference may be either positive or negative, and the magnitude can neither be measured exactly nor calculated. If included in the measured emf, this potential would result in erroneous  $pH$  values.

<sup>1</sup> The assignment of  $pH$  values to these standards has been described in earlier Bureau papers: Tetroxalate ( $pH$  1.68 at 25° C) [1]; tartrate ( $pH$  3.56) [2]; phthalate ( $pH$  4.01) [3]; phosphate ( $pH$  6.86) [4]; and borax ( $pH$  9.18) [5]. Figures in brackets indicate the literature references at the end of this paper.

Fortunately, the concentrated solution of potassium chloride that composes the salt bridge reduces the liquid-junction potential to a small constant value for most solutions of intermediate acidity,  $pH$  3 to 11. When solution X contains appreciable amounts of the highly mobile hydrogen and hydroxyl ions ( $pH$  less than 3 or greater than 11), however, the liquid-junction potentials may differ considerably from the relatively constant values maintained in the region of intermediate  $pH$ . For accurate  $pH$  measurements in these regions of high acidity or high alkalinity, therefore, it is particularly important that reference standards of low and high  $pH$  be available.

This need is readily demonstrated. A  $pH$  measurement is essentially a determination of the difference between  $pH_x$ , the  $pH$  of the unknown solution, and  $pH_s$ , that of the standard. If  $E_x$  is the emf of cell 1 and  $E_s$  that of the same cell when the standard is substituted for solution X, and  $E_{jx}$  and  $E_{js}$  are the corresponding liquid-junction potentials, we have

$$pH_x = pH_s + \frac{E_x - E_s}{2.3026 RT/F} + \frac{E_{js} - E_{jx}}{2.3026 RT/F} \quad (2)$$

where  $R$ ,  $T$ , and  $F$  are the gas constant, the absolute temperature, and the faraday, respectively.

There is no way to evaluate the last term of eq (2). Hence, for the usual  $pH$  measurement the experimental conditions are chosen so as to nullify the greater part of the junction potential. The two potentials,  $E_{js}$  and  $E_{jx}$ , are then assumed to be nearly equal and to cancel rather completely when the difference is taken (eq (2)). Hence the difference of  $pH$  is assumed to be proportional to the difference of emf,  $E_x - E_s$ . Evidently the residual liquid-junction potential will be small when the standard solution and the unknown solution differ but little in  $pH$ , for the concentrations of the free hydrogen or hydroxyl ions (on which the liquid-junction potential largely depends) will be nearly the same in solution X as in solution S.

### 3. Calcium Hydroxide as a pH Standard

The ideal pH standard is a stable solution easily and reproducibly prepared from pure materials. The pH of the solution should not be markedly affected by changes of temperature. The buffer value [6] should be high and the dilution value [7] low; in other words, the pH of the solution should not be altered appreciably by contamination with traces of acidic or basic impurities or by a change in the total concentration of the buffer substances.

The ionization of water is strongly affected by temperature changes, and hence the pH of most highly alkaline aqueous solutions is also sensitive to alteration of temperature. The pH falls with increasing temperature by as much as 0.033 unit/deg C [8]. This imposes, of course, an unfortunate limitation on the use of an alkaline pH standard. It should be noted, however, that a certain degree of temperature control is necessary for pH measurements in the highly alkaline region, not only because the pH of the standard is sensitive to temperature changes but also because the "unknowns," in general, are similarly affected.

The buffer value, or buffer capacity, of solutions containing appreciable concentrations of hydroxide ion is uniformly larger than that of buffer solutions of comparable concentrations in the pH range 3 to 11, but these same solutions usually undergo a larger pH change on dilution [8]. A high buffer capacity is particularly important in an alkaline pH standard, for contamination with atmospheric carbon dioxide during storage and use can never be completely avoided.

In principle, a solution of a strong or moderately strong base will serve as an alkaline standard. In view of the high buffer capacity of aqueous solutions of even incompletely ionized bases at high pH, the addition of a salt of the base is unnecessary. However, it is very difficult, if not impossible, to find a strong base, either inorganic or organic, that is a stable solid. The determination of the concentration of the solution by a titration with standard acid is not only inconvenient and time-consuming but compounds the errors of three separate analytical operations. Buffer solutions of trisodium phosphate are subject to the same objections for, owing to the difficulty of preparing a sample of the phosphate salt of the correct composition, they must be made from the secondary phosphate and standard alkali. A pH greater than 11.2 at 25° C cannot readily be obtained with solutions of the alkali carbonates. To be most useful, an alkaline standard should have a pH of 12 or above.

Substances that form highly alkaline solutions usually become contaminated gradually with carbonate from exposure to the atmosphere when the container is opened. Many are also hygroscopic, and the moisture they acquire is not easily removed by simple drying procedures. If the carbonate were insoluble in water, however, the contaminant could be easily removed by filtration of the solution, and later contamination would be clearly evident when it occurred. If, in addition, the alkaline material were

of moderate solubility, the saturated solution would serve as a standard. Under these conditions, the presence of carbonate would cause no concern; furthermore, no weighings would be necessary.

Because of its ease of preparation, a saturated solution of slaked lime, calcium hydroxide, has often been employed as a reference solution of high alkalinity [9, 10, 11]. Tuddenham and Anderson [11] saturated calcium chloride solutions with calcium hydroxide to achieve pH values from 11 to over 12, as desired. The concentration of the saturated solution of calcium hydroxide in pure water is about 0.02 M and the pH about 12.4 at 25° C. A few measurements made in an earlier study [12], however, suggested that the saturated solution, like that of the more soluble barium hydroxide, might not be sufficiently reproducible to serve as a primary standard. Later work has shown that the solubility of samples of calcium hydroxide free from soluble alkalis and salts is indeed reproducible within 1 percent.

The solubility of calcium hydroxide decreases with rising temperature, being about 4 percent higher at 20° than at 25° C, and 4 percent lower at 30°. Nevertheless, a separation of solid phase does not usually occur at 50° or even at 60° C when a solution saturated at 25° is filtered and subsequently heated to those temperatures [13, 14]. A solution of calcium hydroxide that has been saturated at or near 25° C can accordingly be employed as a pH standard over a considerable range of temperature.

The properties of a solution of calcium hydroxide saturated at 25° C are compared with those of the phthalate and borax pH standards in the following summary:

	Calcium hydroxide	Potassium hydrogen phthalate	Borax
Molar concentration...	0. 0203	0. 05	0. 01
Density (25° C).....	. 9991	1. 0017	-----
Buffer value ( $\beta$ ), mole/pH unit.....	ca. 09	0. 016	. 020
Dilution value ( $\Delta pH_{1/2}$ ), pH units for 1:1 dilution.....	ca. -. 28	+. 05	+. 01
$d pH/dt$ , pH units/deg C.	-. 033	+. 0012	-. 0082

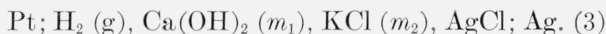
It is seen that the pH change, in absolute measure, on dilution of the calcium hydroxide standard is more than 5 times that on dilution of the phthalate solution of pH 4.0,<sup>2</sup> whereas the temperature coefficient is 4 times that of the borax standard (pH 9.2). It appears that any highly alkaline standard will be subject to these limitations in much the same degree.

### 4. Method of Assigning pH

The emf method by which standard pH values were assigned to solutions of calcium hydroxide has been described [1, 2, 8]. It will be summarized briefly here, but certain novel features of the present treatment will be explained in detail.

<sup>2</sup> At low pH, the dilution value attains large positive values. For the 0.05 M potassium tetroxalate standard (pH 1.7),  $\Delta pH_{1/2}$  is +0.19.

The first step consisted in the measurement of the emf of cells with hydrogen and silver-silver-chloride electrodes, containing the calcium hydroxide solutions with added potassium chloride:



The symbol  $m$  represents molality, or moles per kilogram of water. The molality of a solution does not change with temperature and is therefore favored over volume concentration in measurements of this type. Several different molalities of calcium hydroxide in the range 0.015 to 0.0203 were selected. For each calcium hydroxide concentration, three different molalities of potassium chloride, namely, 0.015  $m$ , 0.01  $m$ , and 0.005  $m$ , were studied.

The second step was to compute values of the quantity  $pwH$ , defined by eq (4), for each mixture of calcium hydroxide and potassium chloride and to determine, by extrapolation, the value of  $pwH^\circ$ , the limit approached by  $pwH$  in calcium hydroxide solutions as the concentration of potassium chloride was reduced to zero. The value of  $pwH$  is computed directly from the measured emf,  $E$ , and the standard potential,  $E^\circ$ , of the cell [15] by

$$pwH \equiv -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) = \frac{E - E^\circ}{2.3026 RT/F} + \log m_{\text{Cl}}, \quad (4)$$

where  $f$  is an activity coefficient on the molal scale,  $R$  is the gas constant (8.31439 j deg<sup>-1</sup> mole<sup>-1</sup>),  $F$  is the faraday (96493.1 coulombs equiv<sup>-1</sup>), and  $T$  is the temperature on the Kelvin scale (deg C + 273.16).

The values of  $pwH$  obtained by eq (4) for each of the three concentrations of potassium chloride proved to be a linear function of  $\log m_1$ , the common logarithm of the molality of calcium hydroxide, in the limited range studied (0.015 <  $m_1$  < 0.0203). The constants of the equation

$$pwH = a + b \log m_1 \quad (5)$$

were determined by the method of least squares and used to compute  $pwH$  for five selected concentrations of calcium hydroxide ( $m_1 = 0.015, 0.0175, 0.019, 0.02, \text{ and } 0.0203$ ) at each of the three chloride concentrations and at the 13 temperatures included in the study. In agreement with our earlier observations,  $pwH$  for a given value of  $m_1$  was found to vary linearly with  $m_2$ , the molality of potassium chloride. The limit,  $pwH^\circ$ , in the absence of chloride was then determined by fitting the values of  $pwH$  for the five selected calcium hydroxide solutions to the equation

$$pwH = pwH^\circ + cm_2 \quad (6)$$

by the method of least squares.

In the third step, the procedure necessarily departs from thermodynamic rigor, for the  $pH$  lacks exact

thermodynamic definition. The formal relationship between  $pwH^\circ$  and  $pH_s$  is

$$pH_s \equiv -\log f_{\text{H}} m_{\text{H}} = pwH^\circ + \log f_{\text{Cl}}, \quad (7)$$

where  $f_{\text{Cl}}^\circ$  is the activity coefficient of chloride ion in the chloride-free solution of calcium hydroxide.

The NBS standard  $pH$  scale is based on the convention that the last term of eq (7) be expressed by the Debye-Hückel equation

$$-\log f_{\text{Cl}}^\circ = \frac{A\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \quad (8)$$

with a reasonable choice of the ion-size parameter,  $a_i$ . In eq (8),  $\mu$  is the ionic strength, while  $A$  and  $B$  are constants for the water medium at a particular temperature [16]. The most probable value of  $a_i$  for chloride ion in a mixture of simple electrolytes is regarded to lie between 4 and 6, but values as low as 3 or as high as 8 cannot be termed unreasonable. Inasmuch as the convention adopted does not specify a *single* value of  $a_i$ , the  $pH_s$  is not defined exactly through eq (7) and (8). The uncertainty amounts to a few thousandths of a  $pH$  unit at an ionic strength of 0.01 and to slightly more than  $\pm 0.01$  unit at an ionic strength of 0.1 [8].

Because calcium hydroxide is not completely ionized,<sup>3</sup> the ionic strength of calcium hydroxide solutions is somewhat less than  $3m_1$ . However, the hydroxide ion molality,  $m_{\text{OH}}$ , can be evaluated with adequate accuracy from  $pwH^\circ$  and the ion-product constant,  $K_w$ , for water at the appropriate temperature:<sup>4</sup>

$$\log m_{\text{OH}} = \log K_w + pwH^\circ. \quad (9)$$

The first dissociation step is presumed to be complete and the second incomplete; hence, the molalities of the ions  $\text{Ca}^{++}$  and  $\text{CaOH}^+$  are given by

$$m_{\text{Ca}} = m_{\text{OH}} - m_1 \quad (10)$$

and

$$m_{\text{CaOH}} = 2m_1 - m_{\text{OH}}, \quad (11)$$

and the ionic strength is

$$\mu = 2m_{\text{OH}} - m_1. \quad (12)$$

## 5. Experimental Procedures and Results

### 5.1. Solubility of Calcium Hydroxide

There is some disagreement among literature values for the solubility of calcium hydroxide, as well as some indication that the apparent solubility is dependent upon crystal size [18, 19]. Bassett [18]

<sup>3</sup> See, for example, the paper of Bell and Prue [17]. The second dissociation constant is about 0.05.

<sup>4</sup> Eq (9) depends for its validity upon the approximate equality of the activity coefficients ( $f_{\text{Cl}}$  and  $f_{\text{OH}}$ ) of ions of like charge in solutions of moderate concentration and upon the fact that the activity of water in such solutions does not depart greatly from unity. The formula is consequently more accurate the more dilute the solution.



has made an extensive study of the solubility from 0° to 100° C and lists two values over a considerable range of temperature; his "true solubility" is from 6 to 15 percent lower than the solubility of very small crystals. The true solubility at 25° C, in moles per kilogram of water (molality), was found by Bassett to be 0.02018, in reasonable agreement with 0.0205 found earlier by Moody and Leyson [20], but significantly lower than 0.0209 obtained by interpolation between the data at 10° and 42° as determined by Haslam, Calingaert, and Taylor [21].

For the solubility of large crystals at 25° C, however, Johnston and Grove [13] found a value of 0.01976 *m*, and quite recently Peppler and Wells [19] have concluded that the solubility of large, well-formed crystals is 0.0184 *m* at 30°. Inasmuch as the solubility of calcium hydroxide appears to be only about 4 percent lower at 30° than at 25°, there remains a discrepancy of about 2.5 percent between these two determinations of the solubility of large crystals.

In the present study, the solubility of several samples of calcium hydroxide prepared in various ways was determined by shaking the material vigorously with about 15 times its volume of water in a glass-stoppered bottle. Between periods of shaking, the bottle was maintained at a controlled temperature by immersion in a water thermostat. The excess of solid was removed on a sintered-glass funnel of medium porosity, and the concentration of the filtrate was determined by titration with a standard solution of hydrochloric acid to the endpoint of phenol red. Weight burets were used in the titrations. The solubility determinations were reproducible to  $\pm 0.5$  percent or better.

In the initial experiments with calcium hydroxide of reagent grade, solubilities as high as 0.0229 *m* at 25° C were obtained, but this figure was lowered somewhat by repeated digestion of the hydroxide under hot water. This behavior could result from the extraction of soluble alkaline impurities or from a gradual stabilization of crystal form during the digestion. Thereafter, the samples of hydroxide were prepared from "CP" low-alkali calcium carbonate and the effect was no longer observed.

The finely granular calcium carbonate was ignited in platinum dishes at 1,000° C for about 45 min, and the resulting lime, after cooling in a desiccator, was added with stirring to water. The mixture was heated to boiling with continual stirring and was then filtered. The calcium hydroxide obtained in this way was dried at 110° C and powdered.

The solubility of five samples of hydroxide prepared in this manner was found to be 0.02037 *m*, with a standard deviation of 0.00011, and this figure was substantially unchanged after seven extractions of the product with water. To test the effect of aging, the calcium hydroxide was stored under water in a polyethylene bottle and samples removed from time to time for solubility tests conducted as described above. After 1 month, the solubility of four samples was found to be 0.02032 *m*, with a standard deviation of 0.00006, and after 6 months had elapsed a figure of 0.02022 *m* was ob-

tained as the mean of two determinations. The average solubility is 0.0203 *m* at 25° C. At 20° C the solubility was found to be 0.0211 *m* and at 30° C, 0.0196 *m*.

These figures are in excellent agreement with the true solubility of Bassett [18], who found 0.0211 *m* at 20°, 0.0202 *m* at 25°, and 0.0195 *m* at 30° C. It appears that they represent satisfactorily reproducible concentrations achieved by shaking granular calcium hydroxide, prepared from low-alkali calcium carbonate, with water at 20°, 25°, or 30° C. However, they do not preclude a solubility lower by perhaps 1 to 3 percent for large well-defined crystals of the material. It should be noted that a change of 1 percent in the concentration of calcium hydroxide corresponds to about 0.004 in the *pH* of the nearly saturated solution.

## 5.2. Electromotive-Force Measurements

The calcium hydroxide solutions for the emf measurements were prepared by dilution of nearly saturated stock solutions whose concentrations had been established by titration with standard acid. A weighed amount of potassium chloride was then added to each solution flask, or a portion of a 0.3-*M* solution of the salt introduced from a weight buret. The dilution and the addition of chloride in an atmosphere of carbon-dioxide-free nitrogen were accomplished with the aid of an arrangement very similar to that described by Bates and Acree [22]. The potassium chloride was a bromide-free fused sample prepared in the manner described in an earlier publication [23].

The cells were rinsed, flushed, and filled in the usual manner. Solution was admitted from the solution flask, the cell emptied and flushed with pure hydrogen, and the cycle repeated before the final portion of solution was admitted. The preparation of the electrodes has been described elsewhere [8]. Each cell contained two pairs of electrodes, and the duplicate measurements were averaged.

Initial measurements were made at 25° C, those from 0° to 30° C on the second day, and those from 30° to 60° C on the third day. With these highly alkaline solutions, the final measurements at 25° C, when they were obtained, did not agree as closely with the initial values as those for solutions of low or intermediate *pH* often do. Differences of 0.3 to 0.5 mv were not uncommon. The emf data were corrected in the usual way to a partial pressure of 1 atm of hydrogen.

## 6. Determination of *p<sub>w</sub>H* and *p<sub>w</sub>H*<sup>o</sup>

A value of *p<sub>w</sub>H* was computed from each corrected emf value by eq (4), and the constants *a* and *b* of eq (5) were obtained for each of the three molalities of potassium chloride (*m*<sub>2</sub> equal to 0.015, 0.01, or 0.005) in the cell solutions. The data are summarized in table 1. The third column gives the number of cells studied, and the sixth column lists  $\sigma$ , the standard deviation of a single *p<sub>w</sub>H* value from the line defined by the constants *a* and *b*. The last five columns give



$pwH$  at five selected values of  $m_1$ , the molality of calcium hydroxide. These figures were computed by eq (5) with the values of  $a$  and  $b$  given in the table. For each  $m_1$ , the limiting value of  $pwH$ ,

namely,  $pwH^\circ$ , as the molality ( $m_2$ ) approached zero, obtained by eq (6), is entered on the fourth line at each temperature. The standard deviation,  $\sigma_i$ , of this intercept ( $pwH^\circ$ ) is listed on the fifth line.

TABLE 1.  $pwH$  and  $pwH^\circ$  for mixtures of calcium hydroxide ( $0.015 < m_1 < 0.0203$ ) and potassium chloride ( $m_2$ ) from  $0^\circ$  to  $60^\circ C$ ; constants of the equation  $pwH = a + b \log m_1$

$t$	$m_2$	Number of cells	$a$	$b$	$^a \sigma$	$pwH$ for $m_1$ equal to				
						0.0203	0.02	0.019	0.0175	0.015
0	0.015	11	15.121	0.9450	0.003	13.521	13.515	13.494	13.460	13.397
	.010	10	15.137	.9548	.002	13.521	13.515	13.494	13.459	13.396
	.005	8	15.110	.9432	.004	13.513	13.507	13.485	13.452	13.389
	.000	-----	-----	-----	-----	$pwH^\circ =$ 13.510	13.504	13.482	13.449	13.386
						$^b \sigma_i =$ 0.005	0.005	0.004	0.004	0.003
5	.015	11	14.909	.9480	0.005	13.304	13.298	13.277	13.246	13.180
	.010	10	15.095	1.0578	.004	13.305	13.298	13.274	13.237	13.166
	.005	8	14.901	0.9492	.004	13.294	13.288	13.267	13.233	13.169
	.000	-----	-----	-----	-----	$pwH^\circ =$ 13.291	13.285	13.263	13.226	13.161
						$\sigma_i =$ 0.006	0.006	0.002	0.003	0.011
10	.015	11	14.705	.9463	0.004	13.103	13.097	13.076	13.042	12.979
	.010	10	14.838	1.0258	.004	13.102	13.096	13.073	13.036	12.967
	.005	8	14.714	0.9584	.005	13.092	13.086	13.065	13.030	12.966
	.000	-----	-----	-----	-----	$pwH^\circ =$ 13.088	13.082	13.060	13.024	12.958
						$\sigma_i =$ 0.006	0.006	0.003	0.000	0.006
15	.015	11	14.495	.9360	0.003	12.911	12.905	12.884	12.851	12.788
	.010	10	14.606	1.0093	.004	12.910	12.904	12.881	12.845	12.778
	.005	8	14.478	0.9334	.004	12.898	12.892	12.872	12.838	12.776
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.893	12.887	12.867	12.832	12.769
						$\sigma_i =$ 0.004	0.004	0.003	0.004	0.007
20	.015	11	14.300	.9281	0.004	12.729	12.723	12.703	12.670	12.607
	.010	10	14.376	.9746	.004	12.727	12.720	12.699	12.664	12.599
	.005	8	14.331	.9533	.006	12.717	12.711	12.690	12.656	12.592
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.712	12.706	12.684	12.649	12.584
						$\sigma_i =$ 0.005	0.004	0.003	0.002	0.002
25	.015	11	14.139	.9312	0.002	12.563	12.557	12.537	12.503	12.441
	.010	10	14.166	.9502	.003	12.558	12.552	12.531	12.497	12.433
	.005	8	14.124	.9325	.007	12.545	12.539	12.519	12.485	12.423
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.537	12.531	12.511	12.477	12.414
						$\sigma_i =$ 0.005	0.005	0.004	0.004	0.002
30	.015	11	13.967	.9268	0.004	12.398	12.392	12.372	12.339	12.277
	.010	9	13.975	.9354	.003	12.392	12.386	12.365	12.332	12.269
	.005	7	14.030	.9707	.004	12.387	12.381	12.359	12.324	12.259
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.381	12.375	12.352	12.317	12.250
						$\sigma_i =$ 0.002	0.002	0.002	0.002	0.002
35	.015	11	13.830	.9387	0.006	12.241	12.235	12.214	12.181	12.118
	.010	9	13.817	.9366	.002	12.232	12.226	12.205	12.172	12.109
	.005	7	13.825	.9441	.003	12.227	12.221	12.200	12.166	12.103
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.219	12.213	12.192	12.158	12.095
						$\sigma_i =$ 0.003	0.003	0.003	0.002	0.003
40	.015	11	13.658	.9276	0.006	12.088	12.082	12.062	12.029	11.966
	.010	9	13.682	.9444	.004	12.083	12.077	12.056	12.022	11.959
	.005	7	13.586	.8924	.005	12.076	12.070	12.050	12.018	11.959
	.000	-----	-----	-----	-----	$pwH^\circ =$ 12.070	12.064	12.044	12.012	11.954
						$\sigma_i =$ 0.002	0.002	0.000	0.002	0.005
45	.015	10	13.516	.9287	0.007	11.944	11.938	11.918	11.884	11.822
	.010	7	13.546	.9492	.004	11.939	11.933	11.912	11.878	11.814
	.005	7	13.451	.8978	.007	11.932	11.926	11.906	11.876	11.814
	.000	-----	-----	-----	-----	$pwH^\circ =$ 11.926	11.920	11.900	11.871	11.809
						$\sigma_i =$ 0.005	0.002	0.000	0.003	0.005
50	.015	11	13.331	.8995	0.007	11.809	11.803	11.783	11.751	11.691
	.010	9	13.252	.8549	.009	11.807	11.800	11.781	11.750	11.693
	.005	7	13.323	.9016	.008	11.796	11.791	11.771	11.739	11.678
	.000	-----	-----	-----	-----	$pwH^\circ =$ 11.790	11.786	11.766	11.735	11.674
						$\sigma_i =$ 0.003	0.004	0.005	0.006	0.011
55	.015	10	13.226	.9150	0.007	11.677	11.672	11.651	11.619	11.557
	.010	7	13.269	.9430	.002	11.673	11.667	11.646	11.612	11.549
	.005	7	13.161	.8832	.010	11.666	11.660	11.641	11.609	11.550
	.000	-----	-----	-----	-----	$pwH^\circ =$ 11.661	11.654	11.636	11.603	11.545
						$\sigma_i =$ 0.002	0.002	0.000	0.003	0.006
60	.015	11	13.081	.9024	0.006	11.554	11.548	11.528	11.496	11.435
	.010	9	13.245	1.0001	.005	11.553	11.546	11.524	11.488	11.421
	.005	7	13.058	0.8945	.008	11.544	11.538	11.518	11.486	11.421
	.000	-----	-----	-----	-----	$pwH^\circ =$ 11.540	11.534	11.513	11.480	11.418
						$\sigma_i =$ 0.005	0.003	0.002	0.003	0.012

<sup>a</sup> Standard deviation of  $pwH$ .

<sup>b</sup> Standard deviation of the intercept,  $pwH^\circ$ .

## 7. pH of Calcium Hydroxide Solutions

The ionic strengths of the five solutions of calcium hydroxide at 0°, 25°, and 60° C, computed by eq (9) and (12), are as follows:

$m_1$	$\mu$ at—		
	0° C	25° C	60° C
0.0203	0.054	0.049	0.047
.02	.053	.049	.046
.019	.050	.047	.044
.0175	.047	.043	.041
.015	.040	.037	.035

The values of  $pH_s$  given in table 2 and plotted as a function of the molality of calcium hydroxide in figure 1 were calculated by eq (7) and (8) with the use of these ionic strengths. Each  $pH_s$  value is the mean between that obtained with  $a_1=4$  and  $a_1=6$ ; these two different estimates of  $pH_s$  differed by 0.009 unit for the solution saturated at 25° (0.0203  $m$ ) and by 0.007 for the 0.015- $m$  solution. In the light of the statistical probable error in  $pH^0$  and the partially arbitrary selection of  $a_1$ , the  $pH_s$  is assigned an uncertainty of  $\pm 0.01$  unit. The effect

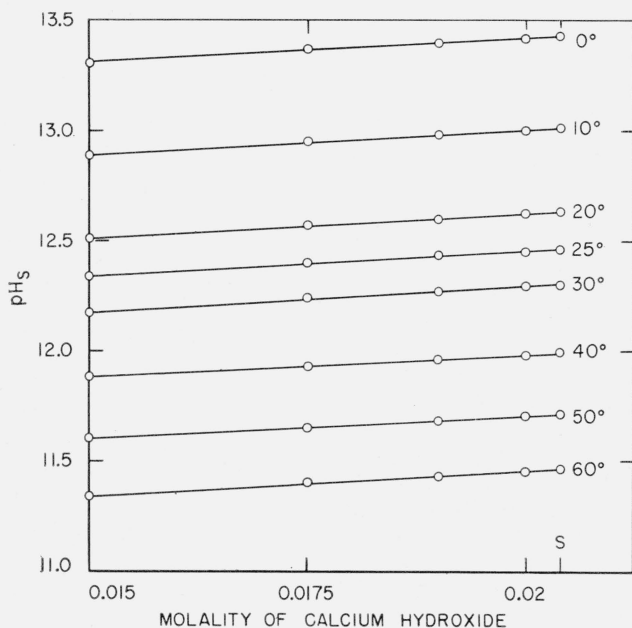


FIGURE 1.  $pH_s$  of solutions of calcium hydroxide from 0° to 60° C, as a function of molality.

The molality of a solution saturated at 25° C is indicated by S.

of  $a_1$  on the calculated  $pH_s$  is shown in figure 2. The solid line passes through the values listed in table 2, and the dotted lines indicate the displacement resulting from a choice of  $a_1=3$  and  $a_1=8$ .

TABLE 2.  $pH_s$  of five solutions of calcium hydroxide from 0° to 60° C

$t$	0.0203 $m$	0.02 $m$	0.019 $m$	0.0175 $m$	0.015 $m$
° C					
0	13.428	13.422	13.401	13.371	13.311
5	13.208	13.202	13.182	13.147	13.086
10	13.004	12.999	12.978	12.947	12.883
15	12.809	12.805	12.786	12.754	12.694
20	12.629	12.623	12.602	12.570	12.508
25	12.454	12.449	12.429	12.398	12.338
30	12.296	12.291	12.270	12.237	12.174
35	12.135	12.129	12.110	12.078	12.019
40	11.985	11.980	11.961	11.931	11.877
45	11.841	11.836	11.816	11.789	11.731
50	11.704	11.701	11.683	11.653	11.596
55	11.575	11.568	11.552	11.521	11.466
60	11.454	11.448	11.428	11.398	11.340

<sup>a</sup> Saturated at 25° C.

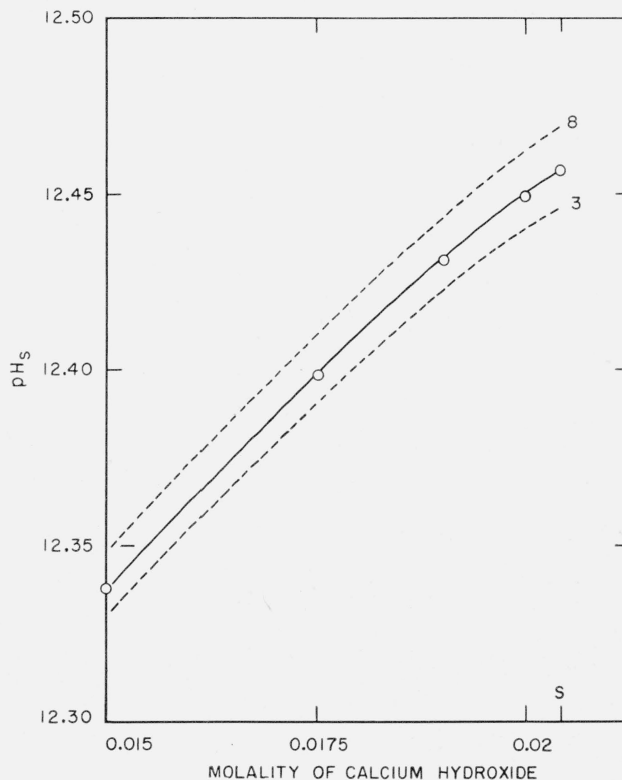


FIGURE 2. Effect of choice of  $a_1$  (eq 8) on the  $pH_s$  values for calcium hydroxide solutions.

Solid line represents the mean values of  $pH_s$  obtained with  $a_1=4$  and  $a_1=6$ ; dotted lines show the displacement resulting from choice of  $a_1=3$  (lower line) and  $a_1=8$  (upper line).

## 8. Standardization in the Range $pH$ 9 to 12.5

As has been pointed out earlier in this paper, a plot of the emf of cell 1 as a function of  $pH$  is a straight line of slope  $2.3026RT/F$  when the  $pH$  is neither too low nor too high. At high alkalinities a voltage departure or change in slope is to be expected. There will be an accompanying aberration of the practical  $pH$  scale near its upper end, operating to yield  $pH$  values that are too low. It is appropriate to consider next the probable magnitude of the error and means of minimizing or eliminating it by proper standardization of the  $pH$  assembly.

The error has its origin in an experimental defect of the  $pH$  method, namely the changing liquid-junction potential with alteration of the concentration of highly mobile hydroxide ions. It is often not noticeable below  $pH$  11, but earlier work with carbonate buffer solutions [12] has indicated that it may be detectable at  $pH$  10. This earlier study suggested further that the magnitude of the discrepancy at  $25^\circ C$  is about 0.01 unit at  $pH$  10, 0.02 unit at  $pH$  11.1, and about 0.05 unit at  $pH$  12.6. The error thus appears to increase in a fairly regular manner with the  $pH$  of the test solution.

It is of some importance, therefore, to determine whether this apparent regularity extends to solutions of calcium hydroxide. The difference of potential between one hydrogen electrode dipping in a solution saturated with calcium hydroxide at  $25^\circ C$  and another dipping in the standard 0.025  $M$  phosphate buffer ( $pH_s = 6.86_0$  at  $25^\circ C$ ) was therefore determined. A cell consisting of two hydrogen-electrode compartments [12] was used. Contact between the solutions was established through a saturated solution of potassium chloride. The observed difference of potential was 0.3288 v at  $25^\circ$ , corresponding to a  $pH$  of 12.42<sub>0</sub> for the solution of calcium hydroxide. This solution was assigned a  $pH_s$  of 12.454 from measurements of cells without a liquid junction (compare table 2). The discrepancy of 0.03<sub>4</sub> unit at  $pH$  12.45 is reasonably consistent with a linear progression of the error from  $pH$  9.18 (the  $pH$  of the borax standard), which lies in the upper end of the error-free region of the practical  $pH$  scale [12], to  $pH$  12.88, where an error of about 0.05 unit has been found [24].

As a consequence, a  $pH$  meter standardized at  $pH$  9.18 will yield a slightly low reading between  $pH$  9.18 and 12.45, and a meter standardized at  $pH$  12.45 will yield a slightly high reading in the same region of the scale. The error evidently will be  $(0.034/3.27)(pH_x - pH_s)$  unit. Hence, we have from eq (2)

$$pH_x = pH_s + \frac{1.0105(E_x - E_s)}{2.3026RT/F} \quad (\text{at } 25^\circ C) \quad (13)$$

$$pH_x = pH_s + 17.08(E_x - E_s) \quad (\text{at } 25^\circ C) \quad (14)$$

Inasmuch as the liquid-junction potential is somewhat dependent upon the structure of the liquid-

liquid boundary, it is advisable to determine the error for the particular assembly that is being used. Freshly prepared borax and calcium hydroxide solutions should be used for this purpose. If the error differs much from 0.03 or 0.04 unit, the numerical coefficients of eq (13) and (14) should be adjusted accordingly. The difference as indicated by a  $pH$  meter may be influenced somewhat by errors in scale length and in the temperature compensator, if these have not been calibrated.

Because the  $pH$  meter reads  $pH$  units directly, it may be convenient to apply a correction to the indicated  $pH$ , rather than to compute the correct figure by eq (13) or (14) from a measurement of the emf. The temperature compensator of the meter is, however, designed to permit the selection of different values of the slope  $pH$ /emf, corresponding to the value of  $F/(2.3026RT)$  at different temperatures. Hence, this device permits  $pH$  to be read directly from the scale of the instrument, even though the functional relationship between the emf of the cell and the  $pH$  value varies rather widely, as it may do when the temperature of the cell changes.

When the temperature compensator indicates  $25^\circ C$ , the instrument converts emf differences into  $pH$  differences according to the relationship  $\Delta pH = 16.90\Delta E$ ; at  $20^\circ C$ , the conversion is made according to  $\Delta pH = 17.19\Delta E$ . It is evidently possible, then, to compensate the liquid-junction error at the high end of the scale, permitting correct values at  $25^\circ C$  to be read directly from the meter, if the temperature compensator is set at  $22^\circ C$ , for at this temperature  $F/(2.3026RT)$  is not far from 17.08 (compare eq (14)). The values of this quantity at other temperatures are:

$^\circ C$	
10	17.80
15	17.49
20	17.19
25	16.90
30	16.63

The alkaline error of the glass electrode made from Corning 015 glass is very much lower in solutions of calcium salts than in solutions of lithium or sodium salts [25]. However, in a saturated solution of calcium hydroxide, this source of error may be of concern at temperatures from  $40^\circ$  to  $60^\circ C$ . Many of the newer commercial electrode glasses contain no calcium, and hence the voltage departures in calcium solutions are probably negligible.

## 9. A Standard Solution of Calcium Hydroxide

A solution of calcium hydroxide saturated at room temperature is recommended as a  $pH$  standard for the highly alkaline range. A considerable excess of pure, finely granular hydroxide is shaken vigorously in a stoppered bottle with water at room temperature. The gross excess of solid is allowed to settle,



the temperature recorded to the nearest degree Celsius, and the suspended material removed by filtration with suction on a sintered-glass funnel of medium porosity.

It has been recommended that a slurry containing excess calcium hydroxide be used for standardization purposes [11]. However, large errors are sometimes incurred in *pH* measurements of suspensions [26], and it seems best to rule out this uncertainty by removal of the solid phase.

For the saturation, a polyethylene bottle is very satisfactory; in fact, it may be found convenient to keep the solid continuously under water in a well-stoppered polyethylene bottle ready for final saturation and filtration when a fresh solution is needed. Contamination of the solution with atmospheric carbon dioxide prior to filtration is obviously of little concern. Contamination of the filtered standard solution renders it turbid and is a cause for replacement.

The temperature coefficient of solubility is negative, but the solution supersaturates readily and no precipitation of solid is ordinarily observed at 60° C. Unfortunately, however, the change of solubility with temperature is sufficiently large to require that the saturation temperature be noted and the *pH<sub>s</sub>* values (column 2, table 2) adjusted by the appropriate amount. These values for saturation temperatures of 20°, 25°, and 30° C are:

Saturation temperature	Solubility ( <i>m</i> )	<i>pH<sub>s</sub></i> at (° C)—			Correction to column 2, table 2
		20	25	30	
°C					
20	0.0211	12.64	12.47	12.31	+0.015
25	.0203	12.63	12.45	12.30	0
30	.0195	12.61	12.44	12.28	-.016

The calcium hydroxide should be prepared from well-washed calcium carbonate of low-alkali grade. The carbonate is heated slowly to 1,000° C and ignited for at least 45 min at that temperature. After cooling, the calcium oxide is added slowly to water with stirring and the suspension heated to boiling, cooled, and filtered on a sintered-glass funnel of medium porosity. The solid is dried in an oven and crushed to a uniform finely granular state for use.

It is advisable to determine the concentration of a saturated solution of one portion of calcium hydroxide prepared from each particular lot of calcium carbonate, as described earlier in this paper. The

molality (*m*) and molarity (*M*) of the saturated solution are practically identical, differing by only 0.3 percent. If the concentration of the solution saturated at 25° C appears to exceed 0.0206 *M*, the presence of soluble alkalis is indicated. If calcium carbonate of a higher grade cannot readily be obtained, the impurity in the available carbonate or hydroxide should be extracted by careful washing with water.

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WASHINGTON, February 6, 1956.