

Field Measurement of Alkalinity and pH

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-H



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By IVAN BARNES

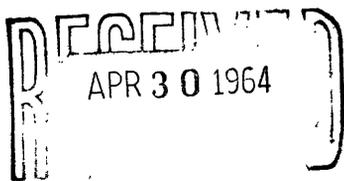
G E O C H E M I S T R Y O F W A T E R

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-H

Method for determinations of pH in the field and of end points for alkalinity titrations



U. S. Geological Survey



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GEOCHEMISTRY OF WATER

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ABSTRACT

The behavior of electrometric pH equipment under field conditions departs from the behavior predicted from Nernst's law. The response is a linear function of pH, and hence measured pH values may be corrected to true pH if the instrument is calibrated with two reference solutions for each measurement. Alkalinity titrations may also be made in terms of true pH. Standard methods, such as colorimetric titrations, were rejected as unreliable or too cumbersome for rapid field use. The true pH of the end point of the alkalinity titration as a function of temperature, ionic strength, and total alkalinity has been calculated. Total alkalinity in potable waters is the most important factor influencing the end point pH, which varies from 5.38 (0° C, 5 ppm (parts per million) HCO_3^-) to 4.32 (300 ppm HCO_3^- , 35° C), for the ranges of variables considered. With proper precautions, the pH may be determined to ± 0.02 pH and the alkalinity to ± 0.6 ppm HCO_3^- for many naturally occurring bodies of fresh water.

INTRODUCTION

Accurate pH data were necessary in a detailed study of the carbonate chemistry of a stream (Birch Creek, Inyo National Forest, Inyo county, Calif.). Study of the methods and data showed that individual measurements of pH were as much as 0.5 pH unit in error. The large (0.5 pH) errors occurred when the sample had a pH considerably different from that of the reference (buffer) solutions. Errors of this magnitude cannot be tolerated when the pH meter is used to determine the end point of the alkalinity titration.

MATERIALS AND METHODS

The meter used throughout was a Beckman (Beckman Instrument Co., Fullerton, Calif.) model N pH meter. Reference electrodes were 5-inch fiber-wick saturated calomel electrodes having 30-inch leads, Beckman Instrument Co. No. 39170. Glass electrodes were 5-inch general purpose glass electrodes having 30-inch leads, Beckman Instrument Co. No. 40498. Buffer solutions were obtained from the sources listed in table 1.

TABLE 1.—*Suppliers of buffer solutions*

<i>pH (25° C)</i>	<i>Supplier</i>
4.00 ± .01	Beckman Instrument Co.
7.00 ± .02	Do.
8.00 ± .02	Fisher Scientific Co.

The pH of each buffer is plotted against temperature in figure 1.

All electrodes were tested in the laboratory before use in the field. The test consisted of calibrating the instrument at pH=8.00 at 25° C and measuring the pH of the pH₄ buffer. The pH₈ buffer has a pH of 8.00 ± .02 at 25° C, and the pH₄ has a pH of 4.00 ± .01. The observed pH value of the pH₄ buffer (pH₄) was in the range 4.00 to 4.03 for all pairs of electrodes. The glass and the calomel electrodes were transported to the field in the manufacturer's original packings. The glass electrodes were transported dry and the calomel electrodes were transported with the working end covered by a rubber cap filled with a saturated KCl solution. No evidence of physical damage to the electrodes was observed when the electrodes were unpacked for use in the field. All glass electrodes were soaked in water for at least two days before use.

The pH meter was turned on 1 hour before measurements were made. The meter was left on during each sampling period (24–36 hours). The electrodes were immersed 2 to 3 inches in the stream at all times, except during sampling. For temperature control all buffers and the standard (0.01639N H₂SO₄) acid for alkalinity titrations were kept in plastic bottles immersed in the stream, except during actual use.

The following steps were found necessary for accurate pH and alkalinity determinations:

1. Measure water temperature with the thermometer in shade.
2. Set temperature compensator on meter to water temperature.
3. Wash electrodes in a stream of buffer whose nominal pH is near that of the water.
4. Immerse electrodes 1 inch in the buffer.
5. Balance and set meter at the nearest integral value of the buffer pH.
6. Rinse electrodes in water.
7. Collect water sample in beaker.
8. Measure the pH of the sample.
9. Pipet 50 ml of sample into dry beaker.
10. Titrate with standard acid and record pH with each increment of acid in the range from pH 5 to pH 4.
11. Rinse electrodes in water.
12. Wash electrodes in a stream of pH₄ buffer.
13. Measure pH of pH₄ buffer.

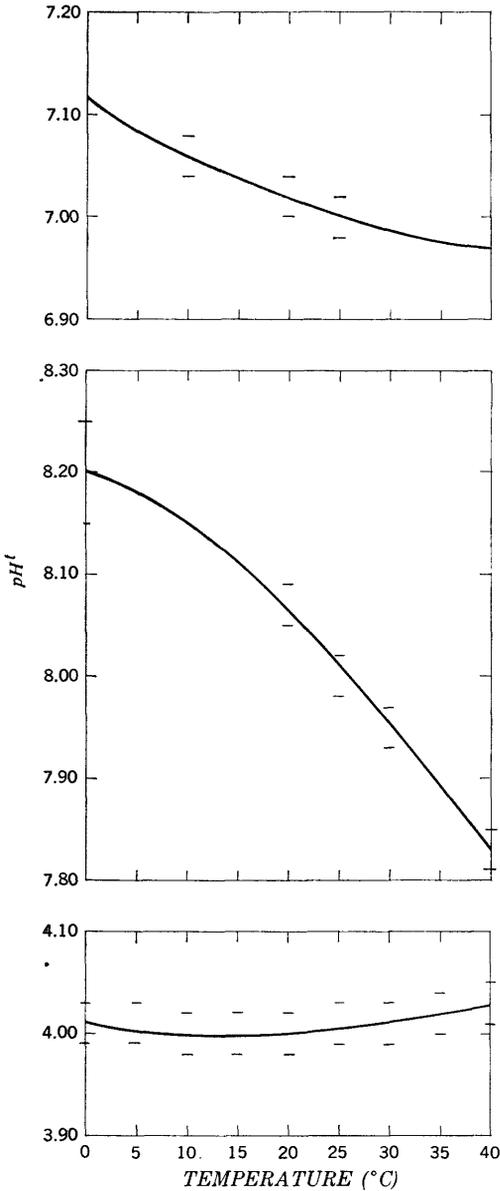


FIGURE 1.—pH of buffer solutions as functions of temperature.

14. Replace electrodes and reagent bottles in water.

The temperature measurement (in the shade, to avoid radiant heating) is necessary because the pH of the buffer solutions is temperature dependent. The temperature compensator corrects the meter reading to the output of the electrodes which changes with tempera-

ture, but it does not correct for the changes of pH of buffers having changing temperature.

Rinsing the electrodes in a stream of the solution to be measured (steps 3, 6, 11, and 12) avoids the necessity for wiping drops of solution from the electrode tip. The glass membrane is quite sensitive to abrasion, and wiping the electrode with even the least abrasive tissue introduces needless risk of damaging the electrode. Under field conditions, especially when the wind is high, sand and grit may be unwittingly rubbed on the glass membrane if the electrodes are wiped. If the water is polluted, oil films and other contaminants on the glass electrode may require different procedures.

The electrodes are immersed in 1 inch of solution both for maximum accuracy of measurement and also to thermostat the electrodes.

Visual interpolation is unnecessary and increased accuracy is obtained if the meter is set on a scale mark. As a regular practice (to avoid confusion), the meter should be set on an integral pH value nearest the nominal pH of the buffer.

Following diurnal variations in pH requires reading the meter by both daylight and artificial light. Commonly accepted practices of instrumental measurement were used. Readings were made by daylight and by means of a flashlight and gasoline lantern at night. For maximum accuracy the eye, needle, scale marking, and light source should be in the same vertical plane; otherwise misleading shadows result. During daylight measurement the meter should be shaded for the same reason.

Measurements of pH should be made in static samples. A reproducible streaming potential corresponding to -0.10 pH unit was observed at a stream velocity of 1 ft per sec (0.3 m per sec). In systems where flow varies, streaming potentials may also be expected to fluctuate. In the present study the sample beaker was immersed in the stream for temperature control. Where it is not feasible to immerse samples in a reservoir of the water body being studied during measurements, insulated beakers or DeWar bottles are recommended. Temperature changes in the sample during measurement are possible when air temperatures are not close to water temperatures or if samples are exposed to bright sunlight.

It is essential to record acid volume and pH over the pH range from 5 to 4. Until the true response of the electrodes is known, the significance of the observed pH is unknown. Owing to the changing response of the measuring system, the pH of the end point (say the true value is 4.5) may be indicated as any value from 5.0 to 4.5 by the meter. The measurement of the pH_4^a will permit calculation of true pH of the water (pH_4^b) from the observed pH values of the water (pH_4^c).

When the electrode fails to give a stable reading, that is, when the meter indicates a fluctuating value for the pH of a sample, the glass electrode can frequently be tested by touching a finger to the barrel of the electrode. A large and immediate change in the indicated pH or a more pronounced fluctuation generally indicates the electrode is no longer serviceable and should be discarded. Presumably the electrode has become polarized, or has suffered other damage, but neither the exact nature of the trouble nor its causes are known. Attempts at rejuvenation of the electrode in the field, by either washing in acid or by cyclic washing with acid and base, have failed in every case to restore the electrode to proper behavior. Most glass electrodes are restored to their proper behavior after several weeks of dry storage.

ELECTRODE BEHAVIOR

Bates (1960) pointed out that the emf (electromotive force) response of many glass electrodes is a linear function of pH over the pH range from 3 to 10. The response is in many instances predictable according to Nernst's law, which is conveniently written in the form

$$\text{emf}_a - \text{emf}_b = \frac{2.303RT}{F} (\text{pH}'_a - \text{pH}'_b), \quad (1)$$

where emf_a and emf_b refer to the observed potentials between the glass and reference electrodes in samples a and b respectively, and R is the gas constant (8.31439 abs j per deg mole), T is the temperature in degrees Kelvin, F is the Faraday (96,484 abs coulombs), and pH'_a and pH'_b are the true pH values of solutions a and b respectively. The above equation reduces to

$$\text{emf}_a - \text{emf}_b = 0.19845T(\text{pH}'_a - \text{pH}'_b) \quad (2)$$

where the emf is in millivolts. Perfect electrodes would yield a particular emf for a particular true pH. The lack of pH' predictability of the emf for electrodes at a particular true pH is evidenced by the calibration procedures recommended by instrument manufacturers. The calibration procedures merely fix emf_b as a convenient function of pH'_b , where emf_b refers to the emf between the glass and reference electrodes in a buffer b , and pH'_b is the true pH of buffer b . The uncertainty of emf_b as a function of pH'_b in no way invalidates the Nernst law, but it does require a calibration procedure if pH' values are to be read directly.

The Nernst law not only specifies a linear relation between observed potentials and pH, but it specifies the slope of the function be $0.19845T$. The slope of the function was tested in 60 samples by measuring the pH of the pH_4 buffer (pH'_4) after setting the meter at

pH=8.00 for the pH₈ buffer. The frequency distribution of pH₄^o values is shown in figure 2. The possibility that the variation of pH₄^o will be affected by temperature is negated by the clearly random data of figure 3, which shows no relation between pH₄^o and temperature. In one instance the pH of the pH₄ and pH₇ buffers was measured after calibration at pH=8.00 for the pH₈ buffer, as shown in figure 4. If pH₄^t, pH₄^o, pH₈^t, pH₈^o, and pH₇^o are known and if it is assumed that the pH response of the measuring system is a linear function of pH, pH₇^t may be calculated. The known value of pH₇^t of 7.03 may be compared with the calculated true value of 7.02. It was concluded that the pH response of the electrodes over the pH range from 4 to 8 was linear.

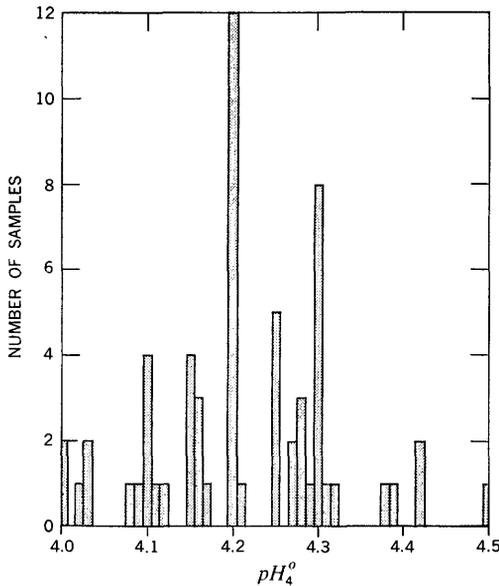


FIGURE 2.—Histogram showing frequency distribution of pH₄^o.

The relationships used for computing pH^t from pH^o are illustrated in figure 5. From the general form of the function

$$\text{pH}^t = s\text{pH}^o + b \quad (3)$$

and a knowledge that the slope (*s*) is given by

$$s = \frac{\text{pH}_w^o - \text{pH}_8^o}{\text{pH}_w^t - \text{pH}_8^t} = \frac{\text{pH}_8^o - \text{pH}_4^o}{\text{pH}_8^t - \text{pH}_4^t} \quad (4)$$

it may be shown that

$$\text{pH}_w^t = [\text{pH}_8^t(\text{pH}_w^o - \text{pH}_4^o) + \text{pH}_4^t(\text{pH}_8^o - \text{pH}_w^o)](\text{pH}_8^o - \text{pH}_4^o)^{-1}, \quad (5)$$

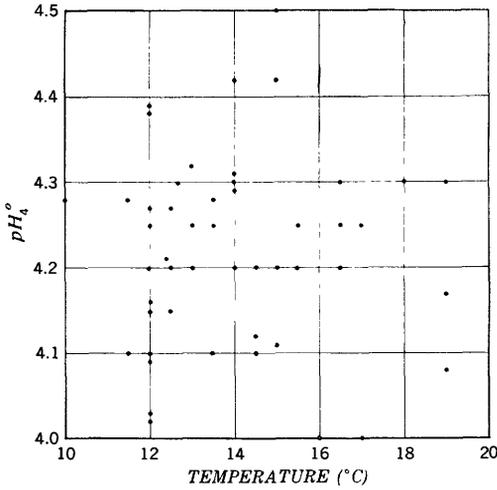


FIGURE 3.—Plot showing random distribution of pH₄^o vs. temperature.

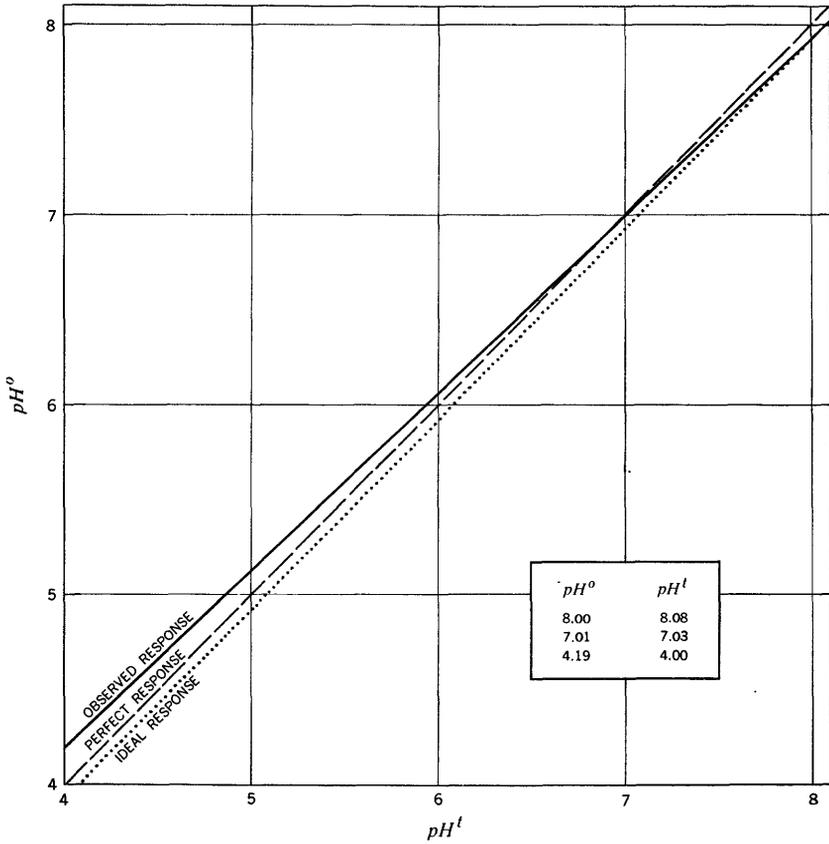


FIGURE 4.—Linearity of pH response of electrodes from buffer comparison. Data collected 11:55 a.m. (Pacific daylight time), June 5, 1961, Birch Creek, Inyo County, Calif. Temperature, 18° C.

where pH_w^t and pH_w^o are, respectively, true and observed pH values of the water sample. If some other buffer solution had been used rather than the pH_8 buffer, substitution of pH_2^t and pH_2^o for pH_8^t and pH_8^o would be appropriate. It is essential that pH_b^t be known at the temperature of the water sample. Buffers whose true pH is known over a range of temperatures are available commercially or may be prepared by the user. Bates (1960) gives data on primary reference buffers.

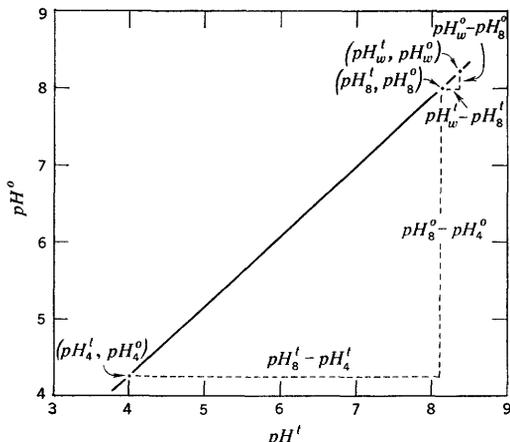


FIGURE 5.—Linear function between observed and true pH data. Data collected 8:56 p.m. (Pacific daylight time), June 5, 1961, Birch Creek, Inyo County, Calif., temperature, 12.5° C.

BICARBONATE DETERMINATION

The bicarbonate titration may be expressed by



The titration may be to either a potentiometric or colorimetric end point. Colorimetric end points are convenient for field use but are of questionable accuracy due to wide variation in illumination and to fatigue of the investigator. Observations of potentiometric titrations should not be affected by light conditions as long as graduations on the meter are visible, and because they are less subjective than the observation of a colorimetric end point, the potentiometric end points are less affected by the fatigue of the operator, unless rapid repetitive measurements are required.

It has been shown in the preceding discussion that the observed (pH^o) and the true (pH^t) pH values do not necessarily agree, and that the difference is a random one. Were the differences between pH^o and pH^t either constant or systematically distributed, a single calibra-

tion or set of calibrations would suffice to define the end point in terms of pH°. It is necessary either to obtain the end point in terms of true pH values or to determine a titration curve for the end point of each alkalinity titration. Experience has shown that it is not economical to determine titration curves hourly. The briefer the time for the determination of each variable, the more time is available for other observations. The end point of the titration was determined in terms of true pH values as shown below. The relationships derived permit calculation of the true bicarbonate content of waters in the office and permit full utilization of field time for observations.

End points of potentiometric titrations usually are determined either by picking the maximum slope from a plot of emf vs. titrant volume or by plotting $\frac{\Delta \text{ emf}}{\Delta \text{ titrant}}$ against total titrant and choosing the maximum in this curve as the end point (fig. 6). The discrepancy between the two methods in the end-point determination is due to large increments of acid and represents 6.8 ppm (parts per million) HCO_3^- . The results given in figure 6 are typical for field titrations where the true pH is not directly measured and emphasize the need for several pH-titrant volume data for each titration. The discrepancy could be decreased by assuming $\frac{\Delta \text{ pH}}{\Delta \text{ titrant}}$ to be constant over each $\Delta \text{ pH}$, but the slope is obviously not constant and the reliability of such a "correction" is questionable. The inconstancy of the measuring system precludes a prior knowledge of the end point and does not permit a predetermined schedule of increments of titrant to educe $\Delta \text{ titrant}$ near the end point. Regardless of which method is used to determine the end point of the titration, the criterion for the end point is that the rate of change of pH with increment of acid be a minimum.

The true pH for the bicarbonate end point can be readily calculated for any set of conditions which may be of interest. The following calculations make allowance for the effect of total concentration of carbonate species (H_2CO_3 , HCO_3^- , $\text{CO}_{2(\text{aq})}$ and CO_3^{2-}), ionic strength (salt effect), and temperature.

Two sets of end points were calculated, on the basis of two different assumptions. The first assumption (case 1) was that there was no loss of CO_2 from the sample. Case 1 would correspond to a rapid titration with minimal stirring and a restricted access of the atmosphere to the surface of the solution. The second set of calculations (case 2) was made on the assumption that the sample was always in equilibrium with the partial pressure of CO_2 (P_{CO_2}) of the normal earth's atmosphere ($P_{\text{CO}_2} = 10^{-3.5}$ atm) at the temperature of the solu-

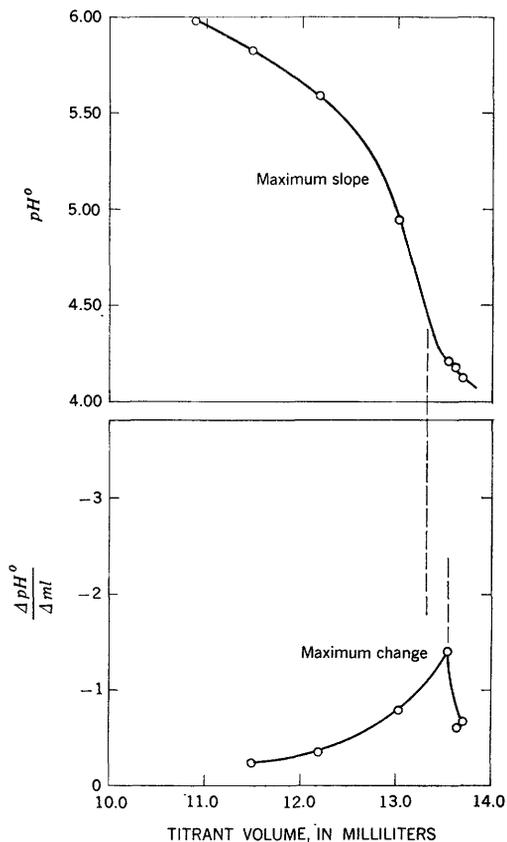


FIGURE 6.—End point of titration by two methods. Data collected 2:45 p.m. (Pacific daylight time), May 26, 1961, Birch Creek, Inyo County, Calif.

tion. Such an equilibrium could be maintained by slow titration and rapid stirring and by bubbling air through the sample.

For the assumption that no CO_2 is lost,

$$A = m_{H_2CO_3} + m_{HCO_3^-} + m_{CO_3^{2-}} \tag{7}$$

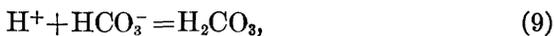
where

A is a constant.

Differentiating

$$0 = dm_{H_2CO_3} + dm_{HCO_3^-} + dm_{CO_3^{2-}}. \tag{8}$$

From the reaction



$$(dm_{H^+})_1 = dm_{H_2CO_3}. \tag{10}$$

From the reaction



$$(dm_{\text{H}^+})_2 = -dm_{\text{CO}_3^{-2}}. \quad (12)$$

From the reaction



$$(dm_{\text{H}^+})_3 = -dm_{\text{OH}^-}. \quad (14)$$

If the increments of m_{H^+} are added,

$$(dm_{\text{H}^+})_T = (dm_{\text{H}^+})_1 + (dm_{\text{H}^+})_2 + (dm_{\text{H}^+})_f + (dm_{\text{H}^+})_3, \quad (15)$$

where

$(dm_{\text{H}^+})_T$ is the total H^+ added

$(dm_{\text{H}^+})_f$ is the increase in free H^+ .

From the functional definition,

$$\text{pH} \equiv -\log \alpha_{\text{H}^+}, \quad (16)$$

and

$$\alpha_{\text{H}^+} = 10^{-\text{pH}}. \quad (17)$$

From the equilibrium constants,

$$m_{\text{H}_2\text{CO}_3} = K_1 10^{-\text{pH}} m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \quad (18)$$

and

$$m_{\text{CO}_3^{-2}} = \frac{m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{K_2 \gamma_{\text{CO}_3^{-2}}} 10^{\text{pH}}, \quad (19)$$

Now

$$A = K_1 10^{-\text{pH}} m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} + \frac{m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{K_2 \gamma_{\text{CO}_3^{-2}}} 10^{\text{pH}} + m_{\text{HCO}_3^-}, \quad (20)$$

and it follows that

$$m_{\text{HCO}_3^-} = \frac{A}{K_1 10^{-\text{pH}} \gamma_{\text{HCO}_3^-} + \frac{10^{\text{pH}} \gamma_{\text{HCO}_3^-}}{K_2 \gamma_{\text{CO}_3^{-2}}} + 1}. \quad (21)$$

The activity coefficient for H_2CO_3 may be estimated from the data cited by Harned and Owen (1958) on their page 736 and the equation cited on their page 532. The salting coefficient was estimated to be 0.06 at 25° C. The maximum ionic strength considered in this paper is 0.01. Substituting in the equation,

$$\log \gamma_{\text{H}_2\text{CO}_3} = k_m \mu \quad (22)$$

where k_m is the salting coefficient, and

$$\gamma_{\text{H}_2\text{CO}_3} = 1.001. \quad (23)$$

The assumption

$$m_{\text{H}_2\text{CO}_3} = \alpha_{\text{H}_2\text{CO}_3} \quad (24)$$

is seen to be correct to within 0.1 percent at 25° C. The assumption will be made throughout the following calculations.

Activity coefficients of ionic species were calculated from the Debye-Hückel limiting law in the form

$$\log \gamma_i = -\frac{Az^2\mu^{1/2}}{1 + Ba_i\mu^{1/2}} \quad (25)$$

where

- γ_i is the activity coefficient of species i ,
- z is the charge on the i th species,
- A and B are functions of temperature,
- a_i is the effective ionic diameter in angstroms.

Values of A and B used in the computation were taken from Klotz, 1950, p. 330, as shown in table 2.

TABLE 2.—Values of parameters for the Debye-Hückel equation

Temperature (°C)	A	B
0.....	0.4883	0.3241
5.....	.4921	.3249
10.....	.4960	.3258
15.....	.5000	.3266
20.....	.5042	.3273
25.....	.5085	.3281
30.....	.5130	.3290
35.....	.5175	.3297

The values of a_i were 4.0 for HCO_3^- and 4.5 for CO_3^{2-} . Values for the equilibrium constant

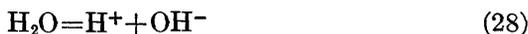
$$K_1 = \frac{\alpha_{\text{H}_2\text{CO}_3}}{(\alpha_{\text{H}^+})(\alpha_{\text{HCO}_3^-})} \quad (26)$$

from the work of Harned and Davis (1943) and

$$K_2 = \frac{\alpha_{\text{HCO}_3^-}}{(\alpha_{\text{H}^+})(\alpha_{\text{CO}_3^{2-}})} \quad (27)$$

from Harned and Scholes (1941) are given in fig. 7.

For the hydrolysis of water,



$$K_w = (10^{-\text{pH}})(m_{\text{OH}^-})\gamma_{\text{OH}^-}. \quad (29)$$

Values of K_w were those of the International Critical Tables as reported in Dorsey, 1940, p. 378. From 29, above,

$$m_{\text{OH}^-} = K_w(\gamma_{\text{OH}^-})^{-1}(10^{\text{pH}}). \tag{30}$$

From equation 17,

$$(m_{\text{H}^+})_f = 10^{-\text{pH}}(\gamma_{\text{H}^+})^{-1}. \tag{31}$$

A description of the hypothetical solutions is given in table 3.

TABLE 3.—*Hypothetical NaHCO₃ solutions*

Total carbonic species as HCO ₃ ⁻ (ppm)	m	Lowest possible ionic strength (μ)
5.....	8.2×10^{-5}	8.2×10^{-5}
10.....	1.64×10^{-4}	1.64×10^{-4}
50.....	8.20×10^{-4}	8.20×10^{-4}
100.....	1.64×10^{-3}	1.64×10^{-3}
150.....	2.46×10^{-3}	2.46×10^{-3}
200.....	3.28×10^{-3}	3.28×10^{-3}
250.....	4.11×10^{-3}	4.11×10^{-3}
300.....	4.92×10^{-3}	4.92×10^{-3}

The calculated end points in table 4 are for titrations undertaken at 0°, 5°, 10°, 15°, 20°, 25°, 30° and 35° C. A similar set of calculations was made for an ionic strength of 0.01 (0.01*m* for 1:1 salts) to determine the effect of different concentrations of neutral salts on the end point.

For case 2, changes in $m_{\text{HCO}_3^-}$ can occur through the reaction



$$-(dm_{\text{HCO}_3^-})_1 = (dm_{\text{H}^+})_1 \tag{33}$$

and from the reaction



$$(dm_{\text{H}^+})_2 = -(dm_{\text{CO}_3^{2-}}) = (dm_{\text{HCO}_3^-})_2. \tag{35}$$

Changes in concentration of total bicarbonate may be computed from

$$(dm_{\text{HCO}_3^-})_T = (dm_{\text{HCO}_3^-})_1 + (dm_{\text{HCO}_3^-})_2. \tag{36}$$

The total increment of H⁺ is

$$(dm_{\text{H}^+})_T = (dm_{\text{H}^+})_1 + (dm_{\text{H}^+})_2 + dm_{\text{H}^+} - dm_{\text{OH}^-}. \tag{37}$$

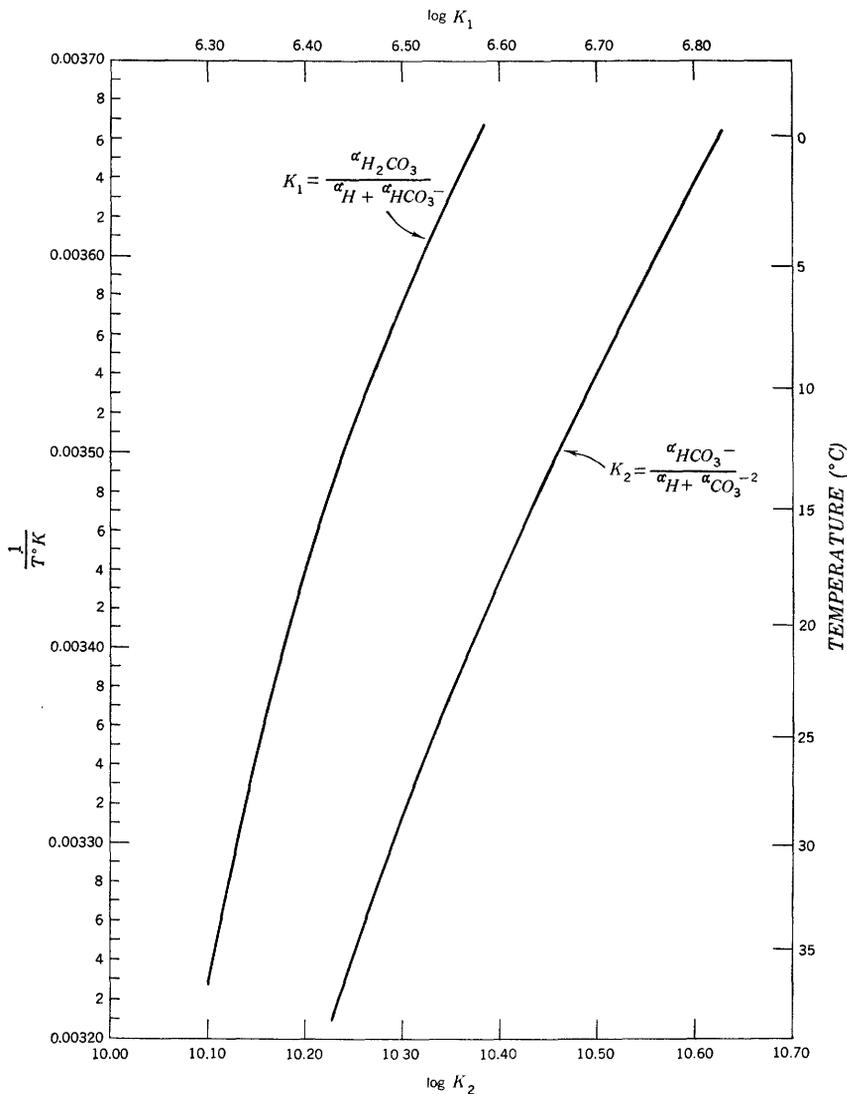


FIGURE 7.—Equilibrium constants for carbonate and bicarbonate hydrolysis reactions given as functions of temperature. Data for K_1 curve from Harned and Davis (1943, p. 2030); data for K_2 curve from Harned and Scholes (1941, p. 1708).

TABLE 4.—End points for alkalinity titration

Total carbonic species as HCO_3^- (ppm)	Ionic strength μ	End points at temperatures ($^{\circ}\text{C}$) indicated—							
		35	30	25	20	15	10	5	0
Case 1:									
5.....	8.2×10^{-4}	5.27	5.28	5.29	5.30	5.32	5.34	5.36	5.38
10.....	1.64×10^{-4}	5.10	5.10	5.11	5.13	5.15	5.16	5.19	5.22
50.....	8.20×10^{-4}	4.72	4.72	4.73	4.75	4.77	4.78	4.81	4.84
100.....	1.64×10^{-3}	4.56	4.57	4.58	4.59	4.62	4.63	4.65	4.69
150.....	2.46×10^{-3}	4.47	4.48	4.49	4.50	4.52	4.54	4.56	4.60
200.....	3.28×10^{-3}	4.40	4.42	4.42	4.44	4.46	4.48	4.50	4.53
250.....	4.11×10^{-3}	4.35	4.36	4.37	4.39	4.41	4.43	4.45	4.49
300.....	4.92×10^{-3}	4.31	4.33	4.33	4.34	4.36	4.39	4.41	4.44
5.....	.01	5.28	5.28	5.30	5.30	5.32	5.34	5.36	5.39
10.....	.01	5.10	5.10	5.12	5.13	5.15	5.16	5.19	5.22
50.....	.01	4.71	4.72	4.73	4.75	4.77	4.79	4.81	4.84
100.....	.01	4.55	4.57	4.57	4.59	4.61	4.63	4.66	4.69
150.....	.01	4.47	4.47	4.48	4.50	4.52	4.54	4.56	4.59
200.....	.01	4.41	4.41	4.43	4.43	4.46	4.48	4.50	4.53
250.....	.01	4.35	4.36	4.37	4.39	4.41	4.42	4.45	4.48
300.....	.01	4.32	4.32	4.33	4.34	4.36	4.39	4.41	4.44
Case 2.....	Lowest possible value (see table 3).	5.68	5.66	5.65	5.63	5.62	5.61	5.59	5.58
	.01.....	5.68	5.66	5.65	5.63	5.62	5.61	5.59	5.58

¹ For $\text{HCO}_3^- > 150$ ppm, 5.60.

² For $\text{HCO}_3^- = 50$ ppm, 5.59.

Substituting bicarbonate changes,

$$(dm_{\text{H}^+})_T = -(dm_{\text{HCO}_3^-})_1 + (dm_{\text{HCO}_3^-})_2 + (dm_{\text{H}^+}) - (dm_{\text{OH}^-}), \quad (38)$$

and the carbonate change,

$$(dm_{\text{H}^+})_T = -(dm_{\text{HCO}_3^-})_1 - (dm_{\text{CO}_3^{2-}}) + (dm_{\text{H}^+}) - (dm_{\text{OH}^-}). \quad (39)$$

Substituting $-dm_{\text{CO}_3^{2-}}$ for $(dm_{\text{HCO}_3^-})_2$ in the equation for total bicarbonate changes,

$$-(dm_{\text{HCO}_3^-})_1 = -(dm_{\text{HCO}_3^-})_T - (dm_{\text{CO}_3^{2-}}). \quad (40)$$

Combining the last two equations,

$$(dm_{\text{H}^+})_T = -(dm_{\text{HCO}_3^-})_T - 2dm_{\text{CO}_3^{2-}} + dm_{\text{H}^+} - dm_{\text{OH}^-}. \quad (41)$$

Let

$$m_{\text{H}_2\text{CO}_3} = B. \quad (42)$$

Values for $(m_{\text{HCO}_3^-})_T$ may be computed from

$$(m_{\text{HCO}_3^-})_T = \frac{B10^{\text{pH}}}{K_1 \gamma_{\text{HCO}_3^-}} \quad (43)$$

and values for $m_{\text{CO}_3^{-2}}$ from

$$m_{\text{CO}_3^{-2}} = \frac{10^{2\text{pH}} B}{\gamma_{\text{CO}_3^{-2}} K_2 K_1} \quad (44)$$

Titration curves were again computed for pH increments of 0.01 pH. In both sets of titration curves the criterion for the end point was that

$$\left[\frac{\partial \text{pH}}{\partial (m_{\text{H}^+})_T} \right]_{T, \mu}$$

be a minimum. The results of the computation are given in table 4.

The data in table 4 show that the end point varies no more than 0.04 pH unit over a 5° C temperature interval. A deviation of 2.5° C from the assumed temperature should introduce no more than a 0.02 pH unit error in the end point. The salt error or effect of ionic strength is no greater than 0.01 pH unit over the range considered, to as much as 580 ppm (as NaCl). Hence any ionic strength in that range (8.2×10^{-5} to 0.01) may be assumed without introducing more than 0.01 pH unit error, or a total error (temperature and ionic strength) of 0.03 pH unit for the end point. Although temperature and ionic strength have relatively minor effects, both the amount of bicarbonate present and the extent to which carbon dioxide may be lost from the system during titration influence the pH at the end point substantially. In case 2 titrations, the initial amount of bicarbonate present is a minor factor.

Several obvious methods of determining the end point for a particular solution suggest themselves. The most obvious is to plot a part of the titration curve as true pH vs. HCO_3^- , that is, plot pH against equivalent HCO_3^- for the titrant acid. Plot on the same scale the data from table 4 for the nearest temperature. Overlay the curves. Their intersection is the end point having a maximum error of 0.03 pH unit in the computed end-point. Errors in the measured pH, of course, lead to greater errors in the end point pH. End points so obtained should be accurate enough for most work.

The end points thus calculated are in terms of true pH. The non-ideal behavior of the electrometric system used gives rise to a problem in approaching the end point of the titration. If the emf-pH function departs appreciably from Nernst's law, the true pH cannot be obtained by inspection of the observed pH data without a knowledge of the extent of the departure. To determine what effect the uncertainty of true pH during titration would have on the bicarbonate determination, plots were made of pH' against the number of milliliters of standard (0.01639N H_2SO_4) acid. For the 21 samples chosen, the

bicarbonate concentrations ranged from 140 to 260 ppm. The average slope was -0.550 ml/pH, over the pH range from 4.1 to 5.1. It is of interest to note that straight lines could be drawn through the points which represented the data for each titration to within ± 0.03 ml of acid. The maximum slope was -0.855 ml/pH and the minimum -0.333 ml/pH. In consequence, if enough points (preferably 3 or more) are available between a pH of 4.1 and 5.1, interpolation as to the number of milliliters of acid at the end point can be within ± 0.03 ml of acid. For the acid used,

$$\text{ppm}_{\text{HCO}_3^-} = 20 \times \text{ml acid}, \quad (45)$$

hence the interpolated end point is within ± 0.6 ppm HCO_3^- for the samples used. For 20 of the 21 determinations, straight lines could be drawn giving the number of milliliters of acid to within ± 0.02 ml acid or ± 0.4 ppm HCO_3^- . The interpolation of acid-pH data to the correct end point would seem sufficiently accurate for most purposes.

The problem remains to obtain true pH data sufficiently close to the end point to warrant an interpolation. A suggested procedure is use of a color indicator to show when the end point is being approached. Data could then be recorded in the vicinity of color change. The pH data would then be converted to true pH and used to interpolate to a correct end point for maximum accuracy, if the suggested calibration procedure with two reference solutions is followed. For field use, indicators having sharp color changes such as methyl purple should be used in view of the variable light conditions.

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