At all concentrations, even in very dilute solutions, it seems to be valid that the decomposition velocity of diacetone alcohol is a function of the thermodynamic activities of the electrolytes present. A short discussion of the measurements for other reactions as compared with those presented in this paper is given.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BOTANY OF THE UNIVERSITY OF WASHINGTON]

THE ACIDITY OF THE WATERS OF SOME PUGET SOUND BOGS[1]

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RECEIVED JUNE 11, 1927 PUBLISHED DECEMBER 10, 1927

Introduction

This investigation was undertaken in order to ascertain the degree of acidity of certain bog waters and to study the relation of such acidity to the carbon dioxide content of the water, the color of the water and the stage of plant succession. It was thought that such data would be useful for interpreting the physiology of plants characteristic of bogs and also for explaining the rather marked corrosive action of such waters upon concrete and cement products.

Experimental

The waters studied were collected from four typical Puget Sound bogs. Two of the bogs, Esperance and Sunnydale, were characterized by the presence of methane dissolved in the waters and by the occurrence of a small pond which each bog surrounded. Bogs of this type have been designated as "wet bogs." The other two bogs, Ronald and White Center, experience a very great lowering of the water table in the summer months, evolve no methane and do not surround open bodies of water. Such bogs have been termed "dry bogs." A more detailed description of these bogs, their flora and the nature of the dissolved gases has been previously published.[2]

Effect of Dissolved Carbon Dioxide Upon Acidity

Samples of water were collected from at least two different points in each bog and the amounts of dissolved carbon dioxide carefully determined. This was accomplished by the complete removal of the dissolved gases by boiling the samples under diminished pressure for an hour.[2] Analyses of the liberated gases followed. Owing to the high dilution it was assumed that all of the carbon dioxide was present in the waters as carbonic acid,

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[1] Read before the Chemical Section of the Pacific Division of the American Association for the Advancement of Science, June, 1927.

[2] *Bot. Gaz.*, **84**, 264–278 (1927).

and from the primary ionization constant of the acid the hydrogen-ion concentration as P_H was calculated from the following

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = K = 3 \times 10^{-7}$$
$$P_H = \log 1/(H^+)$$

In Table I are given the parts per million of dissolved carbon dioxide in the different waters, the molality of such solutions and the calculated P_H. The calculations are given in the fourth column of the table and represent the maximum possible acidity due to the presence of carbonic acid.

TABLE I

THE CONCENTRATIONS OF CARBON DIOXIDE DISSOLVED IN THE WATERS OF THE DIFFERENT BOGS AND THE CALCULATED ACIDITIES PRODUCED BY THE PRESENCE OF THE GAS

Name of bog	Carbon dioxide, p.p.m.	Molality	P_H, calcd.
Esperance			
Hole No. 1	76.9	0.00174	4.64
Hole No. 2	71.9	.00163	4.65
Hole No. 3	68.3	.00155	4.67
Sunnydale			
Hole No. 1	71.6	.00163	4.66
Hole No. 2	40.0	.00091	4.77
Ronald			
Hole No. 1	33.8	.00077	4.82
Hole No. 2	55.8	.00126	4.71
White Center			
Hole No. 1	36.3	.00083	4.80
Hole No. 2	32.4	.00074	4.83
Lake Esperance	12.3	.00028	5.04

Several investigators[3] have explained the acidity of bog or moor water as due to carbonic acid. The data presented in Table I, in some cases, check remarkably with those reported by Endell and thus tend to support this view. However, some preliminary experiments, the results of which are given in Table II, show that the acidity of bog waters is also due to an acid or acids other than carbonic acid. In these experiments a sample of water was collected from Esperance Bog, one was taken from the pond in the bog and another was a sample secured a year previous from Ronald Bog, which had been allowed to stand in a tightly stoppered bottle in the laboratory during this period. The acidity, using two different indicators for each sample, was determined with a double wedge comparator. The P_H was then determined electrometrically but, by the time

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[3] (a) Endell, *J. prakt. Chem.*, **82**, 414–422 (1910); (b) Stremme, *Z. prakt. Geol.*, **16**, 122–128 (1908); (c) Cowles and Schwitalla, *Ecology*, **4**, 402–416 (1923).

equilibrium was reached with this method, all of the carbon dioxide had been driven from the solution by the passage of the hydrogen gas. From the data given in Table II it will be noted that in one instance the removal of carbon dioxide decreased the acidity, while in the others the acidity was slightly increased. Varying results were obtained with the different indicators and these results may be explained by differences in sensitivity, effect of the characteristic yellow color of all of the waters and possibly by a difference in the adsorption of the indicator by the colloidal material.

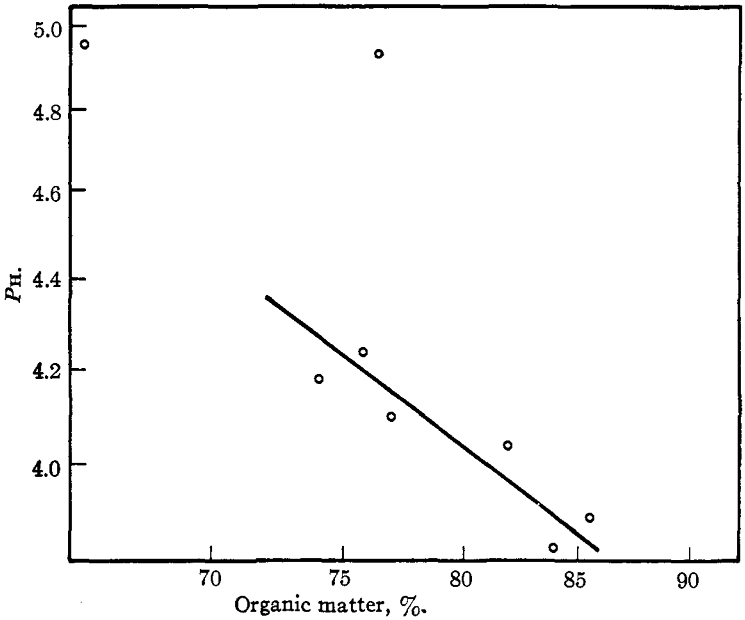

Fig. 1.—The relation between the acidity and the organic matter in bog waters.

A sample of water taken from a lake containing a small quantity of free carbonic acid showed a *P*H of 6.3 with chlorophenol red, while the electrometric method gave a *P*H of 7.95. The water of this lake had the characteristic yellow color of bog water and contained considerable quantities of colloidal matter. The carbon dioxide, in this particular case, produced the acidity and its removal caused a decrease past the neutral point. The colloidal material apparently had no effect upon the acidity. Much the same result was obtained with the water from Esperance Pond, except that the removal of the carbon dioxide did not produce an alkaline water. Comparing these data with those given for the bog waters, it is evident that the acidity of such bog waters is primarily due to an acid or acids in addition to the carbonic acid. The acid or acids are apparently stronger than the carbonic acid and the presence of the latter produces a buffering effect.

These observations are in accordance with those of Smorodinzew and

Adowa[4] who noted a difference in the colorimetric and electrometric methods for the determination of the *P*H of bog waters secured in the vicinity of Moscow. On thirty different samples their maximum plus variation was 0.71 with an average of 0.17. The maximum minus variation was 1.21 with an average of 0.46. The *P*H of undiluted water from sphagnum measured electrometrically varied from 3.88 to 4.62, which is in accord with the measurements made on waters from bogs in the Puget Sound region as reported below.

To demonstrate still further that the acidity was due to acids other than carbonic acid, the experiments outlined in Table III were performed. In series No. 1 the sample of water was taken from the Sunnydale Bog, that in Series No. 2 represents the water from the pond in this bog, while those in Series 3 and 4 were taken from Esperance Bog, the sample used in Series No. 4 being secured from a hole dug very close to the pond.

All *P*H determinations with the exception of some of those given in Table II were made by the ordinary method given by Clark[5] with the use of a Leeds and Northrup potentiometer. The hydrogen electrodes were prepared from platinum foil and their accuracy was checked by buffer solutions. Because of the high resistance of some of the samples of water, the most sensitive type of wall galvanometer was utilized. Normal calomel electrodes, prepared from redistilled mercury, were employed and these were repeatedly checked against each other and also against electrodes used in other research work. The hydrogen was always passed through the water being tested and over the electrode for at least half an hour before readings were made.

TABLE II

COMPARISON OF COLORIMETRIC AND ELECTROMETRIC METHODS FOR THE DETERMINATION OF THE ACIDITY OF BOG WATERS

Source of sample	Electrometric *P*H	Colorimetric *P*H	Indicator
Esperance Bog	4.60	5.1	Chlorophenol red
		4.7	Bromocresol green
Ronald Bog	3.81	4.3	Bromophenol blue
		3.9	Bromocresol green
Esperance Pond	6.50	6.3	Chlorophenol red
		6.1	Bromothymol blue

Endell[3a] in a study of the bogs of the Rhone region found that the colloidal material when separated by dialysis showed no acid reaction. If this is the case the acid substance is in true solution. Baumann and Gully,[6] however, believe that the acid properties are due to colloidal properties, surface tension and adsorption by the cell membrane.

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[4] Smorodinzew and Adowa, *Arch. Hydrobiol.*, **17** (4), 673–677 (1926).

[5] Clark, "The Determination of Hydrogen Ion," Williams and Wilkins, Baltimore, Md., 1923.

[6] Baumann and Gully, *Mitt. Bayr. Moorkulturanst.*, **4,** 31–156 (1910).

TABLE III

SERIES OF EXPERIMENTS WITH DIFFERENT WATERS DEVISED TO ILLUSTRATE THAT ACIDITY IS PRODUCED BY ACIDS OTHER THAN CARBONIC ACID

Series No. 1, *P*H	Series No. 2, *P*H	Manner of treatment of samples
4.02	5.92	Original samples of bog water.
4.03	5.88	After boiling for 5 minutes, cooling to original temperature and replacing the evaporated water with freshly boiled distilled water.
4.63	6.08	Dilution to twice the original volume with freshly boiled distilled water.
3.86	5.49	Concentration to 0.5 of original volume and cooling to original temperature.
3.56		Concentration to 0.2 of original volume and cooling to original temperature.
Series No. 3, *P*H	**Series No. 4, *P*H**	
4.30	4.92	Original samples of bog water.
4.29	4.83	After evaporating a definite volume to dryness at 90°, redissolving in freshly boiled distilled water and making up to original volume.

From the data presented in Table III the following facts are evident. (1) The *P*H is the same after the sample has been boiled as it was before. The passage of hydrogen through the samples of the water lowered the partial pressure of the carbon dioxide to such an extent that it was completely expelled from solution and heating of the sample produced no further changes in acidity. (2) The acid substance is not appreciably volatile and is not affected by temperature changes. (3) The acid either forms a true solution in water and is very soluble or else it is a reversible colloid. (4) The change in acidity upon dilution and concentration is very similar to that which occurs with an acid buffered by a small amount of one of its salts.

Relation of Color to Acidity

The water of all four bogs studied, together with that of Lake Esperance, varied in color from a light yellow to a deep yellow. The intensity of the color was measured with a Lovibond tintometer, using yellow glass standards. The results are shown in Table IV. The samples were collected from two different places in four different bogs on February 27, 1926.

There appears to be rather an indefinite relation between color and acidity. The intensity of the color seems to increase with acidity. The later the stage of plant succession, the greater will be the color.

Acidity of Bog Waters

In Table V, is given the acidity of waters, collected over a period of fifteen months, from four different bogs. These samples were taken a month or so after the rainy season had started and in February, at the

TABLE IV

THE RELATION OF COLOR TO ACIDITY

Name of bog	Acidity, P_H	Water as collected Observer, J. R. L.	 Observer, K. W.
Ronald	3.83	2.00	2.00
	3.89	1.875	1.625
Sunnydale	4.23	1.50	
	4.04	1.50	1.50
White Center	4.17	1.125	1.25
	4.09	1.50	1.50
Esperance[a]	4.93	0.625	0.625
Lake Esperance[a]	4.95	1.125	1.125

[a] At the time these samples were taken the bog was flooded and much water drained from the bog into the lake and water from surrounding country drained into the bog.

height of the season. It was practically impossible to secure samples during the dry season owing to the marked lowering of the water table in

TABLE V

THE ACIDITY OF DIFFERENT BOG WATERS UNDER VARIOUS CONDITIONS

Sample no.	Date collected	Name of bog	Acidity, P_H	Description of conditions
1	11–28–24	Ronald	3.85	Minute particles of sphagnum suspended in sample. Determination run immediately after collection.
2	11–28–24	Ronald	3.85	Same as No. 1 but with all particles of sphagnum removed by filtration.
3	11–28–24	Ronald	4.11	A 2.5 liter bottle was filled with water used in No. 1. Thoroughly washed air was rapidly bubbled through the sample for forty-eight hours.
4	11–28–24	Ronald	3.83	2.5 liters of the water used in No. 1 was sealed in a bottle and kept for one year.
5	2–27–26	Ronald	3.83	Water from holes in two different portions of the bog taken at the height of the rainy season.
6	2–27–26	Ronald	3.89	
7	12–2–25	Sunnydale	4.40	35 feet from the pond in the bog.
8	2–27–26	Sunnydale	4.23	100 feet from the pond in the bog.
9	2–27–26	Sunnydale	4.04	150 feet from the pond where the conditions were much drier and the bog in a late stage of succession.
10	11–25–25	White Center	4.16	60 feet from marginal ditch.
11	12– 2–25	White Center	4.02	Center of bog.
12	2–27–26	White Center	4.09	200 feet from marginal ditch.
13	2–27–26	White Center	4.17	Center of bog.
14	11–25–26	Esperance	4.60	20 feet from the pond.
15	2–27–26	Esperance	4.93	30 feet from the pond. The entire bog was flooded.
16	10–31–25	Esperance	6.50	Water taken from pond.
17	2–27–26	Esperance	4.95	Water taken from pond. The entire bog was flooded.

the bog. The time at which the samples were collected appears to be of no consequence. The dominating factor influencing the degree of acidity is evidently the stage of succession of the bog, the acidity being directly proportional to the stage of succession.

It is a well known fact that aeration practically eliminates the toxicity of bogs to plant life. This is apparently due to two factors: (1) the removal of carbonic acid and the introduction of dissolved oxygen; (2) the partial oxidation of the organic material either chemically or by means of bacteria.

Sample 3 in Table V originally had a *P*H of 3.85, but after thoroughly washed air had been passed through it continuously for forty-eight hours its acidity was decreased. The air was washed by first bubbling it through several bottles containing the bog water. This decrease in acidity indicates a partial oxidation of the acid-producing substance.

The acidities of the waters shown in Table V were all determined electrometrically and were not due to the presence of carbonic acid. In Table I is given the maximum acidity that might be expected from the presence of carbon dioxide.

The "dry" bogs, those containing no open water, have a greater acidity than the "wet" bogs. Furthermore, the acidity of the dry bogs is more constant than that of the wet bogs. The stage of succession and the drainage toward the pond, in the case of wet bogs, appear to be the dominating factors affecting the acidity.

In Table VI are given the results of the analyses of the different waters taken the same day from the four bogs. Two samples were taken at different places in each bog. In the third, fourth and fifth columns are given, as parts per million, the total solids, the ash and the organic matter. There appears to be a very definite relationship between the per cent. of organic matter and the acidity as expressed by

$$\%\ \text{O. M.} \times P_{\text{H}} = K$$

This relationship is illustrated in Fig. 1.

TABLE VI

ANALYSES OF THE DIFFERENT BOG WATERS AND THE RELATION OF THE ORGANIC MATTER TO *P*H

Sample no.	Acidity, *P*H	Total solids, p. p. m.	Ash, p. p. m.	Organic matter p. p. m.	Organic matter Per cent.	*P*H × per cent. O. M.
5	3.83	88.6	14.6	74.0	83.52	3.20
6	3.89	89.1	13.1	76.0	85.30	3.32
8	4.23	77.2	18.8	58.4	75.65	3.20
9	4.04	82.7	15.2	67.5	81.62	3.30
12	4.09	45.2	10.4	34.8	76.99	3.15
13	4.17	83.9	21.8	62.1	74.01	3.09
15	4.93	54.7	12.9	41.8	76.41	3.77
17	4.95	75.8	26.2	49.6	65.43	3.24

Summary

1. While the acidity of bog waters of the Puget sound region may be due to carbonic acid, it is not the dominating cause of the acidity.

2. The maximum acidity that could be produced by carbonic acid is much less than that actually observed.

3. Colorimetric and electrometric methods for the measurement of acidity gave different results.

4. The acidity as measured electrometrically is not appreciably altered by evaporation of the waters and their dilution to the original volume.

5. There appears to be rather an indefinite relationship between color intensity and acidity.

6. The stage of succession of the bogs is directly proportional to the acidity.

7. "Dry" bogs show a greater acidity than "wet" bogs.

8. The per cent. of organic matter in the four bogs studied is a logarithmic function of the acidity. The amount of the organic matter present thus appears to be the controlling factor of acidity.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

A MICRO METHOD FOR THE DETERMINATION OF SURFACE TENSION AND DENSITY

BY V. RICHARD DAMERELL

RECEIVED JUNE 13, 1927 PUBLISHED DECEMBER 10, 1927

Although several micro methods for the determination of surface tension[1] and density[2] are known, none of the apparatus employed in these is applicable to both determinations. The purpose of this article is the description of an exceedingly simple apparatus by which surface tension and density can be determined on amounts of liquid as low as one-tenth of a cubic centimeter, with a theoretical accuracy of from one part in 100 to one part in 300, depending on the liquid.

Apparatus.—A ten centimeter portion of 5 mm. soft glass tubing was heated to softness in a Bunsen burner with wing top attachment and quickly pulled to arm's length. By running a three centimeter column of water up and down the resulting capillary, an eight centimeter portion that had practically uniform bore was found, and a ten centimeter length was cut out so that the eight centimeter portion was on one end. This

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[1] (a) Du Noüy, *J. Gen. Physiol.*, **1**, 521–524 (1919); (b) Kiplinger, THIS JOURNAL, **42**, 472–476 (1920); (c) Sugden, *J. Chem. Soc.*, **119**, 1483–1492 (1921); (d) Ferguson, *Proc. Phys. Soc. London*, **36**, 37–44 (1923); (e) Richards, Speyers and Carver, THIS JOURNAL, **46**, 1196–1207 (1924).

[2] (a) Wartenberg, *Ber.*, **42**, 1126–1131 (1909); (b) Wiedbrauck, *Z. anorg. allgem. Chem.*, **122**, 167–170 (1922); (c) Detre, *Deut. med. Wochschr.*, **49**, 985 (1923).