[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

A Study of Acetic Acid–Acetate Buffers in Potassium Chloride and Sodium Chloride Solutions Using the Quinhydrone Electrode[1]

BY ELWYN F. CHASE

Harned and Owen[2] have observed a variation of the dissociation constant of acetic acid which indicates a "medium effect." It has therefore seemed worth while to determine the classical dissociation constant over a wide range of molecular acetic acid concentration in solutions 0.9 molar in potassium chloride or sodium chloride and 0.1 molar in sodium acetate.

The apparatus and method used were those of Kilpatrick and Chase.[3] The same assumptions were made (namely, that strong electrolytes are almost completely ionized; that the activity coefficients of substances present in small amounts are dependent solely upon the electrolyte present in large amount; and that the potentials developed at the liquid junctions of the cell, as made, cancel) with the additional assumption that the activity coefficient of the hydrogen ion does not vary greatly with the concentration of the molecular acetic acid present. The nitrogen was passed through the solution for five minutes after the addition of the quinhydrone and then turned off during the taking of the readings. Three of these were made at five minute intervals in the first fifteen minutes. Usually the last two were constant within a few hundredths of a millivolt. Different determinations on the same or fresh solutions varied sometimes a few tenths of a millivolt (0.1 millivolt is equivalent to approximately 0.4% in C_{H^+}). Four samples of quinhydrone, three samples of glacial acetic acid and two samples of sodium acetate were used. The sodium and potassium chlorides were from Kahlbaum "with certificate of guarantee." Buffers were made from acetic acid and sodium acetate, and also from constant boiling hydrochloric acid and sodium acetate. The values given in Table I were obtained using buffers made up with Kahlbaum glacial acetic acid and sodium acetate.

The K_c values for all the buffers made up checked within 3% for solutions low in molecular acetic acid concentration but containing more than 0.03 molar acetic acid. Below this value one sample of quinhydrone gave values for K_c which increased with decreasing molecular acetic acid concentration, indicating a possible acid impurity in that sample of quinhydrone. MacInnes and Jones[4] used quinhydrone in the differential titration of hydrochloric acid with sodium hydroxide. When using

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(1) Paper presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(3) Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

(4) MacInnes and Jones, THIS JOURNAL, **48**, 2831 (1926).

Table I

K_c for Acetic Acid in Solutions 0.1 M in Sodium Acetate and 0.9 M in Potassium Chloride or Sodium Chloride

	KCl		NaCl	
C_{HAc} moles per liter	C_{H^+} moles per liter × 10^5	K_c × 10^5	C_{H^+} moles per liter × 10^5	K_c × 10^5
0.00101	0.0307	3.04	0.0346	3.42
.00202	.0595	2.94		
.00303	.0872	2.88		
.00404	.115	2.85		
.00505	.144	2.86	0.160	3.17
.00605	.174	2.88		
.00807	.231	2.86		
.0101	.288	2.86	0.321	3.18
.0202	.574	2.84		
.0303	.855	2.82		
.0404	1.14	2.82		
.0505	1.43	2.84	0.160	3.17
.0606	1.73	2.86		
.101	2.89	2.87	3.24	3.22
.302	8.79	2.90		
.504	15.2	3.02	16.7	3.32
1.01	31.6	3.14	34.8	3.46
3.02	113	3.73	126	4.16
5.04	230	4.56	248	4.93

large amounts of quinhydrone they found a second smaller maximum occurring after the maximum which indicated the end-point of the titration. This could be explained on the basis of an acid impurity in the quinhydrone.

In Fig. 1 the results are plotted. The classical dissociation constant of acetic acid increases with increasing molecular acetic acid concentration in a solution in which the electrolyte concentration is constant. This is also apparent in the results of Harned and Robinson[5] and Harned and Murphy[6] when recalculated to give K_c. Some results from their work in molal salt solutions have been included in the plot as indicated. When the potassium chloride results are extrapolated to zero molecular acetic acid concentration, K_c in a solution free from acetic acid molecules is found to be approximately 2.83×10^{-5}. The value calculated from the work of Harned and Murphy in one molal potassium chloride solution, which is also 0.2 molal in acetic acid, is 2.74×10^{-5}. However for solutions from 0.003 molar to 0.300 molar in acetic acid, and 0.1 molar in sodium acetate and 0.9 molar in potassium chloride, K_c can be represented by $2.85\ (\pm 0.05) \times 10^{-5}$. Similarly, the extrapolated value for the sodium chloride solutions is 3.15×10^{-5}, while the value from Harned and Murphy in one molal sodium chloride solution, which also contained 0.2 molal

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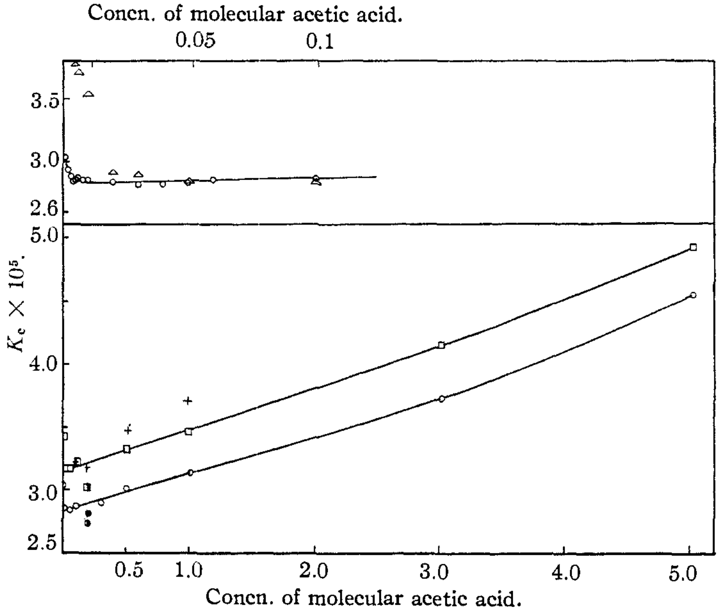
(5) Harned and Robinson, This Journal, **50**, 3157 (1928).

(6) Harned and Murphy, *ibid.*, **53**, 8 (1931).

acetic acid, is 3.02×10^{-5}. For solutions from 0.005 molar to 0.100 molar in acetic acid, and 0.1 molar in sodium acetate and 0.9 molar in sodium chloride, K_c can be represented by $3.19\ (\pm 0.03) \times 10^{-5}$.

The circles in the upper curve on the plot show the results at low acetic acid concentration on a larger scale. The triangles show some results with the uncertain sample of quinhydrone where the effect of a possible acid impurity causes K_c to increase below 0.03 molar acetic acid concentration. The final increase for the other samples of quinhydrone may be due to a much smaller concentration of the same impurity.



○—in KCl; □—in NaCl; △—in KCl with uncertain sample of quinhydrone; +—H. and R. in 1 molal NaCl; ●—H. and R. in 1 molal KCl; ◧—H. and M. in 1 molal NaCl; ◐—H. and M. in 1 molal KCl.

Fig. 1.—Effect of molecular acetic acid concentration on the dissociation constant of acetic acid in KCl and NaCl solutions.

During the work some of the buffers were kept and the hydrogen-ion concentration redetermined. Those most dilute in acetic acid showed signs of some growth such as mold. The hydrogen-ion concentration of the solutions low in acetic acid decreased with time while it remained constant for months in those containing considerable acetic acid. MacInnes and Shedlovsky[7] have reported a similar effect with dilute acetic acid solutions.

The writer wishes to express his thanks to Martin Kilpatrick, Jr., for

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[7] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1420 (1932).

his interest in the work, and also to the University of Pennsylvania for the laboratory facilities extended.

Summary

The variation of the classical dissociation constant of acetic acid with changing molecular acetic acid concentration in solutions 0.1 molar in sodium acetate and 0.9 molar in potassium or sodium chloride has been determined using the quinhydrone electrode. The stability of acetic acid-acetate buffers has been investigated.

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The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Perchloric Acid at 25°[1]

BY J. N. PEARCE AND A. F. NELSON

In a recent paper Pearce and Nelson[2] have reported upon the vapor pressures and activity coefficients of aqueous solutions of several alkali salts. The present paper deals with the results of a similar study of aqueous solutions of perchloric acid and these will be presented briefly. The acid is non-volatile and hence its solutions should be readily amenable to thermodynamic treatment from vapor pressure data.

The apparatus and technique, the accuracy attained and the methods of calculation are fully described in the previous paper. It may suffice to state that the vapor pressure of the solvent is calculated by means of the simple relation

$$p_1 = \frac{n_1}{n_1 + n_2} P$$

Here n_1 is the number of moles of water vapor collected in the phosphorus pentoxide absorber, while n_2 is the total number of moles of hydrogen and oxygen electrolytically generated and calculated from the amount of silver deposited in a silver coulometer. P is the corrected barometric pressure.

Chemically pure perchloric acid was further purified according to the method recommended by Willard.[3] It was twice redistilled at 162-163° under a pressure of 200 mm. Mother solutions were prepared from the concentrated acid. The exact concentrations of these were determined on a weight-concentration basis by titration with a solution of sodium hydroxide which had been standardized previously against a Bureau of Standards

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(1) A brief summary of a thesis presented by Arthus F. Nelson to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932).

(3) Willard, *ibid.*, **34**, 1480 (1912).