[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Dissociation Constant of Boric Acid from 10 to 50°

BY BENTON BROOKS OWEN

The importance of boric acid and borax as solid standards for the preparation of buffer solutions has been responsible for numerous determinations of the dissociation constant of boric acid.[1] The widespread disagreement among the values obtained by various experimenters may be attributed to well-known uncertainties inherent in the earlier methods of investigation. Since some of the more important sources of error have been obviated in methods[2] now available, it seemed desirable to redetermine the dissociation constant of this acid by suitable cell measurements over a useful range of temperatures.

Discussion of the Method

The cells employed were of the type[2b]

$$H_2/HA(m_1),\ MA(m_2),\ MCl(m_3)/AgCl,\ Ag$$

for which the extrapolation function[2b]

$$B\mu + pK = E/k - E^\circ/k + \log m_3 + \log \rho = pK' \quad (1)$$

can be conveniently employed to determine pK when $\mu = 0$. Here HA represents the weak acid for which the thermodynamic dissociation constant, K, is sought. The cation in the salts, MA, and MCl, is usually an alkali metal, or mixture of two. Values of E° were taken from Equation (7) of the paper by Harned and Ehlers,[3] and the constants used to calculate $k = 2.303\ RT/F$ were taken from the "International Critical Tables." The calculation of the buffer ratio, $\rho = m_{HA}/m_{A^-}$, has been discussed elsewhere[2b] for moderately weak acids, but for acids as weak as boric, the calculations must be modified to deal with hydrolysis of the salt, MA.

For the general case of a simple unibasic acid

$$\begin{aligned} m_{HA} &= m_1 - m_{H^+} + m_{OH^-} \\ m_{A^-} &= m_2 - m_{OH^-} + m_{H^+} \end{aligned} \quad (2)$$

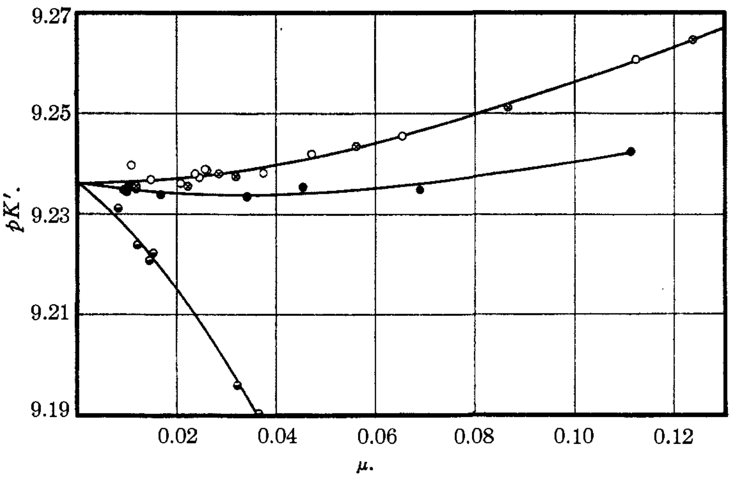

Fig. 1.—Extrapolations for pK at 25°: ○, Series 2; ⊗, Series 3; ●, Series 4; ◒, Series 5.

with $\rho \approx 1$, we may, for our purpose, neglect m_{OH^-} when $pK \leqq 5$, and m_{H^+}, when $pK \geqq 9$. (In the intermediate range, $5 < pK < 9$, both m_{H^+} and m_{OH^-} are negligible.) Therefore, for boric acid we may neglect m_{H^+}, and estimate m_{OH^-} with sufficient accuracy from the approximation

$$m_{OH^-} \approx K_w m_2/K m_1 \quad (3)$$

Values of K_w were obtained from the paper by Harned and Hamer,[4] and of K by successive approximations.[2b] Final extrapolations for pK at 25° are shown in Fig. 1.

Materials and Technique

Kahlbaum purest fused borax was re-fused in platinum for three or four hours[5] in an electric muffle, and poured into a wide platinum dish to cool and fracture. It was immediately bottled without being ground. Borax so treated remained water-white and sparkling for months.

Baker "Analyzed" sodium chloride was precipitated by hydrogen chloride, recrystallized, and fused in platinum. The fused salt was analyzed for free base (about 0.02%), brought to exact neutrality, and twice recrystallized. The potassium chloride was a "C. P." product recrystallized four times. Both salts were air-

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(1) For bibliography, see "International Critical Tables,' Vol. VI, p. 260 and Vol. VII, p. 288, 1929, and Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1924, Vol. V, p. 55.

(2) (a) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); (b) Harned and Ehlers, *ibid.*, **54**, 1350 (1932); (c) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932); (d) Fuoss and Kraus, *ibid.*, **55**, 476 (1933); (e) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); (f) Saxton and Langer, *ibid.*, **55**, 3638 (1933).

(3) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(4) Harned and Hamer, *ibid.*, **55**, 2194 (1933).

(5) Smith and Van Haagen [*Carnegie Inst. Wash. Pub.*, **267**, pp. 20 and 63 (1915)] found that the usual borax "glass" contains about 0.2% of moisture which cannot be eliminated except by prolonged fusion.

dried, ground in agate and finally heated in platinum for five hours at 450° in an electric muffle.[6]

The hydrochloric acid was Baker "Analyzed" redistilled. A 0.1 *N* air-free stock solution was standardized against Bureau of Standards acid potassium phthalate *via* a carbonate-free solution of sodium hydroxide. Subsequent titration against the pure borax[7,8] was concordant to 0.04%.

Preparation, storage, dilution and all other manipulations of the buffer solutions (and standard solutions) were carried out in an atmosphere of pure hydrogen.[9]

TABLE I

THE COMPOSITIONS OF THE BUFFER SOLUTIONS

Series	Constituents	m_1/m_2	m_2/m_3[a]
1	Borax, NaCl	1	0.9584
2	Borax, NaCl	1	1.1349
3	Borax, KCl	1	0.9012
4	Borax, NaCl, HCl	1.1778	.9699
5	Borax, NaCl, HCl	2.6893	1.1839

[a] All concentrations are expressed in moles per kg. of water.

The cells were filled with hydrogen and maintained above atmospheric pressure while the buffer solutions were forced in. Fresh electrodes were prepared for each cell from silver oxide[10] and pure chloroplatinic acid.[11] Cells were measured in duplicate, and the mean of their electromotive forces recorded in Tables II and III. The average difference between duplicate cells was 0.03 mv. The standard cells and thermometers had recently been certified by the Bureau of Standards. Temperature regulation varied from 0.01° at 25° to perhaps 0.03° at 10 and 50°.

TABLE II

THE OBSERVED ELECTROMOTIVE FORCES AT VARIOUS TEMPERATURES

	Series 1					Series 2		
$m \times 10^6$	E_{10}	E_{15}	$m_3 \times 10^6$	E_{20}	E_{25}	E_{30}	E_{40}	E_{50}
5408	0.88570	0.89138	5038	0.89891	0.90472	0.91041	0.92193	0.93348
5658	.88449	.89009	6810	.89136	.89685	.90264	.91380	.92505
8807	.87377	.87924	9700	.88237	.88775	.89325	.90426	.91544
13738	.86303	.86829	10988	.87934	.88466	.89014	.90109	.91218
15662	.85986	.86504	11458	.87819	.88354	.88896	.89976	.91099
20113	.85383	.85887	11982	.87725	.88252	.88792	.89867	.90975
			12292	.87653	.88183	.88716	.89789	.90883
			17440	.86767	.87284	.87809	.88853	.89929
			22003	.86200	.86711	.87223	.88249	.89302
			30602	.85394	.85885	.86373	.87360	.88361
			52523	.84130	.84588	.85050	.85980	.86941

Discussion of Results

The observed *pK* recorded in Table IV are the average values obtained from several concordant series, except for 10 and 15° where only one series was measured. The maximum disagreement between series was 0.003 at 50°.

These values can be expressed by the equation

$$pK = 9.023 + 8 \times 10^{-5} (76.7 - t)^2 \qquad (4)$$

which is of the form which Harned and Embree[12] have shown to be characteristic of a variety of weak electrolytes, but the coefficient of the quadratic term is somewhat greater than 5×10^{-5} suggested by them as a general factor. The difference is not very great when translated into *pK* units. Indeed, if 5×10^{-5} be used, an equation can be derived which would fit the observed values within 0.008. Perhaps an accurate determination of this factor, or proof of its universality must be reserved for an adequate theoretical treatment of the process of ionization.

Combining the derivative of Equation (4) with the van't Hoff equation, we obtain

$$\Delta H = 3.68 \times 10^{-4} RT^2 (76.7 - t) \qquad (5)$$

from which the values of ΔH in Table IV were calculated.

TABLE III

THE OBSERVED ELECTROMOTIVE FORCES AT 25°

Series 3		Series 4		Series 5	
$m_3 \times 10^6$	E_{25}	$m_3 \times 10^6$	E_{25}	$m_3 \times 10^6$	E_{26}
6086	0.89962	4785	0.90155	3790	0.88621
11671	.88300	5093	.89994	5452	.87646
14954	.87675	5312	.89901	6649	.87119
16789	.87375	5969	.89592	6939	.87019
29417	.85966	8481	.88685	14687	.84935
45470	.84901	17642	.86806	16664	.84578
65089	.84060	23541	.86078	34506	.82344
70442	.83889	35690	.85005	51704	.80967
97375	.83173	57630	.83820	65727	.80089

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(6) Ref. 5, p. 55.

(7) Rimbach, *Ber.*, **26**, 164 (1893).

(8) Kolthoff, THIS JOURNAL, **48**, 1447 (1926).

(9) Harned and Owen, *ibid.*, **52**, 5091 (1930).

(10) Harned, *ibid.*, **51**, 416 (1929).

(11) Harned, *ibid.*, **48**, 326 (1926).

(12) Harned and Embree, *ibid.*, **56**, 1050 (1934).

TABLE IV

THE DISSOCIATION CONSTANT AND HEAT OF DISSOCIATION OF BORIC ACID

$t°$	pK(obs.)	pK(eq. 4)	$K \times 10^{10}$	ΔH(cal.)
10	9.380	9.379	4.17	3920
15	9.327	9.328	4.70	3750
20	9.280	9.280	5.25	3570
25	9.236	9.237	5.80	3360
30	9.197	9.197	6.35	3140
35		9.162	6.89	2900
40	9.132	9.131	7.39	2630
45		9.103	7.89	2350
50	9.080	9.079	8.33	2040

The internal consistency of the various series points to an accuracy of about ±0.002 in pK, or 0.1 mv. in $E - E°$. It should be remarked, however, that Equation (1) would not be strictly applicable if HBO_2 shows any considerable tendency to form complexes in the most dilute solutions. The curvature of the lines in Fig. 1 demonstrates the limitations of Equation (1) in this respect,[13] but does not, in the author's opinion, prohibit its use as a practical extrapolation function, especially when $\rho \approx 1$, and the curve is almost horizontal. A variety of investigations[14] indicate complete dissociation of the tetraborate ion into metaboric[15] acid and its ions in dilute solution. Therefore, by virtue of the extrapolation to infinite dilution, the constants in Table IV must pertain to this acid. Increasing concentration of free acid favors the formation of the stronger[14d] tetraboric acid, so at finite concentrations the expression "dissociation constant of boric acid" is ambiguous.[8] A striking demonstration of this increase in acid strength is given in Fig. 1, where the effect of the buffer ratio is many times greater than that which we might normally ascribe to the medium effect of the undissociated acid upon its ions.[16]

Summary

The dissociation constant of metaboric acid (or the first dissociation constant of orthoboric acid) and the corresponding heat of dissociation have been determined over the temperature range from 10 to 50°. At 25° $K = 5.80 \times 10^{-10}$ and $\Delta H = 3360$ cal.

The results have been expressed as a temperature function in formal agreement with the equations proposed by Harned and Embree[12] for the dissociation of weak electrolytes.

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[13] The same effect can be observed in the presence of "zwitter" ions. *Cf.* Nims and Smith, *J. Biol. Chem.*, **101**, 401 (1933), and Owen, THIS JOURNAL, **56**, 24 (1934).

[14] (a) Noyes and Whitney, *Z. physik. Chem.*, **15**, 694 (1894); (b) Kahlenberg and Schreiner, *ibid.*, **20**, 547 (1896); (c) Shelton, *ibid.*, **43**, 494 (1903); (d) Auerbach, *Z. anorg. Chem.*, **37**, 352 (1904); (e) Schmidt and Finger, *J. Phys. Chem.*, **12**, 406 (1908).

[15] It is unnecessary for our purposes to distinguish between *meta-* and *ortho-*boric acids.

[16] Owen, THIS JOURNAL, **54**, 1758 (1932). Also Ref. 2a.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Dipole Moments of Phosgene, Hydrogen Cyanide and Certain Substituted Methanes

BY C. P. SMYTH AND K. B. MCALPINE

Determinations of the dipole moments of phosgene, hydrogen cyanide, nitromethane and chloropicrin are reported in the present paper in order that they may be available for discussions of structure. The dielectric constants of the vapors were measured with the apparatus and method previously described,[1] the gold-palladium cell used by Zahn[2] being employed in the measurements. As in the earlier work, the polarization P was calculated from the dielectric constant ϵ and the molar volume V as $P = [(\epsilon - 1)/(\epsilon + 2)]V$. The errors in P caused by using the ideal gas law to calculate V were eliminated by extrapolating to zero pressure to obtain a value for use in the Debye equation, $P = a + b/T$. Table I gives, at each absolute temperature T, the value of the polarization at zero pressure, P_0, read from the polarization-pressure curves. These straight lines, usually representing six to ten points, become horizontal at high temperatures. The values of a and b, of the atomic polarization, $P_A = a - P_E$, of P_E, the molar refraction extrapolated to infinite wave length, and of the moment μ calculated from b are listed in Table II. The tendency of chloropicrin to decompose made it impossible to run over a range of temperature.

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[1] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933); *J. Chem. Phys.*, **1**, 190 (1933).

[2] Zahn, *Phys. Rev.*, **24**, 400 (1924).