

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## The Formal Electrode Potentials of Palladium in Aqueous Hydrochloric and Perchloric Acid Solutions. Stability of Chloropalladite Ion<sup>1</sup>

BY DAVID H. TEMPLETON, GEORGE W. WATT AND CLIFFORD S. GARNER

Essentially no physicochemical studies appear to have been made as to the state in which bivalent palladium exists in chloride solutions. Wellman<sup>2</sup> has studied the equilibrium between palladous and palladic chlorides and chlorine in chloride solutions, but his data indicate only that the complex ions present in such solutions are formed by the addition of the same number of chloride ions to the simple chlorides, PdCl<sub>2</sub> and PdCl<sub>4</sub>. However, it has been known for some time that salts of the type R<sub>2</sub>PdCl<sub>4</sub> may be crystallized from such solutions,<sup>3</sup> and the existence of the chloropalladite anion, PdCl<sub>4</sub><sup>2-</sup>, in the crystalline state has been well established.<sup>4,5</sup> Hence, it is generally assumed that bivalent palladium in chloride solutions exists mainly in the form of PdCl<sub>4</sub><sup>2-</sup> ions.

The determination of the electrode potentials of palladium in chloride and other solutions is one means of studying the nature of complex ions formed by the palladium and, in addition, allows a direct estimation of the thermodynamic properties of such solutions. No systematic study of the potential has been reported in the literature. Neumann<sup>6</sup> has measured the potential of one "bright" and two "blacked" palladium electrodes in 0.5 *M* palladium chloride, using a normal calomel half-cell as a reference electrode. From Neumann's data, Latimer<sup>7</sup> has calculated the approximate value of -0.83 volt for the standard electrode potential of palladium. Andrews<sup>8</sup> made several measurements on one "bright" and one "blacked" palladium electrode, also in chloride solutions.

In the present investigation, the measurement

(1) Based on a thesis presented by D. H. Templeton to the Graduate Faculty of the University of Texas in partial fulfillment of the requirements for the degree of Master of Arts, June, 1943.

(2) Wellman, *THIS JOURNAL*, **52**, 985 (1930).

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XV, Longmans, Green and Co., London, 1936, pp. 668-673.

(4) Dickinson, *THIS JOURNAL*, **44**, 2404 (1922), has shown by X-ray investigations of crystalline chloropalladites that PdCl<sub>4</sub><sup>2-</sup> is a well-defined anion with a square coplanar configuration.

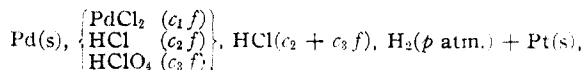
(5) Jones, *ibid.*, **57**, 471 (1935), has demonstrated that K<sub>2</sub>PdCl<sub>4</sub> is diamagnetic, indicating the use of *4d5s5p<sup>2</sup>* square bond orbitals by the palladium.

(6) Neumann, *Z. physik. Chem.*, **14**, 193 (1894).

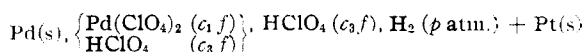
(7) Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 191.

(8) Andrews, *J. Biol. Chem.*, **59**, 479 (1924).

of the electromotive forces of cells of two types has been undertaken. Type I



and Type II



The formal potential,<sup>9</sup>  $E^0$  (for the reaction Pd(s) = Pd<sup>II</sup> + 2e<sup>-</sup>) has been obtained by adding to the observed potential,  $E_{\text{obsd.}}$ , the following two quantities

$$E_C = (RT/2F) \ln c_1 \quad (\text{A})$$

to provide for the formal concentration of palladium salts, and

$$E_H = (RT/F) \ln [\sqrt{p}/\gamma(c_2 + c_3)] \quad (\text{B})$$

to refer the values to the molal hydrogen electrode,  $\gamma$  being the mean ionic activity coefficient of hydrogen ions in  $c_2 + c_3 f$  hydrochloric or perchloric acids, and  $p$  being the partial pressure of hydrogen in atmospheres. The liquid junction potential has been neglected since the salt concentration  $c_1$  was always less than 6% of the total acid concentration ( $c_2 + c_3$ ), which was the same in both half-cells.<sup>10</sup> Constant ionic strength in a given series of experiments could be maintained closely because of the low salt concentration.

### Experimental

**Preparation and Analysis of the Solutions.**—Palladium from three sources was used in the preparation of palladium solutions: c. p. palladium foil, c. p. palladium wire, and c. p. palladous chloride. Gravimetric analysis for palladium by the method of Wunder and Thüringer,<sup>11</sup> as modified by Gilchrist and Wichers,<sup>12</sup> showed a purity of 100.0 and 99.4% for the foil and wire, respectively, and a palladium content of 59.5% for the palladous chloride (theoretical value for PdCl<sub>2</sub> = 60.0%). The foil and wire were converted to palladous chloride by solution in aqua regia followed by repeated evaporation to dryness with hydrochloric acid. Stock palladous chloride solutions

(9) By "formal potential" is meant the potential, referred to the standard molal hydrogen electrode, for the case when the total concentrations of the reduced and oxidized substances are both 1.0 *f* (without reference to their possible incomplete ionization, hydrolysis, formation of complexes, etc.).

(10) A brief discussion of this assumption is given in footnote 8 of the paper by Hughes and Garner, *THIS JOURNAL*, **64**, 1844 (1942).

(11) Wunder and Thüringer, *Z. anal. Chem.*, **52**, 101 (1913).

(12) Gilchrist and Wichers, *THIS JOURNAL*, **57**, 2565 (1935).

were prepared by dissolving the dried palladous chloride (from all three sources mentioned above) in standard hydrochloric acid or in mixtures of known weights of standard hydrochloric and perchloric acids. These solutions were analyzed for palladium by the method mentioned above. The acid concentrations were calculated from the weight data. Other palladous chloride solutions were prepared by weight dilution of these solutions, after which the palladium content was again checked by analysis.

Palladous perchlorate solutions were prepared as follows. A portion of one of the palladous chloride-hydrochloric acid solutions was treated with sodium hydroxide until basic to litmus. The precipitated hydrated palladous oxide was washed with water by decantation until the filtrate gave no test for chloride ion with silver nitrate solution.<sup>13</sup> The precipitate was collected in a porous porcelain filtering crucible and partially dried by suction, after which it was dissolved in standard perchloric acid. The water contained in the oxide had a negligible effect on the concentration of the acid, but a correction was applied for the acid consumed in the neutralization process. Other solutions were made by weight dilution of this solution, and the palladium content of each determined by analysis.

The hydrochloric and perchloric acid solutions were obtained by dilution of reagent grade concentrated acids, the impurities in which were stated to be negligible. Standardization of these solutions was achieved by titrating portions of a sodium hydroxide solution which had just been standardized against potassium hydrogen phthalate obtained from the Bureau of Standards.

All weights and volumetric glassware were calibrated. Weighings were corrected for the buoyancy of air. All solutions were made with distilled water.

**Purification of Hydrogen.**—Tank (electrolytic) hydrogen was passed successively through concentrated solutions of sulfuric acid, potassium hydroxide and sodium plumbite, then over electrically-heated platinized asbestos.

**The Palladium Electrodes.**—Several types of palladium electrode were prepared in search of a reproducible type. (1) A sheet of bright palladium foil was fused to a platinum wire and sealed into a glass tube so that the platinum was completely covered by the glass. (2) An electrode similar to (1) was coated by electrolysis with palladium black. (3) A platinum wire sealed through the end of a glass tube was electroplated with palladium black. (4) Spongy palladium was prepared by electrolysis of one of the palladous chloride-hydrochloric acid solutions, using platinum wire electrodes and a high current density. The finely divided metal was washed repeatedly with water, by decantation. Warmed nitrogen was passed over the palladium to remove most of the water. Heating the metal for some time in a high vacuum removed the remaining moisture and any dissolved hydrogen absorbed from the solution during electrolysis. A small quantity of this spongy palladium was placed in a glass tube with

(13) One of the referees has pointed out that some of the palladium may possibly precipitate as a basic chloride under similar conditions. To test this point a single experiment was carried out under the conditions employed in the original preparation of the palladous perchlorate and it was found that a negligible amount of chloride was retained by the oxide.

holes blown in the walls above the metal to allow access of the solution to the metal. A palladium-blackened platinum wire was immersed in the spongy palladium.

Preliminary measurements of the potentials of several electrodes of each type in the same solution indicated that the first three types of electrode were neither constant nor reproducible enough to warrant their use, but it was found that measurements on the spongy palladium electrodes gave values which agreed within a few millivolts and which were substantially constant. Accordingly, this type of spongy palladium electrode was employed.

**The Cell.**—The type of cell used and the manner of thermostating and handling were essentially the same as described by Hughes and Garner.<sup>14</sup> Each cell was equipped with two palladium electrodes for the purpose of comparison.

**Method of Potential Measurements.**—A Leeds and Northrup Type K-2 potentiometer and Type R galvanometer were used for the e. m. f. measurements. The Eppley standard cell used was checked several times during the investigation against two cells which had been certified recently by the Bureau of Standards.

The spongy palladium electrodes were immersed for one or two days in some of the solution to be used, after which the cells were assembled and placed in the thermostat. Several hours were usually required for the readings to become reasonably constant, although the two hydrogen electrodes in each hydrogen half-cell generally agreed to within 0.1 millivolt as soon as thermal equilibrium was attained.

## Results and Discussion

**Potentials in Hydrochloric Acid Solution.**—The results of measurements made at 25, 15 and 35° with cells of Type I ( $c_3 = 0$ ), are listed in Table I. Concentrations have been expressed as weight formalities,  $f$  (formula weights per kilogram of water). The values of  $E_{\text{obsd.}}$  given in the table represent average values based on the number of cells indicated in the parentheses immediately following each value. The spread between extreme values was generally less than 1 millivolt. The values of  $E_0''$  were computed as indicated earlier in this paper, the values of the activity coefficient of hydrochloric acid being interpolated from the data of Harned and Ehlers,<sup>15</sup> and the partial pressure of hydrogen being calculated from the corrected barometric pressure by subtraction of the vapor pressure of 0.9952  $f$  hydrochloric acid at the given temperature<sup>16</sup> and addition of the hydrostatic head.

As may be seen from the first and sixth columns of Table I,  $E_0''$  is not altered appreciably by a fifty-fold change in the formal concentration of palladous chloride. This constancy of  $E_0''$  indi-

(14) See reference given in footnote 10.

(15) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).

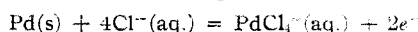
(16) "International Critical Tables," Vol. 111, McGraw-Hill Book Co., New York, N. Y., 1928, p. 301.

TABLE I  
ELECTROMOTIVE FORCES AT 25, 15, AND 35° IN HYDROCHLORIC ACID SOLUTION  
Series 1: 0.9952 *f* HCl ( $\gamma = 0.808$ ) at 25°,  $\mu = 1.00$

PdCl <sub>2</sub> , <i>c</i> <sub>1</sub>	<i>E</i> <sub>obsd.</sub>	<i>E</i> <sub>G</sub>	<i>E</i> <sub>H</sub>	<i>E</i> <sub>Cl</sub>	<i>E</i> <sup>0''</sup>	<i>E</i> <sup>0'''</sup>
0.05021	-0.5902 (4)	-0.0384	+0.0051	+0.0057	-0.6235	-0.6178
.01000	-.5661 (4)	-.0591	+.0052	+.0013	-.6200	-.6187
.00500	-.5597 (6)	-.0680	+.0050	+.0008	-.6227	-.6219
.000996	-.5433 (3)	-.0888	+.0051	+.0004	-.6270	-.6266
				Mean	-.623	-.621
Series 2: 0.9952 <i>f</i> HCl ( $\gamma = 0.822$ ) at 15°, $\mu = 1.00$						
.01000	-.5724 (4)	-.0572	+.0048	+.0012	-.6248	-.6236
.000996	-.5511 (3)	-.0858	+.0046	+.0003	-.6323	-.6320
Series 3: 0.9952 <i>f</i> HCl ( $\gamma = 0.795$ ) at 35°, $\mu = 1.00$						
.01000	-.5599 (4)	-.0611	+.0054	+.0013	-.6156	-.6143
.000996	-.5370 (4)	-.0917	+.0053	+.0004	-.6234	-.6230

cated that only one palladium atom is involved per palladous complex present in substantial concentration in the solutions studied.<sup>17</sup>

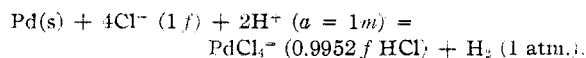
In anticipation of the results of the measurements of Series 4, 5 and 6, calculations have been made of *E*<sup>0'''</sup>, the formal potential for the reaction



by adding the quantity

$$E_{\text{Cl}} = -(2RT/F) \ln (\text{Cl}^-)$$

to *E*<sup>0''</sup>, (Cl<sup>-</sup>) being assumed<sup>18</sup> equal to (*c*<sub>2</sub> - 2*c*<sub>1</sub>). These values of *E*<sup>0'''</sup> have been included in Table I, and their mean given ignoring the fact that there is a definite (although not large) trend with changing formal concentration of palladous salt. From the mean value of -0.621 volt for *E*<sup>0'''</sup> and the mean temperature coefficient of *E*<sup>0'''</sup> at 25°, namely, +0.00046 volt/degree,<sup>19</sup> values of  $\Delta F_{298}^{0'''}$  = 28.6 kcal.,  $\Delta H_{298}^{0'''}$  = 34.9 kcal., and  $\Delta S_{298}^{0'''}$  = 0.021 kcal./deg. were calculated for the cell reaction



These thermodynamic constants, together with the standard virtual entropies<sup>20</sup> of H<sub>2</sub>(g),<sup>21</sup> Pd(s),<sup>22</sup>

(17) Assuming stable complexes of the type Pd<sub>*x*</sub>Cl<sub>*y*</sub>(*w* - 2*x*)<sup>2+</sup> in the solutions involved

$$E^{0''} = (RT/2F)(1 - 1/x) \ln c_1 + \text{constant}$$

where *x* is the average number of palladium atoms per complex. If *x* were 2, for example, the fifty-fold variation of *c*<sub>1</sub> would have altered *E*<sup>0''</sup> by 25 mv. at 25°. The change would be larger, of course, if *x* > 2.

(18) This assumption holds very closely since, as is shown later, the PdCl<sub>4</sub><sup>-</sup> complex is very stable.

(19) Values of +0.00046 and 0.00045 volt/degree were obtained by plotting the mean values of *E*<sup>0'''</sup> at 15, 25 and 35° for *c*<sub>1</sub> = 0.01000 and *c*<sub>1</sub> = 0.000996, respectively, versus the temperature.

(20) The conventional entropy, obtained by subtraction of the limiting nuclear spin entropy from the absolute entropy.

(21) Giauque, THIS JOURNAL, 52, 4816 (1930):  $S_{298}^0[\text{H}_2(\text{g})] = 31.23 \text{ cal./deg.}$

(22) Lewis, Gibson and Latimer, *ibid.*, 44, 1008 (1922):  $S_{298}^0[\text{Pd}(s)] = 8.9 \text{ cal./deg.}$

Cl<sup>-</sup>(aq.),<sup>23</sup> and Cl<sub>2</sub>(g),<sup>24</sup> and the standard free energy of formation of Cl<sup>-</sup>(aq.),<sup>25</sup> lead to the following thermodynamic constants of PdCl<sub>4</sub><sup>-</sup>(aq.): 0.053 kcal./deg. for the standard virtual entropy, and -96.7 kcal., -115 kcal., and -0.063 kcal./deg. for the standard free energy, heat of formation, and entropy of formation, respectively. The above value of the heat of formation may be compared with the value -127.5 kcal., given by Bichowsky and Rossini.<sup>26</sup>

**Potentials in Mixtures of Hydrochloric and Perchloric Acid Solutions.**—Measurements were carried out with mixtures of hydrochloric and perchloric acid solutions in order to study the effect of varying chloride ion concentration independently of hydrogen ion concentration and ionic strength. The results are given in Table II. It may be seen from columns three and eight that *E*<sup>0''</sup> is a function of chloride ion or perchlorate ion concentration. Assuming that perchlorate ions have little or no tendency to form complexes with palladous ion over the range 0 to 4.0 *f* perchloric acid, this variation in *E*<sup>0''</sup> has been interpreted wholly in terms of the formation of chloride complexes of palladous ion. On the assumption that the palladous salt is chiefly in the form of PdCl<sub>4</sub><sup>-</sup> ions in the solutions studied, values of *E*<sup>0'''</sup> have been computed as indicated earlier in this paper. Their relative constancy for given hydrogen ion concentration and ionic strength may be accepted as evidence that this assumption

(23) Latimer, Pitzer and Smith, *ibid.*, 60, 1829 (1938):  $S_{298}^0[\text{Cl}^-(\text{aq.})] = 13.50 \text{ cal./deg.}$

(24) Giauque and Overstreet, *ibid.*, 54, 1731 (1932):  $S_{298}^0[\text{Cl}_2(\text{g})] = 53.31 \text{ cal./deg.}$

(25) Randall and Young, *ibid.*, 50, 989 (1928):  $\Delta F_{298}^0 = -31,330 \text{ cal.}$

(26) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1955, p. 53.

TABLE II  
ELECTROMOTIVE FORCES AT 25° IN MIXTURES OF HYDROCHLORIC AND PERCHLORIC ACID SOLUTIONS

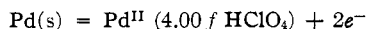
PdCl <sub>2</sub> , c <sub>1</sub>	HCl, c <sub>2</sub>	(Cl <sup>-</sup> ), c <sub>2</sub> - 2c <sub>1</sub>	E <sub>obsd.</sub>	E <sub>C</sub>	E <sub>H</sub>	E <sub>Cl</sub>	E <sup>0''</sup>	E <sup>0'''</sup>
Series 4: Total acid concentration, 4.007 f (γ = 1.762), μ = 4.02								
0.00948	4.007	3.988	-0.4215 (4)	-0.0598	-0.0506	-0.0711	-0.5319	-0.6030
.00975	1.589	1.570	-.4654 (4)	-.0594	-.0504	-.0232	-.5752	-.5984
.00982	0.9301	0.9105	-.4925 (4)	-.0594	-.0505	+.0048	-.6024	-.5976
.00988	.4203	.4005	-.5334 (4)	-.0593	-.0505	+.0470	-.6432	-.5962
.00992	.09875	.07892	-.6134 (4)	-.0593	-.0506	+.1305	-.7233	-.5928
.00992	.05525	.03541	-.6494 (4)	-.0593	-.0507	+.1716	-.7594	-.5878
							Mean	-.596
Series 5: Total acid concentration, 1.993 f (γ = 1.008), μ = 2.00								
.00976	1.993	1.973	-.5028 (4)	-.0594	-.0182	-.0349	-.5804	-.6153
.01016	1.435	1.415	-.5200 (4)	-.0589	-.0183	-.0178	-.5972	-.6150
.01049	0.9593	0.9383	-.5401 (4)	-.0585	-.0183	+.0033	-.6169	-.6136
.01082	.4667	.4450	-.5769 (5)	-.0581	-.0183	+.0416	-.6533	-.6117
							Mean	-.614
Series 6: Total acid concentration, 0.9952 f (γ = 0.808), μ = 1.00								
.00976	.9952	.9757	-.5681 (4)	-.0595	+.0051	+.0013	-.6225	-.6212
.00979	.7008	.6812	-.5853 (5)	-.0594	+.0053	+.0197	-.6394	-.6197
.00982	.4057	.3861	-.6138 (4)	-.0594	+.0051	+.0489	-.6681	-.6192
							Mean	-.620

is valid. In connection with the equilibrium studies of Wellman<sup>2</sup> mentioned earlier, it should be pointed out that these data also show that quadrivalent palladium exists in chloride solutions largely as the chloropalladate ion, PdCl<sub>6</sub><sup>=</sup>.

Using the mean of the values at each ionic strength, and assuming that the effects of changing hydrogen ion concentration over the range 1.0 to 4.0 f are not important,<sup>27</sup> the following relation between E<sup>0'''</sup> and ionic strength has been derived for the temperature of 25°

$$E^{0'''} = -0.6290 + 0.0080\mu, \quad 1.0 < \mu < 4.0$$

**Potentials in Perchloric Acid Solution.**—The results of measurements on cells of Type II are to be found in Table III. In this case, E<sup>0''</sup> represents the formal potential for the cell reaction



and has been found to have the value -0.987 volt at 25°. This is almost certainly a better approximation to the *molar* electrode potential of

TABLE III

ELECTROMOTIVE FORCES AT 25° IN PERCHLORIC ACID SOLUTIONS

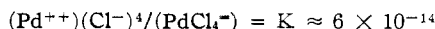
Series 7: 4.007 f HClO<sub>4</sub> (γ = 2.022), μ = 4.02

Pd(ClO <sub>4</sub> ) <sub>2</sub> , c <sub>1</sub>	E <sub>obsd.</sub>	E <sub>C</sub>	E <sub>H</sub>	E <sup>0''</sup>
0.00973	-0.8722 (4)	-0.0595	-0.0542	-0.9849
.00262	-.8591 (4)	-.0763	-.0541	-.9895
			Mean	-.987

(27) It is not considered likely that hydrolytic complexes such as Pd(OH)<sup>+</sup>, Pd(OH)Cl<sub>2</sub><sup>-</sup>, etc., are present in appreciable concentration at such relatively high acid concentrations.

palladium than the value of -0.83 volt obtained by Neumann.<sup>6</sup>

The mean value of E<sup>0'''</sup> for the cells of Series 4 and of E<sup>0''</sup> for the cells of Series 7 have been combined to give an approximate value for the dissociation constant (in terms of concentrations, and not activities) of the chloropalladite ion at 25°



This value is considerably smaller than that estimated by Latimer<sup>28</sup> largely because of Latimer's use of Neumann's value of the standard electrode potential of palladium.

This research was supported by a grant<sup>29</sup> to one of us (C. S. G.) by the University of Texas Research Institute, for which grateful acknowledgment is made.

### Summary

1. The formal electrode potential, E<sup>0''</sup>, of palladous salts in 0.9952 f hydrochloric acid has been determined at 15, 25 and 35°. E<sup>0''</sup> = -0.623 volt for the reaction Pd(s) = Pd<sup>II</sup> + 2e<sup>-</sup> at 25° in the above acid solution and for a fifty-fold change in palladous salt concentration.

2. Measurements have been made of the potentials in mixtures of hydrochloric and perchloric acid solutions of constant total acid concentration and constant ionic strength. The results indicate that bivalent palladium exists in the chloride

(28) Reference 7, p. 192.

(29) Research Project No. 58.

solutions studied mainly as the chloropalladite ion,  $\text{PdCl}_4^{2-}$ .

3. For the half-cell reaction  $\text{Pd}(s) + 4\text{Cl}^-(1f) = \text{PdCl}_4^{2-}(1 - 4f \text{ HCl}) + 2e^-$ , the formal potential  $E^{0'}$  at  $25^\circ$  was found to be related to the ionic strength  $\mu$  by the equation  $E^{0'} = -0.6290 + 0.0080\mu$ ,  $1.0 < \mu < 4.0$ , with a temperature coefficient of  $+0.00046$  volt/degree. Related thermodynamic constants have been presented.

4. The potentials have also been measured in perchloric acid solution in the absence of chloride ion. For the half-cell reaction  $\text{Pd}(s) = \text{Pd}^{II}(4.00f \text{ HClO}_4) + 2e^-$ , the formal potential  $E^{0''}$  has been calculated to have the value  $-0.987$  volt at  $25^\circ$ . An approximate value of  $6 \times 10^{-14}$  has been obtained for the dissociation constant of the chloropalladite anion at  $25^\circ$ .

AUSTIN, TEXAS

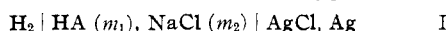
RECEIVED APRIL 22, 1943

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Effect of Sodium Chloride upon the Ionization of Boric Acid at Various Temperatures<sup>1</sup>

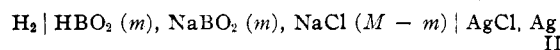
BY BENTON BROOKS OWEN AND EDWARD J. KING<sup>2</sup>

The exact determination of the effects of neutral salts upon the ionization of weak electrolytes is important, but involves so much labor that only formic,<sup>3</sup> acetic<sup>3,4</sup> and lactic<sup>5</sup> acids have been investigated by the thermodynamic method proposed by Harned and Owen.<sup>3,4</sup> This method made use of unbuffered cells of the type



and required a difficult extrapolation. In the present study of boric acid, buffered solutions have been used to increase the accuracy, and the method has been radically altered so as to simplify the extrapolation. In describing the method and treating the experimental results, it will be convenient to employ sodium chloride solutions instead of pure water, in defining standard states. Thus the activity coefficient of any solute at infinite dilution in an  $M$ -molal sodium chloride solution is unity. This device will receive particular attention because it will expedite the calculations in future studies of this nature, and has already proved useful in elucidating the effect of pressure<sup>6</sup> upon ionic equilibria in salt solutions.

**Outline of the Method.**—The cell used in this investigation can be represented by



where  $m$  and  $M$  are concentrations in moles per

(1) This communication contains material from a thesis presented by Edward J. King to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(2) Allied Chemical and Dye Corporation Fellow 1941–1942.

(3) H. S. Harned and B. B. Owen, *THIS JOURNAL*, **52**, 5079 (1930).

(4) H. S. Harned and F. C. Hickey, *ibid.*, **59**, 1284 (1937).

(5) F. C. Hickey, *ibid.*, **62**, 2916 (1940).

(6) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29**, 461 (1941).

kilogram of water. The stoichiometric ratio of boric acid to sodium metaborate is always unity. The total molality of the solutions used in a series of cells is kept constant ( $M$ ), because variations in ionic strength may introduce considerable curvature<sup>7</sup> in the extrapolation. The electro-chemical equation for this cell will be written in the form

$$E_{11} = E^{0*} - k \log m_{\text{H}} m_{\text{Cl}} - k \log \gamma_{\text{H}}^* \gamma_{\text{Cl}}^* \quad (1)$$

where the factor  $k$  equals  $0.00019844 T$ , and the asterisk indicates that the standard state is chosen so that the activity coefficients are unity at infinite dilution ( $m = 0$ ) in a sodium chloride solution of concentration,  $M$ .  $E^{0*}$  is therefore given by the limit

$$E^{0*} = [E_{11} + k \log m_{\text{H}} m_{\text{Cl}}]_{0,M} \quad (2)$$

in which the double subscript ( $0, M$ ) refers, in order, to the value of  $m$  and to the sodium chloride concentration.

According to this same convention, the ionization constant of boric acid in an  $M$ -molal salt solution is written

$$K^* = \frac{\gamma_{\text{H}}^* \gamma_{\text{BO}_2}^* m_{\text{H}} m_{\text{BO}_2}}{\gamma_{\text{HBO}_2}^* m_{\text{HBO}_2}} = \left[ \frac{m_{\text{H}} m_{\text{BO}_2}}{m_{\text{HBO}_2}} \right]_{0,M} \quad (3)$$

Eliminating  $\gamma_{\text{H}}^* m_{\text{H}}$  between equations (1) and (3) and rearranging terms, we obtain

$$[E_{11} - E^{0*} + k \log m_{\text{Cl}} + k \log \rho] = -k \log K^* - k \log \frac{\gamma_{\text{Cl}}^* \gamma_{\text{HBO}_2}^*}{\gamma_{\text{BO}_2}^*} \quad (4)$$

where  $\rho$  is the buffer ratio,  $m_{\text{HBO}_2}/m_{\text{BO}_2}$ .  $K^*$  is readily evaluated by extrapolation, since

$$-k \log K^* = [E_{11} - E^{0*} + k \log m_{\text{Cl}} + k \log \rho]_{0,M} \quad (5)$$

(7) B. B. Owen and S. R. Brinkley, Jr., *THIS JOURNAL*, **64**, 2071 (1942); cf. p. 2074 *et seq*