

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]
**THE DEGREE OF IONIZATION OF ETHYL ALCOHOL. II. FROM
 MEASUREMENTS OF ELECTROMOTIVE FORCE¹**

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In view of the experimental difficulties encountered and the assumptions involved it has seemed hardly worth while to attempt to improve upon the value for the ionization constant of ethyl alcohol, which has been presented in the preceding paper, using the conductivity method, even though this value is much larger in comparison to the corresponding value for water than we should be led to expect from a consideration of the rates of reactions into which these two liquids enter. It has, however, seemed advisable to attempt another determination of this constant employing a method, the accuracy of which does not depend upon the preparation of absolutely pure alcohol and which is at the same time a thermodynamic method. The electromotive-force methods which have previously been used to measure the degree of dissociation of water are satisfactory except for the uncertainties arising from the liquid-junction potentials which have always been present. Some time ago Professor Joel H. Hildebrand suggested to the author that by choosing the proper combination of cells no liquid junction need be included in the measurement of any such quantity. His suggestion has, therefore, been adapted to the determination of the degree of ionization of ethyl alcohol not only because of the desirability of knowing that quantity with considerable certainty but also to demonstrate the possibilities of the method.

The fact that only a very few measurements of the electromotive force of galvanic cells using ethyl alcohol as solvent have been reported, made a large number of preliminary experiments necessary before the final combination of cells to be measured could be decided upon. The three following cells:² (a) H₂, HCl, HgCl, Hg; (b) Hg, HgCl, NaCl, Na(2-phase amalg.); (c) Na(2-phase amalg.), NaOC₂H₅, H₂, were finally selected as being the combination best suited to our purpose. When the concentration of the cell electrolyte is such that the mean activity of the ions,² $a_{\pm} = 1$, the respective reactions occurring in these cells may be written: (a) $\frac{1}{2}\text{H}_2 + \text{HgCl} = \text{H}^+ + \text{Cl}^- + \text{Hg}$; (b) $\text{Hg} + \text{Na}^+ + \text{Cl}^- = \text{HgCl} + \text{Na}$; (c) $\text{Na} + \text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_5\text{O}^- + \text{Na}^+ + \frac{1}{2}\text{H}_2$; these when added

¹ The material here given is taken from a thesis presented by the author in partial fulfillment of the requirement for the degree of Doctor of Philosophy at the University of California.

² The symbols and conventions used in this paper are those which have been adopted by Professor G. N. Lewis and his coworkers and are used by Lewis and Randall in their book, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co. (in press), and in numerous shorter articles already published: **THIS JOURNAL**, 43, 233, 1112 (1921).

give the reaction, $C_2H_5OH = H^+ + C_2H_5O^-$, whose equilibrium constant we desire to determine.

Apparatus.—The potentiometer, the oil thermostats and the general type of hydrogen-electrode vessel used in this investigation have previously been described by Lewis, Brighton and Sebastian.³ The hydrogen generator described by them was modified to include a phosphoric acid drying tower and a long phosphorus pentoxide tube. The heated platinum wire suggested for the removal of possible traces of oxygen was not found necessary. The specific modifications of electrode vessels will be taken up in connection with the discussion of the individual cells. The saturated "Weston" standard cells which were used were prepared by Mr. R. H. Gerke from especially purified materials and are described by him.⁴ The maximum variation among 4 of these cells which were kept for reference was less than 0.0001 volt. The thermostat used in all of the present measurements was constant at 25° to about 0.05°.

Preparation of Solvent.—The alcohol used as solvent in this investigation was prepared according to the method of preliminary purification which has been described in the preceding paper. It was stored in flasks protected from the atmosphere by soda lime and phosphorus pentoxide tubes. Transfer from one vessel to another was effected by means of sealed-in siphon tubes and a pressure of pure dry nitrogen.

Cell (a); H₂, HCl, HgCl, Hg

Cell Vessel and Electrode.—The modifications of the general type of hydrogen-electrode vessel, previously referred to, which have been incorporated in the vessel here used are shown in Fig. 1. The compartments C for 3 calomel electrodes in the same vessel⁵ make possible the comparison of different samples of material under exactly identical conditions and at the same time serve as a check on the constancy of both the hydrogen and the calomel electrodes. This form of vessel has the advantages of compactness and low internal resistance. The hydrogen electrode was of the ordinary type, consisting of a strip of platinum foil coated with platinum black. These electrodes were found to be much more satisfactory when the deposit of platinum black was thin and tightly adherent than when it was thick and loose as recommended by Ellis.⁶ The precaution of heating the electrode to redness immediately previous to platinizing, suggested by Hardman and Lapworth,⁷ was found to favor the formation of a tightly adhering film but the suggestion by them that replatinization is necessary each time the electrode is to be used was not confirmed. This may have been due to the fact that as soon as the electrode was removed from the cell it was placed under pure dry alcohol and allowed to remain so until again required.



Fig. 1.

³ Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

⁴ Gerke, *ibid.*, **44**, 1684 (1922).

⁵ This type of cell was designed by Dr. Buehrer, formerly of this Laboratory.

⁶ Ellis, *THIS JOURNAL*, **38**, 737 (1916).

⁷ Hardman and Lapworth, *J. Chem. Soc.*, **99**, 2242 (1911).

Preparation of Materials.—Hydrogen chloride was prepared by the action of conc. sulfuric acid on conc. hydrochloric acid. The gas was dried by passing through sulfuric acid towers and finally through a long tube containing glass wool to remove any possible spray. The solution to be employed was prepared by collecting this gas in the previously prepared solvent which was usually cooled in a freezing mixture of ice and salt, but this precaution was later found to be unnecessary, at least with the dilute solutions here employed. The more concentrated solutions were analyzed directly by titration with standard barium hydroxide solution, while the less concentrated ones were made by dilution.

Calomel was prepared by the usual methods in water solution, was repeatedly washed and finally dried. It was then ground fine, transferred to a glass-stoppered bottle and shaken for at least 2 weeks with mercury and an alcoholic solution of hydrochloric acid. Cells were made from this stock sample by removing the desired amount of calomel to a second vessel and washing it repeatedly by decantation with portions of the solution to be used as cell electrolyte. The electromotive force of cells so prepared attained a constant final value within a few hours while cells prepared in the same manner from a fresh sample of dry calomel were always 6–8 days and often longer in coming to equilibrium. The mercury used was purified by washing in a dilute solution of mercurous nitrate and nitric acid as recommended by Hildebrand,⁸ and finally by distilling in a current of air after the method of Hulett.⁹

Measurements.—As will be obvious from the method of calculation to be described in a later section, measurements of the electromotive force of cells at various concentrations are desired rather than a series of checks at the same concentration, the experimental variations being smoothed out in the method of plotting. Solutions ranging from 0.009 to 0.3 equivalents of solute per liter of solution were accordingly used.¹⁰ These cells when properly prepared attained approximate equilibrium in 8 to 10 hours and reached a final constant value in 10 to 60 hours, depending upon the strength of the solution, the more dilute cells coming to equilibrium less rapidly. Having reached a steady state, the value of the electromotive force was affected very little by vigorous shaking of the cell and was, in every case, constant to at least 0.0001 volt for as much as 24 hours before the value was accepted. In several cases where it was not necessary to dismantle the cell for a considerable period, readings were taken and found to be surprisingly constant for a number of days.

Results and Calculations.—Since practically nothing is known regarding the activity coefficients of electrolytes in alcoholic solution, the method which has been employed by Linhart¹¹ for determining the value of E° , the potential of a cell when the thermodynamic concentration of the cell electrolyte is unity, was selected as being most applicable. It was found, however, that the experimental difficulties, due to the high internal resistance in cells employing dil. alcoholic solutions as cell elec-

⁸ Hildebrand, *THIS JOURNAL*, **31**, 933 (1909).

⁹ Hulett, *Phys. Rev.*, **33**, 307 (1911).

¹⁰ In such dilute solutions the density change is not sufficient to cause appreciable error should it be desirable to change these figures to weight concentration.

¹¹ Linhart, *THIS JOURNAL*, **41**, 1175 (1919).

trolyte, and also due to the slowness with which the calomel electrode comes to equilibrium in such dilute solutions, make the direct application of this method impracticable.

A first approximation to the thermodynamic degree of dissociation of electrolytes in water solution has been secured in many cases by making the assumption that in some arbitrarily chosen dilute solution it is given by the value of the familiar conductivity function, Λ/Λ_0 , the ratio of the equivalent conductivity at that concentration to the equivalent conductivity at infinite dilution. This assumption has been shown to be sufficiently near to the truth for most calculations providing the concentration chosen be sufficiently low. Since, however, we have no data for any solution in ethyl alcohol from which even a moderately accurate value of the activity coefficient may be calculated we have no means of deciding at what dilution this quantity is even approached by the conductivity ratio. We can test this point and at the same time obtain the value of E° by assuming that at each concentration the activity coefficient, instead of being unity as assumed by Linhart, is given by the value of Λ/Λ_0 .¹² Values of E° calculated from the equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{1}{c^2 \gamma^2} \quad (1)$$

with the assumption that $\gamma = 1$ at each concentration are recorded as $E^{\circ'}$ in Col. of Table I and are represented by Curve I, Fig. 2, while values of E° calculated upon the assumption that at each concentration $\gamma = \Lambda/\Lambda_0$ are recorded as $E^{\circ''}$ in Col. 4 and are represented by Curve II. The values of Λ/Λ_0 were furnished by Professor W. C. Bray who had made the calculations from the data of Goldschmidt¹³ using the method of Kraus and Bray.¹⁴

TABLE I
ELECTROMOTIVE-FORCE MEASUREMENTS IN ACID ALCOHOLIC SOLUTIONS

Conc. HCl in equiv. per liter	E calc. to 760 mm. H ₂	$E^{\circ'}$	$E^{\circ''}$	Λ/Λ_0	γ
0.3020	0.1175	0.0560	-0.0014	0.327	0.221
0.1703	0.1326	0.0416	-0.0081	0.380	0.292
0.0877	0.1538	0.0287	-0.0129	0.445	0.376
0.0274	0.1957	0.0109	-0.0185	0.565	0.531
0.0139	0.2232	0.0022	-0.0202	0.647	0.629
0.00886	0.2406	-0.0022	-0.0209	0.695	0.686

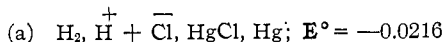
Obviously if this second assumption were correct throughout the range of concentrations employed, the value of $E^{\circ''}$ would be constant and Curve II would be a horizontal straight line. While this is not the case it is suffi-

¹² This method of obtaining the value of E° has previously been employed by Horsch, *THIS JOURNAL*, **41**, 1787 (1919).

¹³ Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1915).

¹⁴ Kraus and Bray, *THIS JOURNAL*, **35**, 1315 (1913).

ciently approached as the dilution increases that an extrapolation may be made with an error of not more than 0.0002 volt, while a corresponding extrapolation of Curve I would be entirely impossible. The value of the ordinate at which Curve II becomes horizontal is of course the value of E° and we have



It will be noticed that quite a few more points are given for values of E° on the plot (Fig. 2) than are recorded in Table I. It will also be noticed that these points fall without exception above the smooth curve. Hardman and Lapworth⁷ have found that the addition of very small amounts of water to hydrogen chloride solutions in alcohol markedly decreases the activity of the acid as shown by the rise in the electromotive force of the hydrogen electrode. This result has been entirely confirmed in the present investigation and is most probably due to the formation

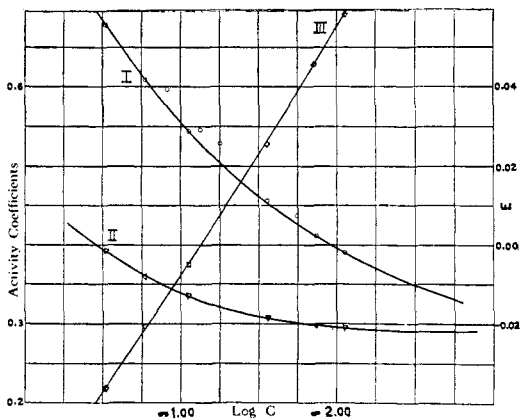


Fig. 2.

The curve given here (Curve I, Fig. 2) was determined using solutions made from alcohol dried with the especially prepared lime which has been described in the preceding article, and though a number of attempts were made to secure a more complete drying by a subsequent treatment with metallic calcium, with sodium amalgam and even with metallic sodium, no point was ever secured which fell below the curve. This fact would seem to show conclusively that the alcohol which has been used was as nearly absolute dryness as it is possible to prepare. The delicacy of this indication of the amount of water present is shown by the fact that the points that have been recorded which lie off the curve are due to exposure of the solution to the moisture of the atmosphere for a slightly longer time than in the case of the other cells. When, in two instances, very small known amounts of water were added to a cell which had reached equilibrium and had been found to give a point falling on the established

of "hydronium ion," a complex between hydrogen ion and molecules of water. Whatever the cause, it is obvious that values of E° which are too high will be given when solutions containing even traces of water are used as cell electrolyte. Having once established a curve we are, therefore, able to determine by a very sensitive method the efficiency of different materials as drying agents for alcohol.

curve, the value of the electromotive force of the cell after it had again been allowed to come to equilibrium was changed to such an extent that the corresponding point fell entirely above the plot.

Several other points which were determined have not been recorded because of small uncertainties arising from what we have called "fluttering" of the electrode. This consisted in rapid fluctuations in the value of the electromotive force by as much as 0.2 or 0.3 mv. to either side of a mean value. This effect was considerably reduced when the hydrogen was shut off for 10 to 15 minutes before a reading was taken. The manner in which this fluttering occurred indicated that it was due to currents of fresh electrolyte being brought into contact with the hydrogen electrode through convection or, when the hydrogen was not shut off, by the rise of bubbles through the solution. This effect could be shown to be due to the hydrogen rather than to the calomel electrode by checking the 3 calomel cells, one against another. It was finally completely eliminated by preventing the cell electrolyte which came into contact with the hydrogen electrode from containing any calomel in solution. This could be effected by completely removing any solution which was introduced with the calomel and then exercising great care when fresh solutions were introduced to prevent stirring of the liquid below the hydrogen inlet. A plug of glass wool inserted between the calomel and the entering hydrogen served to prevent stirring by the bubbles of hydrogen.

Having determined the value of E° we may now calculate back using Equation 1 and obtain the value of γ , the activity coefficient for the hydrochloric acid, at each concentration. Such values have been recorded in Col. 6 of Table I and are represented by Curve III of Fig. 2. For purposes of comparison the values of Λ/Λ_0 , the degree of dissociation from conductivity, are given in Col. 5 of Table I.

Cell (b); Hg, HgCl, NaCl, Na(2-Phase Amalg.)¹⁵

The value of the electromotive force of this cell when the sodium chloride is at unit activity may be calculated from the value of the electromotive force of the same cell using sodium chloride at any actual concentration, provided we know the activity coefficient of sodium chloride in a solution of the concentration used. Our original intention was to employ the cell, Hg, HgCl, NaCl (alc. sat.), Na(2-phase amalg.), but it was found in the preliminary experiments that the calomel electrode was not reliable in neutral solutions of sodium chloride in alcohol. It follows from a consideration of the reaction occurring in this cell, assuming that the solid phases are the same, that the electromotive force will be independent of the solvent. We may, therefore, obtain the desired value from a measurement of this cell in water solution.

¹⁵ The several very important advantages to be gained by the use of a 2-phase amalgam have been pointed out in a recent article by Gerke, Ref. 4.

Electrode Vessels.—The electrode vessels which have previously been used in measurements of cells involving the very reactive amalgams of the alkali metals have of necessity been rather elaborate in order to facilitate the required manipulation and at the same time to protect the amalgam from the action of the atmosphere. The use of a 2-phase amalgam obviates the necessity of excluding air and thus makes possible the use of much simpler apparatus. The combination of the 2 vessels shown in Figs. 3 and 4 has proved very satisfactory.

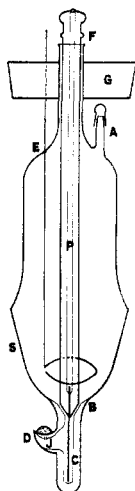


Fig. 3.

In Fig. 3 is shown the vessel used to contain the sodium amalgam. This vessel holds about 15 cc. of liquid which is introduced through the opening at A, which is then closed by a small glass cap to prevent vapor from the solution condensing on the surface of the amalgam. The plunger P made from heavy-walled capillary tubing is kept firmly placed in the ground-glass seat at B by the taut piece of rubber tubing wired on at F. On slightly lifting this plunger by means of the knob at the top it is unseated sufficiently to allow amalgam to run down and fill the small cup at D. This cup was made by blowing a ball on the side of the thick-walled capillary below B, heating this ball on top by means of a small pointed flame and drawing it in. The hole at J through which the amalgam passes was made with the point of a fine needle. Electrical contact is secured by means of the platinum wire C, sealed through the tip of the plunger, and the column of mercury which fills the capillary. The platinum wire is made to extend below the opening at J to prevent the possibility of losing contact through the formation of a small bubble of hydrogen in the capillary, due to the reaction of the amalgam with a film of the cell liquid which is almost sure to creep in when the dropper is in contact with the solution for a considerable time. A platinum wire was introduced through a very small hole at E for the purpose of stirring the amalgam to insure equilibrium with the solid phase, which rises to the surface, before each renewal of the surface of contact with the solution. The total amount of amalgam necessary to fill the capillary below B and the cup at D would form a globule not more than 3 or 4 mm. in diameter. The whole apparatus is suspended by means of the cork stopper G, in one arm of the "H" cell shown in Fig. 4.

The particular advantages of this vessel are its simplicity of construction, the ease and rapidity with which the surface of the amalgam in contact with the cell liquid may be renewed, the small amount of amalgam used in renewing this surface and the small quantity of amalgam which must be left in contact with the solution thus making concentration changes in the relatively large volume of solution, due to reaction with the amalgam, of only secondary importance. This was shown by the fact that even after renewing the amalgam surface in contact with the liquid a considerable number of times over a period of several days the electromotive force of the cell had changed by only a few tenths of a millivolt.

The cell in Fig. 4 is one arm of an ordinary H-type vessel and is shown in order to illustrate the method by which amalgam discharged from the dropper, on renewing the contact surface, was completely removed from the cell electrolyte. By slightly raising the plunger B, the valve at C is opened and the amalgam which has collected at A is allowed to run into the reservoir D. It was found that by making the opening

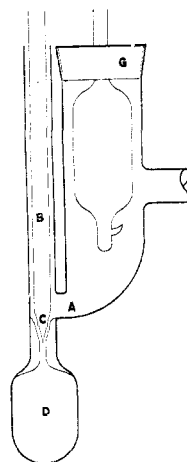


Fig. 4.

at C long and narrow, there was no tendency for the solution to enter the reservoir even when the plunger was completely removed.

Preparation of Materials.—The sodium chloride used was of the best U.S.P. variety which had been twice recrystallized by precipitation with hydrogen chloride. The sodium amalgam was prepared by the electrolysis of a saturated solution of pure sodium hydroxide using a cathode of mercury, which had been purified as previously described, the electrolysis being continued until considerable of the solid phase remained at 25°. The average of three analyses gave 0.641 weight per cent. of sodium in the liquid phase at 25°. The calomel was precipitated in slightly acid mercurous nitrate solution by the addition of dil. sodium chloride solution. After thorough washing, the calomel was stored in contact with mercury under a saturated solution of sodium chloride made slightly acid with hydrochloric acid. Before being introduced into a cell this calomel was repeatedly washed by decantation with portions of the solution to be employed as cell electrolyte.

Measurements and Calculations.—The values for the electromotive force of the 4 cells measured were, respectively, 2.1053, 2.1054, 2.1055 and 2.1055 volts, the average of which is 2.1054 volts,¹⁶ so that we may write: Hg, HgCl, NaCl(sat. in H₂O), Na(2-phase amalg.); $E = -2.1054$. But, as has already been pointed out the electromotive force of this cell is independent of the solvent used, so that we have: Hg, HgCl, NaCl (sat. in alcohol), Na(2-phase amalg.); $E = -2.1054$.

A variation of 30 fold in the values given in the literature for the solubility of sodium chloride in absolute ethyl alcohol at 25° has made a redetermination of this quantity necessary. Mr. Westwater of this Laboratory has found as the average of four closely agreeing measurements, made by precipitation as silver chloride, 0.0906 g. of sodium chloride per 100 g. of solution, or 0.0122 moles per liter.

Since the assumption that the activity coefficients of strong electrolytes of the same type in dilute solution in water are equal is substantially correct we may make the same assumption with regard to solutions in ethyl alcohol. Thus, taking the value of γ at 0.0122 *M* from Curve III of Fig. 2 as being 0.642 we may now calculate by means of Equation 1, the difference in electromotive force between the cells Hg, HgCl, NaCl (0.0122 *M*), Na(2-phase amalg.), and Hg, HgCl, Na⁺ + Cl⁻, Na(2-phase amalg.). This difference is found to be 0.2492 volt which must be added to the above value, thus giving as the final value:

$$(b) \text{ Hg, HgCl, Na}^+ + \text{Cl}^-, \text{ Na(2-phase amalg.)}; E^\circ = -1.8562.$$

Cell (c); Na(2-phase amalg.), NaOC₂H₅, H₂

Electrode Vessel.—The essential features of the vessel used in this investigation are

¹⁶ Since these measurements were completed, the publication of the data of Richards and Conant on the free energy of dilution of sodium amalgam, THIS JOURNAL, **44**, 601 (1922), has made it possible to calculate the value of this electromotive force from the measurement by Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919), of the cell: Hg, HgCl, NaCl (sat.), Na(0.1339% amalgam). The value thus obtained was 2.1055 volts which is seen to be in complete agreement with the value which we have obtained by direct measurement.

shown in Fig. 5. The apparatus consists of the ordinary type of hydrogen-electrode vessel, so modified as to include the previously described device for the removal of spent amalgam and so that the amalgam container may be introduced as near to the hydrogen electrode as possible. The shoulder shown at S in Fig. 3 was roughly ground into the seat at A in Fig. 5, the position of this side tube being so related to that of the hydrogen electrode that when the cell is filled with liquid to the customary level and the amalgam dropper seated, all bubbles of air are forced out. The joint was then sealed with mercury (at B) which also served the purpose of insuring better heat interchange between the bath and the amalgam. The surface of the hydrogen electrode was prepared as has previously been described.

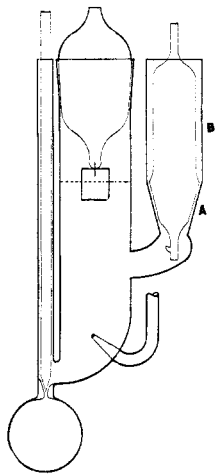


Fig. 5.

Preparation of Materials.—The sodium amalgam used here was the same as that used in the preceding cell. The sodium ethylate solution was at first prepared by the action of sodium amalgam, in contact with a strip of platinum to increase the speed of the reaction, on pure alcohol. This method was later replaced by the more rapid and at the same time more convenient method of allowing a known weight of metallic sodium to react with a known amount of alcohol. This solution must be used immediately after preparation or else kept under an atmosphere of an inert gas to prevent the rapid oxidation to aldehyde, which, while it does not completely interfere with the use of the hydrogen electrode, may give rise to uncertainties as great as 0.003 volt. To prevent any possible concentration change due to reaction, the cup D of the amalgam dropper was not filled with amalgam until the hydrogen electrode had been allowed sufficient time to reach equilibrium. The accepted readings were always

made within a few hours of the time of bringing the amalgam into contact with the solution. Except in the most dilute solutions this precaution was unnecessary.

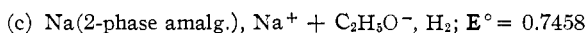
Results.—Several of the cells measured were rendered unreliable through exposure of the solution to the air thus forming appreciable quantities of aldehyde. These results have not been included in the following table.

TABLE II
ELECTROMOTIVE-FORCE MEASUREMENTS IN BASIC SOLUTION

Conc. NaOEt Eq. per liter	E calc. to 760 mm. H ₂	E°	E°	γ
0.1120	0.9135	0.8010	0.7466	0.347
0.0817	0.9220	0.7935	0.7444	0.386
0.0516	0.9395	0.7872	0.7458	0.447
0.04285	0.9459	0.7847	0.7458	0.469
0.01930	0.9767	0.7738	0.7457	0.579
0.00302	1.0543	0.7562	0.7470	0.837

The values appearing in Col. 3 above when plotted to the same scale as used in Fig. 2 fall on a curve which coincides entirely with Curve I of that figure, showing that the activity coefficient for sodium ethylate changes in the same way with the concentration as does that for hydrogen chloride. We might, of course, apply the same method here for determining the value of E° as was employed in the case of hydrochloric acid but since the con-

ductivity data seem to be far less reliable in this case, the assumption of the equality of the activity coefficients for sodium ethylate and hydrochloric acid at each concentration seems the more desirable. The constancy of the values of E° obtained in this way, and recorded in Col. 4 above, is sufficient justification for this assumption. Choosing the mean value of E° we have



Calculation of the Dissociation Constant

As has been pointed out, the sum of the reactions occurring in Cells a, b and c is the reaction $\text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_5\text{O}^- + \text{H}^+$. The value of the electromotive force for this reaction, also by addition, is -1.1320 volts. The dissociation constant for the reaction may, therefore, be calculated by means of the familiar relation,¹⁷ $\Delta F^\circ = -nEF = -RT \ln K$. The value of K so calculated is 7.28×10^{-20} as compared with 2.89×10^{-16} calculated in the preceding article from conductance measurements. The present value is certainly correct to better than 0.002 volt which would produce an error of not more than 10% in the value of K . The discrepancy between these two values may, therefore, be attributed partly to the assumptions involved in the interpretation of the conductivity measurements, but probably to a far greater extent to the assumption that the liquid whose conductance was measured was pure alcohol. When this final value of K is used to calculate, by the method of the preceding paper, the value of N_d , the mole fraction dissociated, the value obtained is 1.58×10^{-11} which when compared with 1.8×10^{-9} shows ethyl alcohol to be only $1/100$ as strongly ionized as is water.

Summary

The electromotive force of a series of galvanic cells in alcoholic solution has been measured for the purpose of determining the dissociation constant of the solvent. These cells were so chosen that the final result is entirely free from assumptions regarding liquid-junction potentials.

The experimental technique developed for handling very reactive amalgams and the design of electrode vessels of relatively low internal resistance, for use with dilute solutions, have been described.

A table of the activity coefficients for hydrochloric acid in ethyl alcohol is given covering a range of concentration up to 0.3 *N*.

The constant for dissociation of the ethyl alcohol into hydrogen and ethylate ions is calculated to be 7.28×10^{-20} ; the mole fraction dissociated is 1.6×10^{-11} .

In conclusion the writer wishes to express his sincere appreciation to Professor Joel H. Hildebrand, under whose direction the present investigation was carried out.

BERKELEY, CALIFORNIA

¹⁷ Lewis, THIS JOURNAL, 35, 1 (1913).