In the third experiment an aqueous solution of carbon dioxide in a sealed quartz tube was exposed for 36 hours.

No formaldehyde nor reducing sugar was produced in any of these experiments.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS OF ETHYL ALCOHOL

BY HERBERT S. HARNED AND MAURICE H. FLEYSHER

RECEIVED AUGUST 5, 1924 PUBLISHED JANUARY 8, 1925

In the present investigation, an extended series of measurements has been made of the cells

$$H_2 \mid HCl(M) \mid AgCl \mid Ag \qquad (I)$$

in which the solvent was either alcohol or an alcohol water mixture. Cells of the types, containing hydrochloric acid in ethyl alcohol,

$$H_2 \mid HCl(c_1) \mid HCl(c_2) \mid H_2 \qquad (II)$$

and

$$Ag \mid AgCl \mid HCl(c_1) \mid HCl(c_2) \mid AgCl \mid Ag \qquad (III)$$

as well as the cells

$$Hg \mid HgCl \mid HCl(c_1) \mid HCl(c_2) \mid AgCl \mid Ag \qquad (IV)$$

have been measured by Lapworth and Partington[1] and by Hardman and Lapworth.[2] Cells II and III combined correspond to Cell I. Direct measurements of Cell I should afford a more accurate measurement of the activity coefficients than measurements of Cells II and III owing to the difficulties inherent in reproducing the liquid-junction potentials. More recently, Danner[3] has measured the electromotive forces of the cells, $H_2 \mid HCl(c) \mid HgCl \mid Hg$, throughout the concentration range from 0.00886 to 0.302 N acid. In this investigation, measurements of the cells, $H_2 \mid HCl(m) \mid AgCl \mid Ag$, throughout a greater concentration range have been made both in alcohol and in alcoholic solutions containing 50 mole per cent. of water. Measurements of the same cell at 0.01 and 0.1 M acid concentrations in a solvent of variable composition have also been made.

Materials

Alcohol.—The method employed for purifying the alcohol was chosen after consulting the large number of methods described in the literature.[4]

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[1] Lapworth and Partington, *J. Chem. Soc.*, **99**, 1417 (1911).

[2] Hardman and Lapworth, *ibid.*, **99**, 2248 (1911); **101**, 2250 (1912).

[3] Danner, THIS JOURNAL, **44**, 2832 (1922).

[4] Some of the more important references are as follows. (1) *Sulfuric acid distillation:* (a) Bishop, Kittredge and Hildebrand, THIS JOURNAL, **44**, 135 (1922). (b)

The procedure finally adopted was as follows.

Commercial 95% alcohol was distilled from concd. sulfuric acid (6 cc. per liter) to remove amines, basic substances and some of the water. Only the middle portion was retained. This distillation as well as the subsequent ones was carried out on a "slow" water-bath and the receiver was protected from atmospheric moisture by calcium chloride tubes. The cork stoppers were protected from the action of alcohol by tin foil coverings.

The distillate was then redistilled from alkaline silver oxide (prepared from 4 g. of silver nitrate crystals and 1.5 g. of solid sodium hydroxide per liter) to remove oxidizable materials and any acid substances, and only the middle portion was retained.

The last distillate was placed in flasks of 3 liters capacity containing recently burned, freshly broken and hard pieces of unslaked lime (2 kg. of lime for each 2.25–2.5 liters of alcohol), kept sealed for at least two weeks and thoroughly shaken twice a day. When alcohol was required, a flask of alcohol and lime was distilled from a "slow" water-bath through a fractionating column. The first fraction was rejected and no attempt was made to force the last amounts of alcohol out of the lime. When the distillation had become very slow it was stopped. This last step constituting the refluxing, fractionation and distillation of a flask of alcohol (distillate collected: 1.5 liters) usually occupied from six to eight hours. The pure alcohol was preserved in amber-colored glass bottles provided with tightly fitting, well-ground glass stoppers which were protected from dust by closely fitting, inverted beakers.

The slow rate of dehydration of alcohol by lime is probably caused by the formation of a layer of calcium hydroxide on the surface. Vigorous shaking at regular intervals is essential. To test the effectiveness of the drying process, a density determination was made of a sample which had stood over lime for one week, a time much shorter than that employed for this purpose in the present investigation. Check determinations gave $d_{4°}^{20°} = 0.78951$, which corresponds to 99.95% alcohol. By longer dehydration with lime Goldschmidt[4j] obtained 99.98% and 99.99% alcohol.

Kailan[4i] has made a study of the absorption of water by alcohol. A flask containing material of $d_{4°}^{20°} = 0.7856$, or 99.88%, was placed in a water thermostat kept at 25° and kept there for 20 days. During that time the stopper was opened six to eight times and left open each time for one minute. At the end of this period of time the density of the alcohol was 0.7858, corresponding to 99.80%. A second experiment consisted in exposing alcohol of 99.97% to the air on a watch crystal for $4^1/_2$ hours at 17°. At the end of that time the alcohol was 99.64% as measured by density determinations. The latter experiment was carried out in a room communicating with one containing a large water thermostat.

One of the sources of error in the electromotive-force measurements to be described was caused by exposing the solutions to the air for from two to four minutes during the processes of weighing and filling the cells. Some atmospheric moisture may have been absorbed during these processes, but certainly not enough to lower the alcoholic content to less than 99.90%.

Preparation of Solutions

Aqueous hydrochloric acid solutions were made from an approximately

Danner and Hildebrand, *ibid.*, **44,** 2824 (1922). (2) *Silver nitrate:* (c) Wilderman, *Z. physik. Chem.*, **14,** 232 (1894). (d) Robertson and Acree, *J. Phys. Chem.*, **19,** 381 (1915). (3) *Silver oxide alkaline with potassium hydroxide:* (e) Winkler, *Ber.*, **38,** 3612 (1905). (4) *Lime:* (f) Mendeleef, *Ann. Physik*, **138,** 239 (1869). (g) Andrews, THIS JOURNAL, **30,** 353 (1908). (h) Kailan, *Monatsh.*, **28,** 927 (1907); (i) **27,** 546 (1906). (j) Goldschmidt, *Z. physik. Chem.*, **89,** 129 (1914).

4 *M* solution of redistilled acid which had been standardized gravimetrically.

Alcoholic hydrochloric acid solutions were prepared by passing pure, thoroughly dried hydrogen chloride into the purified alcohol which was cooled in an ice-bath. These solutions were standardized by gravimetric analysis and their acid content just after preparation was determined to within ± 0.05%.

All solutions were prepared on the basis of a fraction or a multiple of a mole of hydrogen chloride plus 1000 g. of solvent. The solvents used were alcohol and alcohol-water containing 50 mole per cent. of each. The concentration of acid was varied in each of these. Two series were measured in which the acid content was kept constant while the composition of the solvent, alcohol-water, was changed. In preparing the solutions, the greater difficulty was experienced with those containing pure alcohol as the solvent. When hydrogen chloride is dissolved in alcohol, the resulting solution is not a stable one, but there is a slow formation of ethyl chloride and water. Kailan[5] has studied this reaction velocity at 25°. For a given solution the change is very uniform with the time. In general, the more concentrated solutions have a greater velocity than the dilute. The presence of water in the alcohol retards the velocity of this reaction. An alcoholic solution of hydrogen chloride containing about 3% of acid changes to the extent of about 4% per month. This agrees fairly well with the change observed during the present investigation in an alcoholic solution containing 4.3% of hydrogen chloride which changed 3.2% in acid content over a period of 25 days.

It is therefore evident that a standard solution of hydrochloric acid in alcohol could not be kept indefinitely. The dilute solutions measured in this investigation were made up by diluting a standard solution, containing about 3.5%, within two days of its preparation. No alcoholic solution was kept longer than a week. The concentrated solutions were made by diluting a stronger solution in as short a time as possible. All these solutions were measured within 48 hours after preparation. Samples of these solutions were weighed immediately after preparation and precipitated by silver nitrate.

The solutions of 50 mole per cent. of water and alcohol were prepared by weighing aqueous hydrochloric acid and then adding calculated amounts of alcohol and water. The strongest solutions in this class were prepared by weighing aqueous and dilute alcoholic solutions and then adding calculated amounts of water and alcohol.

The solutions, in which the acid concentration is kept constant while that of the solvent is varied, were made by weighing aqueous acid and then adding the requisite amounts of alcohol and water.

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[5] Kailan, *Monatsh.*, **28**, 559 (1907).

A new solution was prepared for each measurement.

Apparatus and Procedure

The cells consisted of tubes in the form of an H, one limb of which contained the silver-silver chloride electrode and the other limb the hydrogen electrode. The silver-silver chloride electrodes were prepared as described by Noyes and Ellis.[6] The hydrogen electrode was a platinized sheet-platinum foil. Since the vapor pressure of alcohol is considerable, the pure dry hydrogen was passed through a long and efficient saturating chain containing the same solution as the cell so as to prevent any evaporation and change in concentration.

When pure alcoholic solutions were used, the cell and saturator were thoroughly dried before the solutions were introduced. In the cases where aqueous alcoholic solutions were employed, the cell and saturator were carefully rinsed a number of times with these solutions.

The cell attained its equilibrium value in about five hours, and readings were taken every half hour thereafter. A mean of at least six readings constituted a measurement. In most cases, the cell remained constant to within ± 0.1 millivolt for many hours. Greater difficulty was experienced and less easy reproducibility was obtained with the solutions containing the greater percentages of alcohol. The electromotive forces were corrected to one atmosphere hydrogen pressure by the customary thermodynamic equation. The total vapor pressures of the alcohol-water mixtures were taken from a plot of the data of Konovalov[7] and the values used were 23.5, 45.0, 53.3, 57.6, 58.6, 59.4, 59.8 and 60.2 mm. of mercury at 0, 25, 50, 75, 85, 90, 95 and 100 mole percentages of alcohol, respectively.

Measurements of the Cells, H_2 | HCl (M) | AgCl | Ag, at 25°

In Table I are given the electromotive forces at one atmosphere of hydrogen pressure of the cells of variable solvent composition containing 0.1 M and 0.01 M acid, respectively. $E_{0\cdot1}$ and $E_{0\cdot01}$ refer to concentrations of the acid denoted by subscripts.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS OF CONSTANT ACID CONCENTRATION AND VARIABLE ALCOHOL-WATER COMPOSITION

Mole % of alc.	100	95	90	85	75	50	25	0
$E_{0\cdot1}$	(0.1227)	0.1915	0.2176	0.2352	0.2620	0.3037	0.3279	0.3521[8]
$E_{0\cdot01}$	.2109	....	....	....	.3556	.4028	.4346	.4639[9]

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[6] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

[7] Konovalov, *Wied. Ann.*, **14**, 34 (1881).

[8] Noyes and Ellis [Ref. 6, p. 2537] obtained 0.3522.

[9] Value computed from $E_{0\cdot1} = 0.3521$ and activity coefficients of the acid in aqueous solution taken from Lewis and Randall's calculation [(a) "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 336].

These results, particularly the series containing 0.1 *M* acid, show that as the alcohol content increases, the rate of decrease of the electromotive force with the composition increases. Thus, $E_{0.1}$ changes 0.0261 and 0.0711 between 90–95 mole per cent. and 95–100 mole per cent. of alcohol, respectively. Consequently, we would expect a difference of approximately 0.003 volt between 99.9 and 100 mole per cent. In the dilute solutions, where no appreciable reaction takes place between the alcohol and acid, it is thought that the alcohol content of the solutions employed was greater than 99.9%, and therefore that these electromotive forces are not more than 0.002 volt high in the so-called 100% alcohol solutions. This error is considerable when the activity coefficient of the acid in alcohol relative to its activity in water is required. When, however, the activity coefficient of the acid in alcohol relative to an activity coefficient of unity at infinite dilution is desired, the above-mentioned error influences the result very little.

In Table II are given the electromotive forces of the cells of variable acid composition in the alcohol and the 50 mole per cent. alcohol-water mixtures at 25°. The results with the alcohol cells corresponding to A, B, etc., in the first column were each obtained from solutions prepared by diluting the most concentrated solutions of the series denoted. Each series was made from a freshly prepared solution and all the results obtained are included. The results with the alcohol-water cells are contained in the fifth column. The series denotation in the first column refers to alcohol cells only. Concentrations are expressed in moles per 1000 g. of solvent.

Table II

Electromotive Forces of the Cells of Variable Acid Concentration

	Solvent Alcohol		Solvent 50 mole % alcohol-water	
Series	*m*	*E*	*m*	*E*
E	0.001	0.3053	(0.001)	(0.5035)
E	.002	.2770	.002	.4765
E	.005	.2392	.005	.4346
E	.01	.2109	.010	.4028
A	.02	.1830	.020	.3730
C	.0249	.1746	.050	.3333
C	.0423	.1548	.1	.3037
A	.05	.1484	.2	.2733
..	.1	(.1227)[a]	.5	.2306
C	.1242	.1153	1.	.1931
C	.1782	.1011	1.5	.1657
A	.2	.0977	2.0	.1441
C	.4437	.0707	2.5	.1234
B	1.	.0398	..	...
C	1.0501	.0398	..	...
D	1.4807	.0252	..	...
D	3.6215	− .0179	..	...

[a] Interpolated from a log *m*-*E* plot.

A large scale plot of log *m* against these electromotive forces was made and a smooth curve was drawn through the points. From an approximate consideration of these plots, it was inferred that the mean variation from the plot for the 50 mole per cent. series was less than ± 0.4 mv. At concentrations up to 0.2 *M* of the alcohol series the mean variation is less than ± 0.5 mv., but for solutions higher than this the consistency is not so great. At the lower concentrations we may compare the results with those obtained by Danner[3] on the cells with a calomel electrode. The differences in electromotive forces of the latter cells at two concentrations should equal a similar difference of the silver-silver chloride cells. Danner's concentrations were converted to molal, and his results as well as those in Table II are plotted on the same scale in Fig. 1; 0.0350 volt has been subtracted from Danner's values to account for the difference in potential between the calomel and silver-silver chloride electrodes. Up to 0.1 *M* concentration there is a very close agreement, but above this

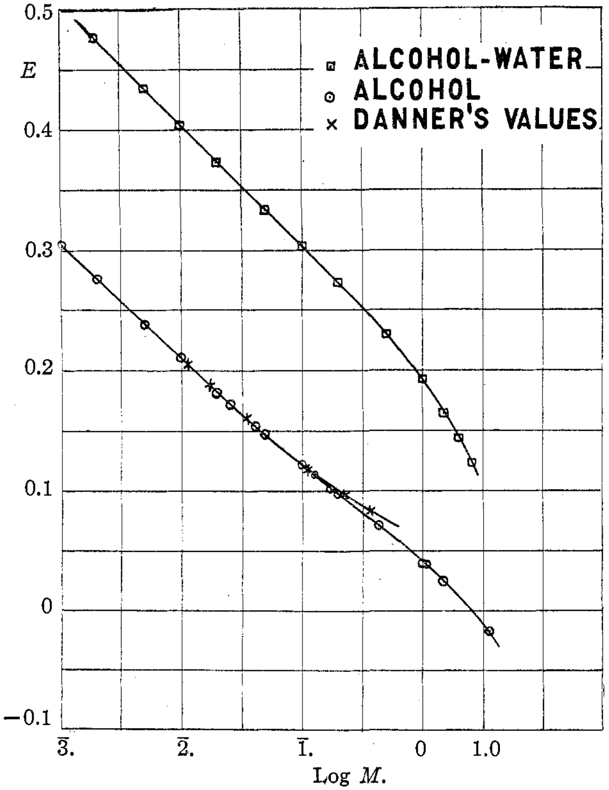

Fig. 1.—Electromotive forces of cells against logarithms of concentrations.

concentration Danner's results lie somewhat higher. Since the presence of water in the alcohol, caused by reaction of the acid and alcohol, is responsible for high values of the electromotive forces and is the most apparent source of error, it would seem that the results of Danner above 0.1 M are somewhat high.

Calculation of the Activity Coefficients in Solutions of Solvents of Constant Composition

From the differences of electromotive forces between two concentrations in Table II, the activity coefficient ratio may be computed by the equation

$$\Delta E = 0.1183 \log \frac{\gamma_2 M_2}{\gamma_1 M_1} \tag{1}$$

where γ_1 and γ_2 are the activity coefficients in the solutions at the concentrations m_1 and m_2, respectively. An effort was made to obtain sufficiently accurate data in very dilute solutions to allow the activity coefficient to be obtained by the extrapolation method employed by Linhart[10] and by Lewis and Randall.[11] The present attempt failed for two reasons. First, the activity coefficient in the alcoholic solutions is less than in aqueous solutions at a given concentration. Consequently, for the purposes of extrapolation in these solutions it is necessary to obtain accurate data in more dilute solutions than was the case with the pure aqueous solutions. Second, the internal resistance of the cells containing very dilute acid decreased the sensitivity of the galvanometer circuit employed to such an extent that it was impossible to obtain sufficiently accurate data.

In view of the fact that the data could not be extrapolated to infinite dilution, it was necessary to choose a value for γ at some concentration for both series. In alcoholic solutions, Danner[3] computed his activity coefficients upon the assumption that at 0.0113 M concentration the activity coefficient equals 0.686 based on a conductance ratio, which according to Bray's calculation of Goldschmidt's data[4j] equals 0.695. This value is thought to be too high because in all cases known, when in dilute solution, the activity coefficient differs from unity by any considerable amount, it is considerably less than the conductance ratio. In the case of uni-univalent electrolytes in dilute solutions, the conductance ratio very nearly equals the van't Hoff coefficient,[12] γ_0, or $\frac{i-1}{\nu-1}$ where "i" is van't Hoff's "i" and ν is the number of ions produced by the dissociation of the electrolyte. If the log γ is proportional to the square root of the concentration, then according to thermodynamic reasoning, it can be shown

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[10] Linhart, This Journal, **41,** 1175 (1919).

[11] Ref. 9 a, p. 333.

[12] Noyes and Falk, This Journal, **34,** 485 (1912).

that γ differs from unity by two-thirds as much as the activity coefficients.[13] In view of the lack of further knowledge of γ, we have assumed that γ_0 equals the conductance ratio, or 0.695 at 0.0113 M concentration. Since γ_0 differs from unity by two-thirds as much as γ, 0.543 is obtained for γ at 0.0113 M concentration. The electromotive force at this concentration read from the plot equaled 0.2065 volt, whence we find the activity coefficient at 0.1 M to be 0.3135. All values of the activity coefficients in the alcohol series based on this approximate value, are given in the third column of Table IV. The activity ratios refered to the value at 0.1 M acid are also given in the second column of Table IV.

It is still necessary to obtain a value for the activity coefficient of the acid in the 50 mole per cent. solvent at some concentration or concentrations, in order to calculate this quantity at all other concentrations by means of Equation 1. To accomplish this approximately, use has been made of the relation between the dielectric constant of the medium and the activity coefficient which follows from Debye and Hückel's theory.[14] To state the matter briefly, it is found that in dilute solutions of a substance at a constant concentration in a solvent of variable composition, log γ is inversely proportional to the dielectric constant of the medium. Therefore, in the present case

$$\log \gamma_1/\log \gamma_2 = D_2/D_1 \qquad (2)$$

where γ_1 and γ_2 are the activity coefficients of hydrochloric acid at a given concentration in water and alcohol, respectively and D_1 and D_2 are the dielectric constants of water and alcohol. The dielectric constants for water and alcohol were taken to be 81 and 26, respectively. By graphical computation of the values of Nernst,[15] the value for the dielectric constant of alcohol-water (50 mole per cent. alcohol) is 37. Let the activity coefficient in 50 mole per cent. alcohol be designated by γ_3 and the dielectric constant by D_3. By using the scale of the abscissas as a measure of $1/D$ and that of the ordinates as that of log γ, we obtain two points from the values γ_1, D_1 and γ_2, D_2 which we connect by a straight line. The point in this line corresponding to the abscissa, $1/D_3$, equals the log γ_3.

Using for the values of γ_1 those given by Lewis and Randall[9a] and for γ_2 the values given in Table IV we obtain values for γ_3 which are 0.858, 0.749, 0.700, 0.634 and 0.543 at the molal acid concentrations 0.002, 0.005, 0.01, 0.02 and 0.05, respectively. In Table III, electromotive-force differences between two concentrations calculated from these values have been compared with the observed electromotive-force differences in Table II. Line 1 contains the concentrations, Line 2 the electromotive-

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[13] Ref. 9 a, p. 346.

[14] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[15] Nernst, *Z. physik. Chem.*, **14**, 1622 (1894).

force differences computed from these values of γ_3 by Equation 1 and Line 3, the observed electromotive-force differences computed from the fifth column of Table II.

TABLE III

CALCULATED AND OBSERVED ELECTROMOTIVE FORCES

Concn. range	0.002–0.005	0.005–0.01	0.01–0.02	0.02–0.05
E (Calcd.)	.0401	.0321	.0305	.0391
E (Obs.)	.0419	.0318	.0298	.0397

There is a fair agreement between the observed and calculated values. For these 50 mole per cent. mixtures of alcohol and water, therefore, the value of γ at 0.01 M is taken to be 0.700 and all other values of γ are referred to this one. Table IV contains the values of γ and also the activity coefficient ratios referred to 0.1 M. Concentrations are given in moles per 1000 g. of solvent.

TABLE IV

THE ACTIVITY COEFFICIENT RATIOS AND ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ALCOHOL AND 50 MOLE PER CENT. MIXTURES OF ALCOHOL AND WATER AT 25°

Solvent: Alcohol			Solvent 50 mole per cent. alcohol-water mixtures		
m	$\gamma/\gamma_{0.1}$	γ	m	$\gamma/\gamma_{0.1}$	γ
0.001	2.864	0.898	(0.001)	(2.047)	(0.986)
.002	2.483	.778	.002	1.732	.834
.005	2.070	.649	.005	1.565	.745
.01	1.797	.563	.01	1.453	.700
.02	1.546	.485	.02	1.297	.625
.0249	1.462	.458	.05	1.125	.542
.0423	1.266	.397	.1	1.	.482
.05	1.212	.380	.2	0.903	.435
.1	1.	.3135	.5	.829	.399
.1242	0.929	.291	1.0	.861	.415
.1782	.854	.268	1.5	.978	.471
.2	.813	.255	2.0	1.118	.539
.4437	.620	.194	2.5	1.337	.644
1.	.502	.157	..	..	..
1.050	.478	.150	..	..	..
1.481	.452	.142	..	..	..
3.621	.426	.134	..	..	..

In Fig. 2, are plotted these activity coefficients as well as those of the acid in pure aqueous solutions against the molal concentrations. It is noticeable that this quantity passes through a minimum at about 0.5 M in the case of the 50 mole per cent. solutions but that no such minimum is observable when only alcohol is employed as solvent. According to recent theories of this subject it is probable that the presence of such a minimum is a function of the increased size (apparent diameter) of an ion brought about by solvation. It appears, therefore, that the hydrogen ion and possibly the chloride ion are more highly solvated in the aqueous solutions.

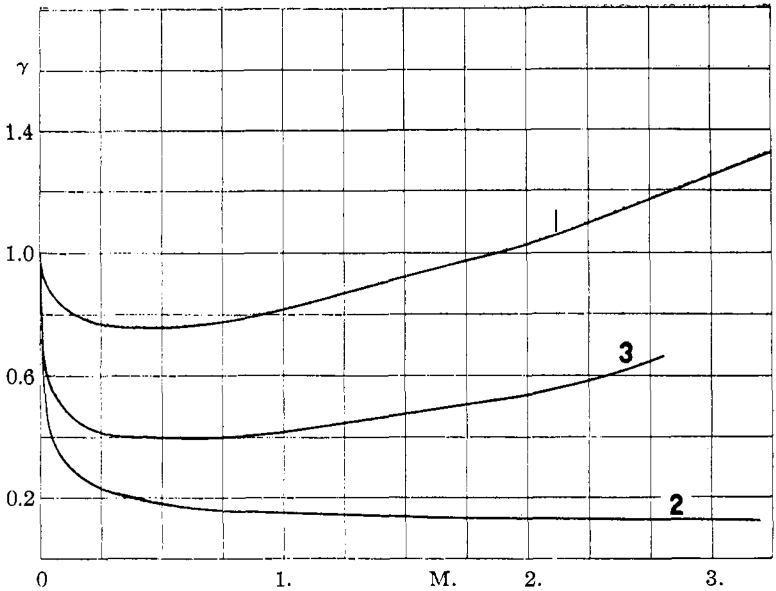

Fig. 2.—Activity coefficient of hydrochloric acid. 1. Aqueous solution. 2. Alcoholic solution. 3. 50 molal per cent. alcohol-water solution.

The Relative Activity Coefficient of Hydrochloric Acid in Solvents of Variable Composition

In Table V are given values of the activity coefficient ratios of 0.1 *M* and 0.01 *M* hydrochloric acid in mixtures of alcohol and water of various composition, relative to the value in pure water, computed by Equation 1 from the electromotive-force data in Table I.

Table V

Activity Coefficients of Hydrochloric Acid in Solvents of Variable Composition at 25°

Mole % of alc.	100	95	90	85	75	50	25	0
0.1 HCl, $\gamma_{\text{alc.}}/\gamma_{\text{water}}$	86.9	22.8	13.7	9.73	5.78	2.57	1.60	1.00
0.01 HCl $\gamma_{\text{alc.}}/\gamma_{\text{water}}$	127.3	..	..	..	8.23	3.29	1.77	1.00

The activity coefficient and activity of the acid are about one hundred times greater in alcoholic than in aqueous solutions.

Summary

1. Electromotive forces at 25° of the cells, H_2 | HCl (*M*) | AgCl | Ag, in alcohol and alcohol-water mixtures have been measured.

2. The relative activity coefficients of the acid in these solutions have

een computed, and the absolute activity coefficients approximately estiıated.

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[Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania]

HE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN SOLUTIONS OF ETHYL ALCOHOL

By Herbert S. Harned and Maurice H. Fleysher

Received August 5, 1924 Published January 8, 1925

In the preceding contribution on the activity coefficient of hydrochloric cid in solutions of ethyl alcohol[1] measurements of cells are given from hich it is possible to compute the electromotive forces of the cells, Ag | gCl | HCl (m_2) | H_2 | HCl (m_1) | AgCl | Ag, which are without liquid nctions. From these measurements and those of the cells, Ag | AgCl | ICl (m_2) | HCl (m_1) | AgCl | Ag, with liquid junctions, it is possible to ompute by an exact thermodynamic method the transference numbers of he ions of the acid. The present investigation contains the results of easurements of these cells with liquid junctions in alcohol and 50 mole er cent. alcohol-water mixtures at 25° and the calculation of the transerence numbers.

The preparation of materials and the methods employed in making up he solutions have been carefully described in the preceding article.

The cell consisted of two parts, one containing a 1mm. capillary and the ther a cup into which the capillary could be fitted and held in place by eans of a rubber stopper. The part containing the capillary always conained the same solution (0.01 *M* hydrochloric acid) which was compared ith solutions of different concentrations contained in the other half of he cell. In making a measurement, each half of the cell was filled with ts solution and the silver electrodes, washed six times with the proper olution, were inserted in the electrode compartments. Before being conected, each part of the cell was allowed to remain at room temperature, bout 25°, for one hour, so that equilibrium between the electrode and soluion was obtained. The connections were then made, a liquid junction was stablished by mixing the solutions from each part in the cup, and the cell laced in the thermostat. The stopcocks leading to the electrode chambers vere kept closed for half to three-quarters of an hour until the cells atained the temperature of the bath. After opening the cocks, readings f the electromotive forces were taken every quarter to half an hour until t least six were obtained, a mean of which constituted a measurement of he cell. Both solutions were renewed for every measurement.

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[1] This Journal, **47,** 82 (1925).