chlorate. This salt bridge presented a very small cross section (0.03 sq. cm.) to the solution in the cell, so that diffusion of chloride into it during a five-minute run was negligible. It was short enough so that the resistance drop was not serious. The electrode for this cell was a chloridized silver wire wound around a 4-mm. glass rod, and it provided sufficient stirring for the small cell without a propeller. A small Anschütz thermometer was used to read the temperature inside the microcell. Four cc. of 0.150 M sodium perchlorate was placed in it. The microcell was clamped so that it was three-quarters immersed in one liter of solution in the titration cell. The latter cell consisted of a $1^1/_2$-liter beaker hung on the vertically sliding assembly with a large ring. Its electrode was wound on a stirrer with a large glass propeller. At zero time, with the solutions at 23.7°, 0.20 cc. of acetone stock solution was added to the microcell from a graduated 1-cc. pipet. Simultaneously 50 cc. of pure acetone was poured into the titration cell from a graduate. The solution in the titration cell was "titrated" with a 25-cc. buret.

For each individual run ten times the half life (five minutes) was used as an infinite time point. The fact that only the solution in the titration cell is diluted 2% by the titration does not introduce any error, since the final titer is taken as representing 100% reaction and the amount by which the titration cell is diluted at any time is proportional to the percentage reaction.

Summary

Concentration cells have been adapted to permit a simple and accurate null-point method for the measurement of the rate of a chemical reaction. The method can be adapted to follow kinetically any ion or substance for which an electrode sensitive to changes in concentration is known, and should be useful in studying most oxidation, reduction, halogenation, hydrolysis

and displacement reactions. The technique offers special advantages in the study of very rapid reactions, and can be applied to micro quantities or very dilute solutions for which ordinary potentiometric methods fail.

In the present paper the method has been applied to a study of the rate of production of both chloride and hydrogen ions in the hydrolysis of 0.001 M t-butyl chloride in 95% water–5% acetone. The electrode reactions selected were

$$Ag + Cl^- \overset{Ag}{\rightleftharpoons} AgCl + e$$

and

$$Quinone + 2H^+ \overset{Pt}{\rightleftharpoons} Hydroquinone - 2e$$
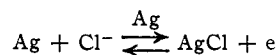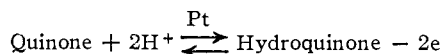
At 25° in 95% water–5% acetone t-butyl chloride liberates both chloride and hydrogen ions by a first order reaction, the half life being 27 ± seconds. Within experimental error the rate is unaffected by pH (between 3 and 12), by ionic strength (between 0.000 and 0.144 M) or by sodium chloride concentrations (between 0.000 and 0.144 M). The total liberation of hydrogen ion is unaffected by the presence of 0.48 M sodium thiosulfate. Evidently the carbonium ion formed does not accumulate to a measurable extent in solution but instead reacts immediately and indiscriminately with the most available molecule, in this case, water.

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Standard Potentials of Hydrogen–Silver–Silver Chloride Cells in Ethylene Glycol Solutions at 25°

BY SAMUEL B. KNIGHT, JOSEPH F. MASI AND DOROTHY ROESEL

In connection with other work being carried on in the Laboratory, it became necessary to determine the standard potentials of the cells

H$_2$ | HCl (m), Ethylene Glycol (x), H$_2$O (y) | AgCl–Ag

at 25° in solutions containing 10, 20, 40 and 60% ethylene glycol by weight. The activity coefficients of hydrochloric acid have been determined in these glycol–water solutions at acid concentrations ranging from 0 to 1 m. The dielectric constants of the glycol–water solutions are high enough so that hydrochloric acid may be considered completely ionized.

A number of investigators have made electromotive force measurements and activity coefficient determinations on cells of the above type using hydroxyorganic solvents other than ethylene glycol. Harned and Thomas[1] have investigated certain methanol–water mixtures, while ethanol–water solutions have been studied by

Harned and Fleysher[2] and Harned and Calmon.[3] The latter have also investigated certain isopropanol–water solutions. Lucasse[4] has studied the cell in glycerol–water mixtures, and Scatchard[5] in sucrose solution. The activity coefficients of hydrochloric acid in all of these mixtures seem to conform to a pattern similar to that found in aqueous solutions, and they may be calculated from 0 to 1 m by means of the Debye–Hückel expression with a linear term.

Experimental

Commercial ethylene glycol was purified by fractionation at 5 mm. pressure in a slow stream of purified nitrogen. The density of the product agreed with that listed by Taylor and Rinkenback[6] for pure ethylene glycol. Stock solutions of hydrochloric acid were made by weight from

(1) H. S. Harned and H. C. Thomas, THIS JOURNAL, **57**, 1666 (1935).

(2) H. S. Harned and M. H. Fleysher, ibid., **47**, 82 (1925).

(3) H. S. Harned and C. Calmon, ibid., **60**, 334 (1938).

(4) W. W. Lucasse, Z. physik. Chem., **121**, 254 (1926).

(5) G. Scatchard, THIS JOURNAL, **48**, 2026 (1926).

(6) C. A. Taylor and W. H. Rinkenback, Ind. Eng. Chem., **18**, 676 (1926).

constant boiling acid, and the molarity was checked by analysing for chlorides gravimetrically. All solutions for electromotive force measurements were made by weight from the stock hydrochloric acid, purified glycol and distilled water having a specific conductance of the order of 1×10^{-7} mhos. The ethylene glycol content of the solutions is correct to within $\pm 0.05\%$.

Density measurements were made on all solutions at $25°$ in pycnometers of about 25-cc. capacity. Vapor pressures of the 10, 20, 40 and 60% glycol-water solutions are from Trimble and Potts,[7] and dielectric constants are from Akerlof.[8]

The cell vessels were a slight modification of those employed by Harned and Morrison.[9] Silver-silver chloride electrodes were prepared by caking silver oxide paste on platinum spirals and heating in a furnace at $450°$ for half an hour according to the directions of Harned,[10] and then electrolyzing in $0.5 N$ hydrochloric acid using a 3-volt d. c. source and 12 milliamp. for two hours according to Owen.[11] Hydrogen electrodes were prepared in the usual manner.

A type K-1 potentiometer and high sensitivity galvanometer were employed for electromotive force measurements. Electromotive force measurements were made on each solution in quadruplet, the readings being taken at half-hour intervals beginning about an hour after starting the hydrogen. The final reading on each cell was corrected to that at 1 atm. of hydrogen. Cell reproducibility was about ± 0.05 mv.

Calculations and Results

The standard potentials were first determined by use of the function E', defined by the equation

$$E' = E + 0.1183 \log m - \frac{0.1183 A\sqrt{c}}{1 + aB\sqrt{c}} -$$
$$0.1183 \log (1 + 0.002 m M_{xy}) = E_m^0 + f(m) \quad (1)$$

where E is the observed electromotive force, m is the molality, A and B are Debye–Hückel constants, a is the mean distance of approach in ångströms, c is the concentration in moles per liter, and M_{xy} is the mean molecular weight of the

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS AT 25°

(1) 10% Glycol by weight, v.p. = 22.8 mm.

m	c	d	E
0.002289	0.002309	1.0095	0.53080
.003470	.003500	1.0095	.51041
.003646	.003670	1.0095	.50802
.004368	.004400	1.0096	.49923
.006208	.006260	1.0096	.48204
.007845	.007920	1.0096	.47048
.008532	.008606	1.0096	.46625
.01005	.01013	1.0096	.45820
.01050	.01059	1.0096	.45617
.01385	.01396	1.0096	.44211
.01652	.01666	1.0097	.43346
.11805	.11884	1.0110	.33856
.3347	.3355	1.0146	.28713
.4924	.4919	1.0169	.26713
.7171	.7137	1.0213	.24687
.9348	.9263	1.0247	.23147
1.2827	1.2626	1.0304	.21157

(2) 20% Glycol by weight, v.p. = 21.7

m	c	d	E
0.001594	0.001631	1.0230	0.54306
.003779	.003865	1.0230	.50012
.006432	.006579	1.0231	.47409
.008572	.008706	1.0231	.46052
.01060	.01084	1.0231	.44992
.01364	.01394	1.0231	.43755
.01565	.01601	1.0232	.43078
.02156	.02204	1.0232	.41561
.02497	.02553	1.0233	.40844
.03946	.04037	1.0237	.38596
.05821	.05949	1.0240	.36774
.08354	.08534	1.0246	.35008
.10237	.1045	1.0247	.34022
.1412	.1441	1.0254	.32492
.4211	.4227	1.0300	.27072
.5698	.5766	1.0331	.25431
.7261	.7322	1.0351	.24093
1.1345	1.1346	1.0415	.21431

m	c	d	E

(3) 40% Glycol by weight, v.p. = 18.9 mm.

m	c	d	E
0.002815	0.002954	1.0494	0.50329
.006563	.006889	1.0494	.46107
.009808	.01029	1.0494	.44152
.01140	.01196	1.0496	.43424
.01247	.01308	1.0498	.42970
.01647	.01729	1.0500	.41628
.01714	.01798	1.0500	.41448
.01927	.02021	1.0500	.40905
.02193	.02301	1.0501	.40256
.02246	.02356	1.0501	.40149
.02387	.02503	1.0501	.39842
.06456	.06767	1.0508	.35100
.16441	.17405	1.0523	.30590
.3193	.3329	1.0547	.27411
.5329	.5531	1.0581	.24723
.6743	.6978	1.0602	.23437
.8580	.8844	1.0629	.22039

(4) 60% Glycol by weight, v.p. = 15.1 mm.

m	c	d	E
0.002802	0.003013	1.0741	0.48722
.003349	.003597	1.0741	.47839
.003946	.004238	1.0741	.47033
.004387	.004712	1.0741	.46514
.006468	.006947	1.0741	.44624
.007246	.007780	1.0742	.44071
.009426	.01012	1.0742	.42800
.01070	.01148	1.0742	.42186
.01599	.01716	1.0743	.40275
.01991	.02137	1.0743	.39213
.10592	.11353	1.0760	.31334
.2098	.2243	1.0776	.28049
.2646	.2826	1.0785	.26896
.2797	.2986	1.0788	.26618
.3983	.4244	1.0809	.24832

solvent. An a value of 4.3 Å. was used since this was the value found by Harned and Ehlers[12] for aqueous solutions and Harned and Thomas[1] for methanol–water solutions.

On plotting E' vs. m, straight lines were obtained

(7) H. M. Trimble and W. Potts, *Ind. Eng. Chem.*, **27**, 66–68 (1935).

(8) G. Akerlof, THIS JOURNAL, **54**, 4125 (1932).

(9) H. S. Harned and J. O. Morrison, *Am. J. Sci.*, **33**, 161 (1937).

(10) H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

(11) B. B. Owen, *ibid.*, **60**, 2229 (1938).

(12) H. S. Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

in the lower concentration ranges, and from them the standard potentials, E_m^0, could be determined to within ±0.05 mv. Table I gives the observed electromotive force, molality, density and ionic strength (concentration) of each of the solutions, and Table II shows values used for the constants of equation 1 in each solvent. The actual values of E_m^0 which were obtained from these plots are not given since extrapolations employing the extended terms of the Debye–Hückel function were also made.

TABLE II

CONSTANTS OF EQUATIONS (1) AND (5)

	A	B × 10⁻⁸	M_{xy}	a
10% Glycol	0.5387	0.3349	19.40	3.6
20% Glycol	.5701	.3413	21.00	3.7
40% Glycol	.6515	.3568	25.16	4.3
60% Glycol	.7750	.3781	31.38	4.3

TABLE III

STANDARD POTENTIALS OF THE CELLS

H_2/HCl(m), Ethylene glycol(x), H_2O(y)/AgCl–Ag

	D	E_m^0	E_N^0	E_c^0
10% Glycol–water	75.7	0.21484	0.41739	0.21531
20% Glycol–water	72.8	.20936	.40784	.21053
40% Glycol–water	66.6	.19720	.38640	.19968
60% Glycol–water	59.38	.18070	.35855	.18437

In the most dilute solutions, the value of the residual function represented by $f(m)$ in equation (1) should equal the contribution of the "extended terms" of the Debye–Hückel function. The addition to the electromotive force produced by the calculated values of the third and fifth order terms may be represented by E_{EXT}. When E' + E_{EXT} is plotted against either m or c for solutions less than 0.01 m a horizontal line should result. Using several values of the parameter a, values of E_{EXT} were obtained for the most dilute solutions in each series from the table of Gronwall, LaMer and Sandved functions as reproduced by Harned and Owen.[13] The values of E' + E_{EXT} are plotted against molality in Fig. 1. The E_m^0 values thus obtained are the most trustworthy and are given as the final values in Table III, although they did not differ by more than 0.03 mv. from those obtained from the plots of E' vs. m as previously described. Unusually low values of a would be required to produce constant values of E' + E_{EXT} in the 10 and 20% glycol solutions as may be seen from Fig. 1.

The standard potentials of the cells, as obtained from equation (1), plus the extended terms have as reference states for E_m^0 a solution of unit molality with the activity coefficient, γ, at unity in a given solvent. E_N^0 may be calculated from E_m^0 for a given solvent by using the equation

$$E_N^0 = E_m^0 + 0.1183 \log \frac{1000}{M_{xy}} \quad (2)$$

(13) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1942, p. 122.

where M_{xy} is the mean molecular weight of the solvent and E_N^0 is the potential for a solution of unit mole fraction of electrolyte at unit rational activity coefficient, f. Also, E_c^0 may be calculated from the relation

$$E_c^0 = E_m^0 + 0.1183 \log d_0 \quad (3)$$

where d_0 is the density of the solvent and E_c^0 is the potential in a given solvent containing electrolyte at unit concentration in moles per liter of solution and at unit activity coefficient. Table III gives the values of E_m^0, E_c^0 and E_N^0 for 10, 20, 40 and 60% glycol–water solutions, along with the dielectric constants of the solvents.
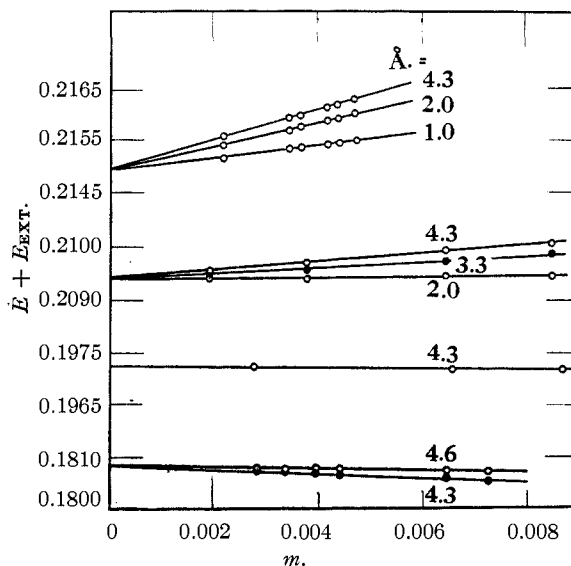

Fig. 1.—Extrapolations in glycol–water mixtures at 25° according to the extended form of equation 1. Curve families from top to bottom are: 10% glycol; 20% glycol; 40% glycol; 60% glycol.

In Fig. 2, values of E_m^0 are plotted against the reciprocal of the dielectric constant of the medium. The origin of the plot represents E_m^0 for pure water. The curve is not quite a straight line but is typical of plots of this type.

Activity Coefficients

The activity coefficients of hydrochloric acid in 10, 20, 40 and 60% glycol–water solutions by weight may be computed from the electromotive force measurements and molalities given in Table I and the standard potentials, E_m^0, given in Table III by means of the equation

$$\log \gamma_{\pm} = \frac{E_m^0 - E}{0.1183} - \log m \quad (4)$$

The values of $\gamma_{\pm}$ were plotted against $\log m$ on a large scale and from such plots the activity coefficients at rounded molalities were read off and assembled in Table IV, together with values for
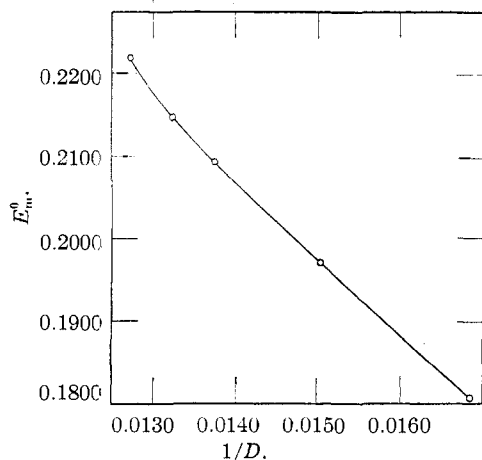
Fig. 2.—A plot of E_m^0 vs. $1/D$ in aqueous ethylene glycol solution. The origin of the plot represents E_m^0 in pure water.

aqueous solutions given by Harned and Owen.[13] It will be noticed that the activity coefficients in the low concentration range (<0.012 m) are smaller for 10% glycol than for either 20 or 40%. No explanation of this anomaly should be attempted until further measurements are available, particularly in the range of low glycol concentrations and over a range of temperatures.

TABLE IV

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYLENE GLYCOL-WATER MIXTURES AT 25°

Molality	X = 0[a]	X = 10	X = 20	X = 40	X = 60
	X = weight per cent. glycol in solvent				
0.001	0.9668		0.959	0.957	0.946
.002	.9541		.942	.939	.926
.005	.9303	0.897	.911	.908	.892
.01	.9065	.871	.878	.876	.858
.02	.8774	.851	.845	.843	.820
.05	.8346	.805	.799	.791	.763
.1	.8027	.770	.764	.750	.717
.2	.7756	.743	.728	.712	.685
.5	.7761	.734	.726	.707	.672
1.0	.8419	.784	.780	.760	

[a] Harned and Owen, ref. 13, p. 340.

The experimental activity coefficients should be capable of representation by a Debye–Hückel equation of the type

$$\log \gamma^{\pm} = - \frac{A\sqrt{c}}{1 + aB\sqrt{c}} + Cc - \log (1 + 0.002 M_{xy}m) \quad (5)$$

Using the constants of Table II and C values of 0.156 and 0.211, respectively, the experimental activity coefficients of the 40 and 60% series were successfully fitted over the entire range from 0 to 1 M. Constant values of a and C could not be found, however, over the whole concentration range in the 10 and 20% glycol solutions. When the constant values of a given in Table II are re-

tained, it is possible to fit equation (5) to the activity coefficients in the low concentration range (<0.1 m) of the 10 and 20% glycol solutions only by using several different values of the parameter C. The desired result cannot be accomplished by adding a quadratic term, $D\mu^2$, to equation (5).

In the ranges of 0 to 0.005 m for 10% glycol and 0 to 0.012 for 20%, the experimental activity coefficients are very successfully reproduced when C values of -2.55 and -0.60, respectively, are used. Other values of C which are needed for the 10% solutions are -1.60 from 0.005 to 0.010 m, and -1.00 from 0.010 to 0.012 m, -0.45 from 0.012 to 0.020 m, $+0.07$ from 0.02 to 0.10 m and $+0.157$ from 0.10 to 1.20 m. In the 20% solutions the required values are -0.22 from 0.012 to 0.025 m, $+0.06$ from 0.025 to 0.080 m and $+0.161$ from 0.08 to 1.2 m.

Harned and co-workers[1,2,3] have obtained straight lines on plotting E' vs. m in 10 and 20% methanol, 10 and 20% ethanol, and 10% isopropanol in concentration ranges from 0 to 1 m. Also they have been able to find a and C values suitable for calculating activity coefficients for the whole concentration range. Our work on 40 and 60% glycol gave similar results. In 10 and 20% glycol solutions, however, the plots of E' vs. m were straight only from 0 to about 0.2 m, after which a new slope was obtained on each solution. There seems to be no logical reason why 20% glycol and 10% ethanol, solvents with the same dielectric constant, should differ in these respects. Nor does it seem logical that the 40 and 60% glycols should behave in a normal fashion while 10 and 20% glycols should require special treatment in calculating $\gamma_{\pm}$ in dilute solutions. All experimental evidence, however, seems to allow the generalization that when the glycol concentration is low, departure from expected results is greatest. This is seen in the abnormally low a value which would be necessary to obtain a horizontal curve in the $E' + E_{EXT}$. vs. m plot of the 10% glycol solutions, and in the variable values of C necessary for calculating activity coefficients in very dilute hydrochloric acid concentrations. The departure from the expected is less marked in the 20% glycol solutions, and finally the 40 and 60% glycol solution show normal behavior.

Summary

1. The standard potentials of the cells

$$H_2 \mid HCl\ (m),\ \text{Ethylene glycol}(x),\ H_2O(y) \mid AgCl\text{-}Ag$$
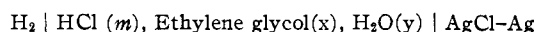
have been determined at 25° from electromotive force measurements on solutions of 10, 20, 40 and 60% ethylene glycol-water mixtures. The accuracy of the standard potentials is believed to be ± 0.05 mv.

2. The mean activity coefficients of hydrochloric acid in these solvents are tabulated at rounded molalities up to 1.0 m.

3. The activity coefficients may be calculated by a Debye–Hückel expression with constant a and C values, except in the case of 10 and 20% glycol solutions less than 0.1 m with hydrochloric acid, for which several values of the parameter C are required.

CHAPEL HILL, NORTH CAROLINA
RECEIVED NOVEMBER 10, 1945

The Standard Potential of the Cell, H₂ | HCl(m) | AgCl-Ag, in 50% Glycerol–Water Solution from 0 to 90°

BY HERBERT S. HARNED AND F. H. MAX NESTLER[1]

Standard potentials of the cell H₂ | HCl(m), H₂O(X), solvent (Y) | AgCl–Ag have been determined in water and in a number of water–organic solvent solutions from 0 to 50 or 60°.[2] Experimental difficulties were encountered when attempts were made to extend these measurements to higher temperatures. In this work, we have made a serious attempt to extend the temperature range and to determine the degree of uncertainty of the determinations at the higher temperatures. A 50% by weight solution of glycerol–water was chosen for these experiments. Since its vapor pressure is 618 mm. at 100°, the measurements could be carried out to this temperature without causing serious error in correcting the hydrogen pressure to one atmosphere.

Experimental Procedure and Electromotive Force Data

The measurements were carried out with minor modifications by the technique described by Harned and Morrison.[3]

Merck synthetic c. p. glycerol was further purified by distilling twice in a vacuum of 3–4 mm. of mercury. From refractive index determinations with a Zeiss immersion refractometer and the tables of Stedman,[4] the composition of this material was found to be 99.78–99.84% by weight. An indirect test of the purity was also made as follows. Assuming that the impurity was water, a 50% by weight glycerol–water solution was prepared and its density determined. Interpolation from the tables of Bosart and Snoddy[5] showed that the composition was known to within a few hundredths of a per cent.

The cell solutions were made by weighing glycerol, water and hydrochloric acid solution standardized gravimetrically. The acid concentration was known to within ±0.02 per cent.

Two series of cell electromotive force measurements were made at each acid concentration, one at lower and the other at the higher temperatures. The lower temperature run was started at 25°, then measurements were made at 5° intervals to 0°. The temperature was brought to 25° for a check reading and then by 5° intervals to 50° and finally back to 25°. The three readings at 25° after this treatment agreed within the satisfactory limit of 0.1 mv. The higher temperature determinations were by no means as satisfactory. These were begun at 50°, carried to 90° by 5° intervals and then brought to 50°. The two readings at 50° showed variations from 0.3 to 1 mv. Our experience indicates that silver–silver chloride electrodes begin to deteriorate at temperatures of 70° or higher, a fact which will be shown to accord with subsequent calculations.

The cell measurements were made in triplicate, and the mean values of these observations recorded. The results were found to accord over the temperature ranges indicated in the last column of Table I with the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

The constants a and b were obtained by plotting the first order five degree differences in electromotive forces against the temperature according to the method used by Harned and Nims.[6] This has the advantage over the method of least squares since any sharp deviations from the quadratic

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H₂ (1 atm.) | HCl (m), H₂O(X), C₃H₅(OH)₃(Y) | AgCl–Ag. Constants of equation $E = E_{25} + a(t - 25) + b(t - 25)^2$.[2] X = Y = 50% by weight. Δ = average deviation in millivolts between observed electromotive forces and those calculated by equation (1) over temperature range given in the last column.

m	E_{25}	$a \times 10^4$	$b \times 10^6$	Δ (mv)	Validity range
0.00359	0.47765	2.52	−2.83	0.10	0 → 90°
.00694	.44543	1.47	−2.98	.04	0 → 70
.00987	.42831	.89	−2.93	.06	0 → 70
.01954	.39521	−0.16	−2.82	.05	0 → 70
.03233	.37130	−0.86	−2.82	.09	0 → 75
.05331	.34754	−1.66	−2.88	.08	0 → 75
.07373	.33189	−2.06	−2.81	.06	0 → 75
.09013	.32234	−2.34	−2.81	.11	0 → 90

(1) This communication contains material from a dissertation presented by F. H. Max Nestler to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1943.

(2) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, 1943, Table 11-3-3A, p. 546.

(3) Harned and Morrison, Am. J. Sci., 33, 161 (1937).

(4) Stedman, Trans. Faraday Soc., 24, 296 (1928).

(5) Bosart and Snoddy, Ind. Eng. Chem., 19, 506 (1927).

(6) Harned and Nims, THIS JOURNAL, 54, 423 (1932).