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.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Standard Potential of the Cell, H_2 | 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 H_2 | HCl(m), H_2O(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

H_2 (1 atm.) | HCl (m), H_2O(X), $C_3H_5(OH)_3$(Y) | AgCl–Ag. Constants of equation $E = E_{25} + a(t - 25) + b(t - 25)^2$. 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

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(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).

equation due to the deterioration of the electrodes at higher temperatures will appear on the plots. In six of the eight series shown in Table I, such sharp deviations appeared at temperatures above 70 or 75°. These results were not included in computing Δ(mv).

Calculation of Standard Cell Potential

The standard electromotive force of the cell, E_0, was computed in the usual manner by employing the equation

$$E + 2k \log m - \frac{2kS_{(f)}\sqrt{md_0}}{1 + A'\sqrt{md_0}} = E_0 + f(m) \quad (2)$$

where k equals $2.3026RT/F$, $S_{(f)}$ is the limiting slope of the Debye and Hückel theory, d_0 the solvent density and $A'\sqrt{md_0}$ is the term which takes into account the mean distance of approach of the ions.[7] Two graphical extrapolations were made of the left side of this equation. In the first, $A'\sqrt{md_0}$ was neglected according to the method of Hitchcock.[8] The second extrapolation was carried out using 4.5 Å. for the mean distance of approach of the ions and the entire expression on the left side of the equation. As far as we could judge, both methods yielded equally satisfactory results. Those given in the last column of Table II represent the mean of the two extrapolations.

TABLE II

STANDARD POTENTIAL OF THE CELL: H_2 | HCl (m), H_2O (50%), $C_3H_5(OH)_3$ (50%) | AgCl-Ag

p_0, d_0 and $S_{(f)}$ are the vapor pressures, densities and Debye limiting slopes of glycerol–water solutions.

t	p_0 (mm.)	d_0	$S_{(f)}$	E^0 (obs.)[a]
0	3.60	1.13595	0.6525	0.20065 (+2)
5	4.98	1.13360	.660	.19760 (+2)
10	6.92	1.13120	.668	.19441 (+1)
15	10.4	1.12875	.6755	.19103 (+4)
20	13.1	1.12630	.684	.18760 (−2)
25	17.4	1.12375	.692	.18398 (−6)
30	23.4	1.12115	.700	.18015 (−3)
35	30.6	1.11845	.709	.17618 (−1)
40	41.3	1.11570	.718	.17202 (+6)
45	53.3	1.11285	.728	.16780 (+2)
50	69.0	1.10995	.737	.16341 (+2)
55	88.7	1.10695	.747	.15890 (−3)
60	114	1.10385	.757	.15420 (−2)
65	142	1.10070	.768	.14936 (+4)
70	180	1.09745	.777	.14437 (−4)
75	224	1.09410	.790	.13912 (+5)
80	278	1.09065	.802	.13394 (−6)
85	345	1.08710	.814	.12838 (+4)
90	420	1.08345	.827	.12280 (+3)

[a] (The numbers in parentheses are the differences in fifth decimal place of (E^0 (calcd.) − E^0 (obs.)). E^0 (calcd.) according to equation (4).

This table contains the data necessary for this computation. The second column contains the vapor pressures used for correcting the hydrogen pressure of the cell to one atmosphere. These were obtained from large scale composition–vapor pressure graphs at 0, 15, 25 and 100°. The values of the 50% glycerol solutions were read off these curves and plots of log p *versus* $1/T$ drawn. From these linear graphs, p was determined at the desired temperatures. This computation was made from the combined data of Fricke,[9] Fricke and Haverstadt,[10] Drucker and Moles[11] and Gerlach.[12]

The densities given in the third column of Table II were obtained from a large scale temperature plot. For the interval 0 to 25°, values from the data of Bosart and Snoddy,[5] Green and Park[13] and Landolt–Börnstein tables[14] were employed. From 30 to 90°, density measurements at 10° intervals were made by us. The results are expressed to five in the fifth decimal place. An error of ±0.01% in composition is approximately equivalent to ±0.00005 in the density.

The dielectric constants for these mixtures used in computing the limiting slopes, $S_{(f)}$, were obtained from Åkerlöf's data by his formula

$$\log D = 1.87171 - 0.00217\,(t - 20) \quad (3)$$

The fundamental physical constants employed in calculating the values of $S_{(f)}$ in the fourth column of Table II were those given by Birge.[15]

Summary

1. The standard potentials of the hydrogen–silver–silver chloride cell in 50% by weight glycerol–water solutions has been determined from 0 to 90°.

2. These may be computed as a function of the temperature by the equation

$$E^0 = 0.18392 - 7.45 \times 10^{-4}(t - 25) - 3 \times 10^{-6}(t - 25)^2 \quad (4)$$

The deviations of observed from calculated results are given in parentheses in the last column of Table II.

NEW HAVEN, CONN. RECEIVED JANUARY 19, 1946

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[7] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, Chap. XI.

[8] Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

(9) Fricke, *Z. Electrochem.*, **35**, 633 (1929).

(10) Fricke and Haverstadt, *ibid.*, **33**, 441 (1927).

(11) Drucker and Moles, *Z. physik. Chem.*, **75**, 410 (1910).

(12) Gerlach, *Z. anal. Chem.*, **24**, 110 (1885).

(13) Green and Park, *J. Soc. Chem. Ind.*, **58**, 319 (1939).

(14) "Landolt-Börnstein Tabellen," Erg. I., Julius Springer, Berlin, 1927, p. 214.

(15) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).