[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Temperature Variation in Transference Numbers of Concentrated Solutions of Sulfuric Acid as Determined by the Galvanic Cell Method[1]

BY WALTER J. HAMER[2]

In a previous contribution[3] measurements of the cell

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg \qquad (1)$$

where the concentration was varied from 0.05 to 17.5 molal and the temperature from 0 to 60° were reported. In this contribution measurements of the cell

$$Hg \mid Hg_2SO_4 \mid H_2SO_4(m) \mid H_2SO_4(m') \mid Hg_2SO_4 \mid Hg \quad (2)$$

measured over the same range of concentration and temperature will be presented. The corresponding cell at the same concentration ratios without liquid junction may be obtained from various combinations of cell (1) and may be represented by

$$Hg \mid Hg_2SO_4 \mid H_2SO_4(m) \mid H_2 \mid H_2SO_4(m') \mid Hg_2SO_4 \mid Hg \quad (3)$$

From measurements of cells (2) and (3) the transference numbers of the hydrogen ion of sulfuric acid may be readily calculated.

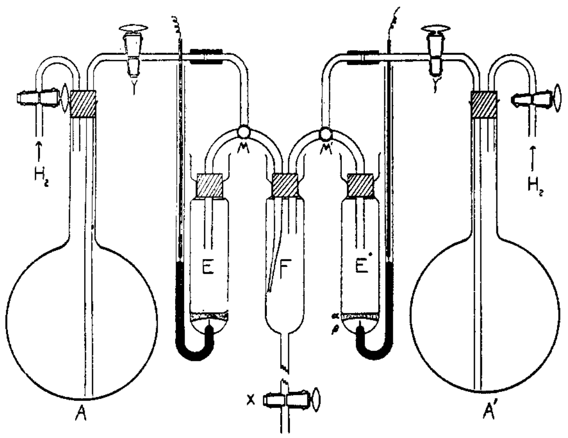

Fig. 1.—Apparatus for the measurements of cell (2).

Experimental Procedure

The electrodes and solutions were prepared in the same manner as described by Harned and Hamer.[3] In Fig. 1 a diagram of the apparatus employed for these measurements is shown. Mercury (β) and mercurous sulfate (α) were introduced into the cells E and E' with the precautions previously described. All the parts of the apparatus could be dismantled except compartment F, which was constructed permanently in the thermostat and had stopcock X below and outside the bath. The entire apparatus to stopcocks Y and Y' was evacuated through stopcock X and then filled (compartment F excepted) with solution by opening stopcocks Y, Y', M and M'. Each cell was filled separately, cell E with the less dense of the two solutions and cell E' with the more dense solution. To prevent air from entering the system during this process, hydrogen was led into the solution flasks as indicated. Cells E and E' were then allowed to stand in the thermostatic bath (maintained constant to within ±0.02°) for from one to two hours. Then the apparatus was raised carefully several cm. and the denser solution from flask A' which had also been kept in the thermostat was introduced into compartment F and the apparatus was then lowered to its initial position. Any air introduced by this process does not come into direct contact with the electrodes and any small trace present does not affect the observed electromotive forces appreciably. This has been shown to be true by Randall and Stone[4] and was confirmed by Harned and Hamer.[3] The compartments were filled only to the level shown to prevent direct contact of sulfuric acid with the rubber stoppers. Immediately after the three compartments were filled, stopcocks M and M' were opened to make electrical connections and the electromotive forces were read immediately. Measurements were then taken at thirty-minute intervals for a period of a day.

A total of six compartments F were constructed, two in each of three thermostats, thus making possible fifteen concentration ratios between five initial and different concentrations. Errors due to small electrode differences were eliminated by first measuring one electrode against another containing the same solution. A new junction was made for each temperature and only one temperature was measured in the period of a day. It was found impractical to measure the same junction throughout a temperature range as was done for cells without the liquid junction.

Liquid Junction Construction.—The apparatus shown and described above is characterized by its simplicity in construction where the junction between the two different concentrations is at the tip of a small tube of one and a half millimeter in diameter. The electromotive force for a junction between two different electrolytes has been shown to depend upon the breadth of the "boundary layer" as well as the method of construction of the junction.[5] However, it is generally conceded from theoretical considerations as well as experimental observations that a junction between the same electrolyte at different concentrations is not only independent of the breadth of the "boundary layer" but also of the method of construction. Scatchard and Buehrer[6] found that this was not strictly true for a

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[3] Harned and Hamer, THIS JOURNAL, **57**, 27 (1935).

[4] Randall and Stone, *ibid.*, **51**, 1752 (1929).

[5] Maclagan, *Biochem. J.*, **23**, 309 (1929); Guggenheim, THIS JOURNAL, **52**, 1315 (1930).

[6] Scatchard and Buehrer, *ibid.*, **53**, 574 (1931).

simple concentration cell with hydrochloric acid, and that the "Clark type of junction" is a more steady and reproducible junction than a "flowing junction" where the "boundary layer" is much sharper. Although they found the difference between the two to be quite small (order of 0.03 mv.) they stated that a stationary junction with a broad "boundary layer" was to be preferred. The differences were attributed by them to heat effects produced within the "boundary layer." It was for this reason as well as conclusions drawn by others[5,7] that the above junction, a broad junction of about one-half centimeter in breadth (measured parallel to the concentration gradient) was chosen for these measurements. With its use steady electromotive forces reproducible to better than ±0.01 mv. were obtained.

Measurements were especially desired in concentrated solutions and due to the large heats of dilution for sulfuric acid solutions, it was impossible to maintain one concentration constant and vary the other. Consequently, a large number of preliminary measurements were made in order to determine the proper concentration ratios which would give steady and reproducible electromotive forces, or, in other words, the ratios for which the heat effects are at a minimum. From these measurements it was found that any ratio where the molalities differed by one molal except for the more dilute solutions or where the differences between the relative partial molal heat contents of the two concentrations under consideration were below approximately 800 calories could be reproduced with an accuracy of better than ±0.01 mv., and when the differences became 2000 calories the accuracy was reduced to ±0.15 mv. For extreme cases of difference of 10,000 calories, the accuracy was extremely low and of the order of 3.5 mv. Smaller differences in concentration or relative partial molal heat contents would likewise be suitable and give steady and reproducible electromotive forces but experimental accuracy is sacrificed somewhat. Table I was constructed on this basis. The electromotive forces given in Table I are the average of four measurements and in no case was the average deviation more than ±0.01 mv. Moreover, these electromotive forces are those recorded immediately after formation of the junction and remained constant (slight variation of ±0.003 mv.) for a period of a day. It is also to be noticed that the differences in the relative partial molal heat contents for m and m' in this table are below 600 calories for all ratios.[8]

In order to test the effect of "heat of mixing" upon the observed electromotive force, we may add successive electromotive forces of Table I, which gives us a series of values at various ratios for which the heat effects are at a minimum as exemplified by the steadiness and reproducibility described above, and then compare these "summed-up" electromotive forces with ones measured. A large number of concentration ratios were measured but for the sake of brevity only a few will be given here at 0° to illustrate. For 0.05–0.2 molal where $\overline{\Delta L_2}$ is equal to 711 calories we should obtain 0.02745 v. The measured value was 0.027444 v. For 0.1–1.0, 0.1–2.0, 0.2–2.0, 0.5–2.0, 1.0–4.0, 5.0–8.0, 10.0–15.0 and for 15.0–17.0 molal where $\overline{\Delta L_2}$ is less than 2000 calories we find the differences between the "summed-up" electromotive forces of Table I and the observed ones to be, respectively, 0.01, 0.019, 0.031, 0.002, 0.078, 0.119, 0.15 and 0.033 mv., which is certainly not large. For the ratios where $\overline{\Delta L_2}$ exceeds 5000 calories, namely, 0.05–10.0, 0.1–10.0, 0.2–10.0, 0.5–10.0, 1.0–10.0, 2.0–15.0, 5.0–15.0, and 0.05–17.0 molal we find the differences to be respectively 1.06, 0.90, 0.82, 0.77, 0.57, 1.47, 0.55 and 3.39 mv.

At least qualitatively, it is apparent that these differences observed *at zero time* are not merely a function of the concentration or the activity ratio but some function of the "heat of mixing." This can be shown by plotting the differences (ΔE) against m/m' or a/a'. A series of curves are obtained which fuse into one another if (ΔE) be plotted against $\overline{\Delta L_2}$. This implies that the ratio 5.0–10.0 molal is less steady and reproducible than 0.05–0.10 molal even though m/m' is the same, due to the larger heat effect obtained in the former case. These differences are unquestionably due primarily to heat effects or to the temperature gradients around the "boundary layer" and become more evident and exert a greater influence upon the electromotive force for concentration ratios where the heats of dilution are larger. They are also probably influenced by the apparatus employed. Scatchard and Buehrer employed a junction in which there was rapid heat conduction and undoubtedly larger ratios may be employed for sulfuric acid in cells in which the junction is so constructed that heat conduction is rapid. However, the relative differences found above will still persist and remain independent of the apparatus. Finally, it must be emphasized that the above differences are obtained only at zero time and decrease with time, but less dependence may be placed in these measurements than in those which remain steady.

Method of Evaluation of Transference Numbers at a Particular Concentration.—The differential equations for the electromotive forces of the cells without and with liquid junction are given, respectively, by

$$dE_s = (3RT/2F)d \ln a \qquad (4)$$

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(7) Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917); also, Taylor, "Treatise on Physical Chemistry," 2d ed., Vol. 1, Chap. XII by H. S. Harned, p. 819 *et seq.*, D. Van Nostrand Co., New York, 1931.

and

$$dE_2 = (3RT/2F)t \, d \ln a = t \, dE_3 \quad (5)$$

where t is the cation transference number at concentration m and temperature T and a is the geometric mean activity of the ions in the same solution. The method of Jones and Dole[8] in which the integration of the differential equation (5) requires a functional relationship between the transference number and the activity is not suitable to this case, since an analytical treatment of sulfuric acid is complicated by the fact that sulfuric acid is an incompletely dissociated unsymmetrical electrolyte which dissociates to give ions of unequal size. Moreover, an expression for the variation of the transference number with the concentration is likewise complicated and an inspection of the final values shows that they do not follow a parabolic equation or any other well defined expression.

Instead, direct integration[9] of the differential equation (5) was employed. For the evaluation of the slope of E_2 against E_3, we shall employ the method of Rutledge[10] of finding, with known limit of error, the derivative function of a differentiable function, from values of the latter observed for equally spaced values of the independent variable. Briefly, this method involves the use of a Lagrange polynomial of degree four which is passed through successive five points until the entire curve is defined. This method is very accurate and ideally suited to this case where the slope shows but a slight curvature, and successive values of the derivative for any one point on the curve were in good agreement, indicating that the errors of observation were small. This method was found preferable to that employed by MacInnes and Beattie since it was unnecessary to formulate an equation for the variation of E_2 with the logarithm of the activity of the solute, and the evaluation of the empirical constants by the method of least squares.

Experimental Data

In Table I the electromotive forces of the cell with liquid junction are given. In practice the sixth decimal was read but results are only given to 0.01 mv. For calculations 0.05 molal was chosen for the fixed concentration and the electromotive forces up to 17.0 molal were obtained by summation. Values at the corresponding concentration ratios for the cells without liquid junction were obtained from Table I of a previous paper by Harned and Hamer.[3] For sake of brevity, plots of E_2 against E_3 and of dE_2/dE_3 against equal

TABLE I

THE ELECTROMOTIVE FORCES FROM 0 TO 60° OF CELL (2)

m	m'	0°	10°	15°	25°	35°	45°	60°
0.05	0.10	0.01394	0.01420	0.01431	0.01451	0.01464	0.01472	0.01478
.10	.20	.01351	.01384	.01400	.01428	.01450	.01469	.01490
.20	.30	.00757	.00792	.00804	.00825	.00844	.00861	.00874
.30	.50	.01055	.01076	.01083	.01101	.01110	.01116	.01124
.50	1.0	.01565	.01594	.01604	.01625	.01638	.01644	.01636
1.0	2.0	.01994	.01998	.02005	.02005	.01996	.01980	.01946
2.0	3.0	.01637	.01627	.01622	.01605	.01580	.01556	.01508
3.0	4.0	.01459	.01442	.01429	.01410	.01381	.01362	.01306
4.0	5.0	.01328	.01310	.01302	.01277	.01250	.01216	.01178
5.0	6.0	.01186	.01168	.01158	.01134	.01109	.01080	.01035
6.0	7.0	.01054	.01035	.01024	.01002	.00981	.00949	.00917
7.0	8.0	.00925	.00908	.00898	.00879	.00858	.00836	.00799
8.0	9.0	.00815	.00799	.00791	.00762	.00754	.00733	.00699
9.0	10.0	.00701	.00686	.00679	.00682	.00647	.00630	.00602
10.0	11.0	.00652	.00636	.00631	.00613	.00600	.00583	.00558
11.0	12.0	.00579	.00569	.00564	.00552	.00539	.00526	.00505
12.0	13.0	.00526	.00516	.00511	.00501	.00491	.00482	.00469
13.0	14.0	.00490	.00478	.00471	.00460	.00449	.00434	.00416
14.0	15.0	.00445	.00433	.00428	.00416	.00404	.00394	.00378
15.0	16.0	.00403	.00397	.00399	.00387	.00382	.00374	.00369
16.0	17.0	.00384	.00373	.00361	.00357	.00347	.00336	.00322

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(8) Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

(9) See MacInnes and Beattie, *ibid.*, **42**, 1117 (1920); Lucasse, *ibid.*, **47**, 743 (1925).

(10) Rutledge, *J. Math. Phys. M. I. T.*, **8**, 1 (1929); *Phys. Rev.*, **40**, 262 (1932). The Lagrange polynomial is merely employed as a tool and there is no implication that the entire curve can be represented by a polynomial. The author is indebted to Professor George Scatchard for the reference to this method of evaluating the slope and for suggestions in its application.

TABLE II

THE CATION TRANSFERENCE NUMBERS OF SULFURIC ACID

m	0°	10°	15°	25°	35°	45°	60°
0.00[a]	(0.840)	(0.829)	(0.824)	(0.813)	(0.801)	(0.788)	(0.761)
.05	.839	.834	.830	.819	.807	.793	.770
.10	.838	.834	.829	.819	.807	.793	.770
.20	.837	.833	.829	.819	.806	.792	.770
.50	.834	.828	.824	.815	.801	.787	.764
1.00	.828	.822	.818	.808	.793	.779	.755
2.00	.816	.808	.803	.793	.779	.763	.737
3.00	.803	.793	.788	.776	.762	.747	.720
5.00	.772	.762	.756	.744	.730	.715	.689
8.00	.720	.708	.702	.690	.676	.663	.641
10.00	.682	.672	.666	.655	.642	.629	.610
12.00	.638	.629	.625	.616	.605	.595	.578
14.00	.591	.584	.580	.573	.564	.556	.543
17.00	.512	.508	.506	.502	.498	.494	.488
α	.0331	.0362	.0370	.0375	.0363	.0331	.0250

[a] Calculated from conductance data.

intervals of E_3 will not be given. Suffice it to say they were smooth curves which deviate but slightly and regularly from a straight line. From the plots of E_2 against E_3, smoothed values of E_2 at twenty-eight equal intervals of E_3 were read. These were then employed in the method of Rutledge and the numerical values of $\mathrm{d}E_2/\mathrm{d}E_3$ were calculated employing the Rutledge equation for the derivative[11]

$$\mathrm{d}y/\mathrm{d}x = \phi + (1/12h)(C_{-2}y_{-2} + C_{-1}y_{-1} + C_0y_0 + C_1y_1 + C_2y_2) \quad (6)$$

In this application, the derivative was carried only to significant figures corresponding to the significant figure of the experimental error and the values of the transference numbers given are accurate to ±0.001. Since twenty-eight equal intervals of 0.01 volt were read for E_3 we have twenty-two shifts of equation (6) along the curve with three derivative determinations in each shift which are averaged in the manner described by Rutledge. This gives us twenty-two slopes or values of $\mathrm{d}E_2/\mathrm{d}E_3$ at the same number of E_3 intervals. To obtain the slope at both ends of the curve, we may either employ smaller values of "h" or only evaluate those derivatives for which we have sufficient points, or "C_xy_x" values when the above value of "h" is retained. The values of $\mathrm{d}E_2/\mathrm{d}E_3$ determined in this manner are then plotted against E_3 and the values of $\mathrm{d}E_2/\mathrm{d}E_3$ or the transference number are read from these plots at the E_3's corresponding to round concentrations of sulfuric acid. Values of the cation transference numbers obtained by this method from 0.05 to 17.0 molal and at various temperatures are given in Table II. Measurements below 0.05 molal cannot be clearly interpreted due to the solubility of mercurous sulfate.[12]

The transference numbers are seen to decrease with concentration except below approximately 0.20 molal, where they remain nearly constant within the experimental error of ±0.001. From

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(11) Rutledge, *Phys. Rev.*, **40**, 262 (1932). In the application here, $\mathrm{d}y/\mathrm{d}x$ becomes $\mathrm{d}E_2/\mathrm{d}E_3$; "$h$" is the interval between successive values of E_3 and was taken equal to 0.01 volt; C's are functions of $(E_3-E'_3)/h$ at successive points on the curve; y is equal to $(E_2-\phi E_3)$; E'_3 is the value of the third point of original five points taken; and ϕ is the straight line slope introduced into equation (6) to reduce the magnitude of the slope in the calculations. Numerical values of the C's were obtained from Table II of the paper by Rutledge referred to above.

(12) Solubility data for mercurous sulfate in sulfuric acid are not known above 1.0 molal and consequently corrections cannot be made in the more concentrated solutions. Since an added electrolyte lowers the electromotive force it is to be expected that corrections for this solubility would raise the values of the transference numbers in the more concentrated range unless the solubility changes in a manner as to produce no change in the slope of E_2 against E_3. In 0.05 molal sulfuric acid solution the concentration of mercurous sulfate is 0.000681 molal at 0° and 0.001060 molal at 60° as computed from the combined solubility data of Drucker, *Z. anorg. Chem.*, **28**, 361 (1901); Wilsmore, *Z. physik. Chem.*, **35**, 305 (1900); Wright and Thompson, *Phil. Mag.*, [5] **17**, 288 (1884); Barre, *Ann. chim.*, [8] **24**, 203 (1911); Brodsky, *Z. Elektrochem.*, **35**, 833 (1929); and Hager and Hulett, *J. Phys. Chem.*, **36**, 2095 (1932). Since the sulfate ion contributes one-third as much to the electromotive force as the hydrogen ion, the error introduced at 0.05 molal if solubility corrections are not made is +0.45% at 0° and +0.51% at 60°. This error is not confined to one cell but to both the cells with and without liquid junction, and the correction must be applied to the slope of E against E_3. Since the slope is approximately 0.8 at this concentration, the error produced in the transference number with neglect of solubility corrections is about 0.08% at 0° and 0.09% at 60°. In addition the solubility of mercurous sulfate has an effect upon the liquid junction potential, but corrections for this effect are quite small, especially when the acid concentrations differ by 1.0 molal or less. For more dilute solutions, interpretations become more difficult. At 0.001 molal the solubility of mercurous sulfate at 0° is 0.000989 molal or 99% of the acid concentration. Corrections for the sulfate ion may be made by calculating the total sulfate ion concentration, which is then substituted in the expression for the electromotive force, but the large concentration of mercurous ion becomes a disturbing factor which cannot be accurately eliminated without some knowledge of the activity of sulfuric acid in the presence of mercurous sulfate.

experimental observations[13] it has been found that the transference numbers of most ions if below 0.5 decrease with increasing concentration and if above 0.5 become larger as the concentration is increased. In dilute solutions this variation is also predicted theoretically from the limiting conductance equations of Debye and Hückel and Onsager.[14] Since the transference numbers of the hydrogen ion of sulfuric acid are above 0.5 and vary with concentration in the direction opposite to that expected, the constancy of the values at approximately 0.20 molal and less seems to indicate that we are in the neighborhood of a maximum in the transference number–concentration curve. It is of interest as well as advisable to test this supposition and at the same time test the consistency of the present data with the best conductance data by calculations of the transference number at zero concentration from the latter data.

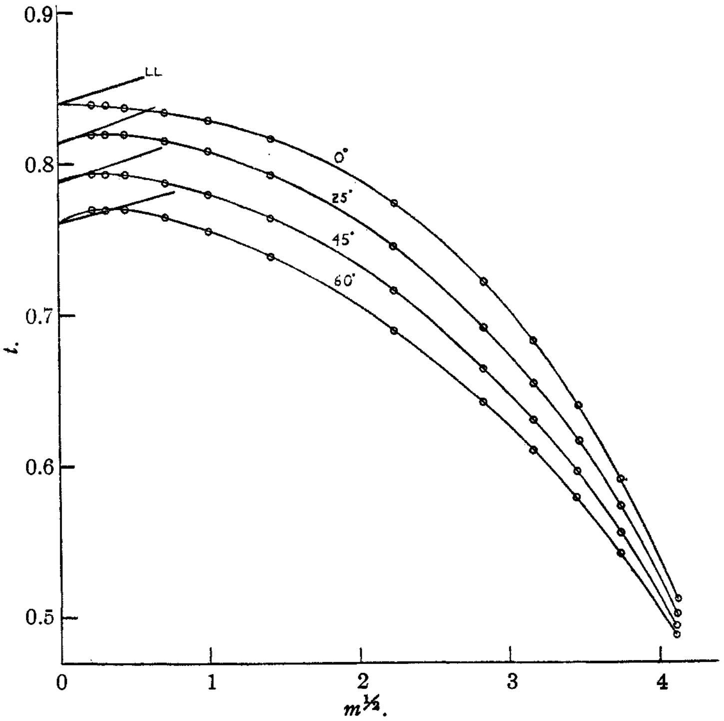

Fig. 2.—Variation of transference number of the hydrogen ion of sulfuric acid with the square root of the molality.

The ionic conductance at zero concentration and at 25° for the hydrogen ion was taken from the paper by MacInnes, Shedlovsky and Longsworth[15] and for the sulfate ion from the data compiled by Partington.[13] For the calculations at the other temperatures, the temperature coefficient for the mobility of the sulfate ion obtained by Noyes and Falk[16] and of the hydrogen ion by Kendall[17] were employed, and from these data the conductance of sulfuric acid and the cation transference numbers at zero concentration were calculated. Values of the latter are given at various temperatures in the first row of Table II.

The value of the limiting slope for the hydrogen ion is given by the equation

$$\begin{aligned} t_{\mathrm{H}} &= t_{\mathrm{H}}^0 + (41.01/\eta\, D^{1/2}T^{1/2}\,\Lambda_0)\,[(z_{\mathrm{H}} - z_{\mathrm{SO_4}})\,t_{\mathrm{H}}^0 - z_{\mathrm{H}}]r^{1/2} \\ &= t_{\mathrm{H}}^0 + \alpha'\,[(z_{\mathrm{H}} - z_{\mathrm{SO_4}})\,t_{\mathrm{H}}^0 - z_{\mathrm{H}}]r^{1/2} \\ &= t_{\mathrm{H}}^0 - \alpha m^{1/2} \end{aligned}$$

where t_{H} and t_{H}^0 are the transference numbers of the hydrogen ion at a concentration, m, and at zero concentration, respectively; Λ_0 is the conductivity of sulfuric acid at zero concentration; T the absolute temperature; η is the viscosity in poises of the pure solvent;[18] D the dielectric constant of water;[19] z_{H} the valence of the hydrogen ion; $z_{\mathrm{SO_4}}$ the valence of the sulfate ion and considered negative; r is equal to $\sum_1^s c_i z_i^2$ and the constant value is the universal constant derived by Debye and Hückel and Onsager. α' and α are constants $41.01/\eta D^{1/2}T^{1/2}\Lambda_0$ and $\alpha'[(z_{\mathrm{H}} - z_{\mathrm{SO_4}})t_{\mathrm{H}}^0 - z_{\mathrm{H}}]6^{1/2}$, respectively, and values of the latter are given at various temperatures in the last row of Table II. Equation (7) follows from the definition of the transference number of an ion, l_i/Λ, and the Debye–Hückel–Onsager conductance equations, and it shows that the transference number of an ion varies linearly in dilute solutions with the square root of the concentration. In equation (7) all terms higher than the first power in $r^{1/2}$ were dropped as we are only interested in the limiting law.

In Fig. 2 the transference numbers are plotted against the square root of the molality at 0, 25,

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(13) Taylor, "Treatise on Physical Chemistry," 2d ed., Vol. I, Chap. XI, by J. R. Partington, p. 683, D. Van Nostrand Co., New York, 1931.

(14) Debye and Hückel, *Physik. Z.*, **24**, 305 (1932); *Trans. Faraday Soc.*, **23**, 334 (1927); Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 272 (1927); *J. Phys. Chem.*, **36**, 2689 (1932); *Trans. Faraday Soc.*, **23**, 341 (1927).

(15) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

(16) Noyes and Falk, *ibid.*, **34**, 454 (1912).

(17) Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

(18) The values for the viscosity of water were taken from the "International Critical Tables," Vol. V, p. 10.

(19) Wyman, *Phys. Rev.*, **35**, 623 (1930).

45 and 60°. These curves were drawn smoothly to the value of the transference number at zero concentration and the limiting slopes ("L.L.") were drawn. For consistency with the best conductance data, the supposition as regards the occurrence of a maximum in the transference number–concentration curve has been justified except at 0°.[20] It is also interesting that the limiting slope is approached at the various temperatures in very much the same manner as was found for extrapolation functions of electromotive force measurements of sulfuric acid solutions[21] and for the relative partial molal heat contents of sulfuric acid.[3] In other words, the limiting slope is approached at higher concentrations at 0° than it is at 60° and the maximum in the curve is more marked at higher temperatures. This is an expected behavior due to the increased ionic association of sulfuric acid at higher temperatures.[22]

Conclusion

For reasons stated above, no attempt has been made to express the variation of the transference numbers with concentration and temperature in the form of equations. The values at any desired concentration between 0.05 and 17.0 molal and at temperatures between 0 and 60° may be obtained by interpolation.

The transference numbers are seen to decrease with temperature. This decrease is in accord with the conclusions drawn from the data obtained for other electrolytes by Noyes and Falk.[23] They stated that if the transference numbers are exactly 0.5 they remain constant with temperature, if less than 0.5 they increase, and if greater than 0.5 they decrease with rise in temperature. This trend is clearly shown here and for a single electrolyte in that the values at 17.0 molal decrease less rapidly with rise in temperature than at 0.05 molal where the magnitude of the transference number is larger.

No complete comparison with Hittorf determined values is possible due to wide divergence found for the latter values when various data[24] are compared and because most of the data is for concentrations below 0.05 molal. Sherrill and Noyes[25] employed 0.816 at 25° for the value of the cation transference number at 0.05 molal and for all concentrations more dilute. The value obtained in this work is 0.819 and corresponds to the maximum value, while the value at zero concentration is 0.8133. At 20° Tower obtained 0.821, 0.824, 0.819, 0.813, and 0.812 at 0.05, 0.10, 0.20, 0.50 and 1.0 molal, respectively, while the values obtained in this investigation at the same concentrations are, respectively, 0.825, 0.825, 0.824, 0.819 and 0.812.

The author takes this opportunity to express his appreciation to Professor Herbert S. Harned who suggested this investigation and for advice during its progress.

Summary

1. Measurements of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{H_2SO_4}(m) \mid \mathrm{H_2SO_4}(m') \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$$

have been made over a concentration range of 0.05 to 17.0 molal and at temperatures 0, 10, 15, 25, 35, 45 and 60°.

2. From measurements of the above cell and corresponding values for a cell without liquid junction reported by Harned and Hamer, the transference numbers of the hydrogen ion of sulfuric acid were calculated for the same ranges of temperature and concentration with use of the Rutledge equation for the derivative determination.

3. Considerations involved in the applicability of the galvanic cell method to very concentrated solutions of sulfuric acid have been discussed.

4. Extrapolations of the cation transference numbers of sulfuric acid to zero concentration and the limiting law based upon the Debye–Hückel–Onsager conductance equations are given at various temperatures.

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[20] An error of 1% in the mobility of the sulfate ion only produces an error of from 0.1 to 0.2% in the transference number at zero concentration and the calculated values are probably within this limit of accuracy.

[21] Hamer, THIS JOURNAL, **57**, 9 (1935).

[22] Hamer, *ibid.*, **56**, 860 (1934).

[23] Noyes and Falk, *ibid.*, **33**, 1436 (1911).

[24] Bein, *Z. physik. Chem.*, **27**, 1 (1898); Jahn, *ibid.*, **37**, 673 (1901); Jahn and Huybrechts, *ibid.*, **58**, 651 (1907); Tower, THIS JOURNAL, **26**, 1039 (1904); Noyes and Stewart, *ibid.*, **32**, 1134 (1910); Noyes and Falk, *ibid.*, **33**, 1454 (1911); **34**, 470 (1912); Whetham and Paine, *Proc. Roy. Soc.* (London), **A81**, 58 (1908).

[25] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).