composition, ±0.01 wt %, viscosity, ±1.9%, and density, ±0.0002 g/ml.

A complete description of the error analysis is given by Yergovich (*10*).

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Hittorf Transference Numbers in Aqueous Copper Sulfate at 25°C

MICHAEL J. PIKAL
Chemistry Department, University of Tennessee, Knoxville, Tenn. 37916
DONALD G. MILLER[1]
Lawrence Radiation Laboratory, University of California, Livermore, Calif. 94550

Hittorf transference numbers have been determined at 25° C for aqueous $CuSO_4$ solutions from 0.046*m* to 1.4*m* (saturation). All solutions were first equilibrated with Cu metal. The results, except at 0.046*m*, can be well represented by the equation:

$$t_+ = 0.4010 - 0.1426m^{1/2} + 0.0186m \qquad (\sigma = 0.005)$$

The results are in satisfactory agreement (<0.01) with Fritz and Fuget's moving boundary results over a more limited concentration range.

Recent interest in the Onsager transport coefficients (*4, 8, 19-21*), l_{ij}, has created a new need for experimental electrolyte transport properties over a large concentration range. Data for the l_{ij} of aqueous 2-2 electrolytes are particularly lacking, owing at least in part to the unavailability of the transference numbers necessary to calculate them (*19, 20*).

Transference measurements have been the subject of numerous investigations for more than a century. However, data available on 2-2 electrolytes are few, and when available, are often the results of studies made before 1910 at temperatures other than 25° C.

The principal purpose of this study is to provide transference data on an appropriate 2-2 electrolyte over a large concentration range, which would then be suitable for l_{ij} calculations. In addition, these data can be compared with the older measurements, thus serving as a basis for estimating the accuracy and suitability of other 2-2 electrolyte data reported by early workers.

Our experiments were carried out at 25° C on aqueous $CuSO_4$ solutions from 0.04*m* to 1.4*m* (saturation), where *m* is the molality. This system was chosen because $CuSO_4$ is a representative 2-2 electrolyte, there are relatively recent moving boundary measurements for comparison done by Fritz and Fuget (*6*) at 25° C over the limited range 0.15–0.5*m*, and there are limited data for comparison in the older literature (1853–1901) up to about 1*m* (*3, 10, 11, 13, 16*).

Despite its known difficulty, we selected the Hittorf method over the moving boundary and concentration cell methods for the following reasons. The Hittorf method is valid at any concentration. The moving boundary method, while accurate at low concentrations, becomes increasingly inaccurate at higher concentrations both because the correction for volume changes at electrodes becomes increasingly large and the assumptions for this correction become increasingly invalid (*1, 2, 7, 15, 18*). The concentration cell method, although valid over the complete concentration range, requires accurate activity coefficient data and either good copper or good sulfate electrodes. Previous experience with $CuSO_4$ concentration cells at LRL has been discouraging. (See appendix.) If good cell results are obtained in the future, they could be used in conjunction with the Hittorf measurements to provide a test of the Onsager Reciprocal Relations.

In order to obtain a successful electrode reaction without formation of Cu_2O, we found it necessary to *equilibrate our* $CuSO_4$ *solutions with Cu metal,* although previous workers (*3, 10, 11, 13*) either did not do or did not report this.

EXPERIMENTAL

The Hittorf apparatus used was identical to that described previously (*23*), except that high purity copper wire (99.999% pure) was used for the anode. The cell design was that of MacInnes and Dole (*14*). Two cells with 10-mm tubing were used, one with 12 ml and the other with 25-ml compartments. A P.A.R. Model TC-100.2BR voltage reference source provided a constant current to the cell. Standard resistors were used at each end to detect possible current leaks into the thermostat. The thermostat was controlled at 25.00° ± 0.01° C. The copper sulfate was purified by preparing a saturated solution at 35° C, using reagent grade copper sulfate, cooling to 0° C, and recovering the crystals. Copper sulfate solutions should not be boiled

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[1] To whom correspondence should be addressed.

to expel gases or for recrystallization purposes because a precipitate of $CuSO_4 \cdot 2Cu(OH)_2$ (X-ray analysis) can be irreversibly formed, especially in dilute solutions (*17*). Deionized water subsequently distilled once was used in all preparative work. The amount of organic impurities in this water is negligible.

It is well known that when copper is in contact with aqueous copper sulfate (with no added acid), copper is oxidized to cuprous oxide (*24*). Although the details of the oxidation mechanism may be uncertain, it seems clear that the following equilibria are involved (*24*):

$$Cu^\circ + Cu^{2+} \rightleftarrows 2\ Cu^+ \tag{1}$$

$$2\ Cu^+ + H_2O \rightleftarrows Cu_2O + 2\ H^+ \tag{2}$$

as well as possible oxidation of Cu^+ by dissolved oxygen. Thus, in addition to the usual electrochemical oxidation or reduction during electrolysis, reactions 1 and 2 also proceed at the electrodes.

To circumvent the problem arising from the formation of cuprous oxide, copper sulfate solutions were equilibrated with copper and deoxygenated prior to use according to the following procedure. Clean reagent-grade copper shot was added to a solution, and dry nitrogen was bubbled through the solution for several hours. The solution was allowed to remain in contact with the copper under nitrogen for several weeks. The solution was then transferred, in an atmosphere of nitrogen, through a fine sintered glass frit into a nitrogen-filled flask. Solutions prepared in this way contained an equilibrium concentration of cuprous ion and hydrogen ion and would undergo no further reaction with copper provided the pH of the solution was not increased.

The increase in hydrogen-ion concentration resulting from equilibration is significant, particularly in the more dilute solutions. For example, the pH values for copper sulfate solutions prior to equilibration were: $0.1m$; pH = 4.1; $0.5m$, pH = 3.5; $1.0m$, pH = 3.2. The corresponding pH values afterward were, respectively: 3.2, 2.9, and 2.75.

The transference numbers were calculated assuming the solutions were pure aqueous cupric sulfate. Because the cuprous ion and increased hydrogen ion concentrations caused by copper equilibration must be regarded as impurities, systematic errors in the calculated transference numbers are possible. Such errors may arise in two ways. First, some cuprous ion may be reduced at the cathode. Second, since any ionic impurity will carry part of the current, not all of the current is carried by just cupric and sulfate ions. Since the equilibrium constant for reaction 1 is small ($K = 1 \times 10^{-6}$) (*5*), the concentration of Cu^+ is quite small—i.e., less than 0.5% of the Cu^{2+} normality for our solutions—and its presence should not introduce a significant error. In view of the high mobility of hydrogen ion, its presence in excess is likely to be more serious, particularly in dilute solutions.

Intuitively, one would expect the relative error in the transference number of Cu^{2+} to increase as the normality ratio, $N_{H^+}/N_{Cu^{2+}}$, increases. Thus, owing to the equilibria described by reactions 1 and 2, any systematic error should increase as the copper sulfate concentration decreases. However, as shown later, the results of this research are in satisfactory agreement with the moving boundary data of Fritz and Fuget (*6*), agreement being particularly good at lower concentrations where moving boundary data are most reliable (*1, 2, 7, 15, 18*). Thus, we conclude that the use of copper equilibrated solutions did not introduce a significant systematic error, at least for measurements above $0.1m$.

The general experimental procedure was essentially the same as described previously (*23*), except that the Hittorf cell was loaded under an atmosphere of nitrogen. Electrolysis was allowed to proceed until a concentration change in the electrode compartment of 10–15% was obtained. To verify that mixing between the electrode compartment and the middle compartment had not occurred, samples of the solution in the anode middle and cathode middle compartments were also analyzed. In no case was there evidence that mixing had occurred. After electrolysis was complete, it was noticed that a small amount of cuprous oxide had formed on the anode. Presumably, this was owing to the pH near the anode increasing slightly because of the migration of the hydrogen ion away from the anode. Therefore, only transference data calculated from the cathode results are reported.

An electrolytic deposition method was used to determine the compositions of the copper sulfate solutions (*22*). Weights were reduced to vacuum. Duplicate analyses generally agreed within about ±0.03%. It is estimated that the probable error in a transference number owing to uncertainties in the analytical determinations is about ±0.002.

RESULTS AND DISCUSSION

The Hittorf transference numbers were calculated from the raw data by the usual procedure (*26*), which may be summarized by the equations for divalent cations

$$1 - t_+ = t_- = \frac{2}{I\tau} \frac{W_0}{10^3} \left|(m_F - m)\right| \tag{3}$$

$$W_0 = \frac{W}{1 + 10^{-3} m_F M_s} \tag{4}$$

where t_+ is the Hittorf transference number of the copper ion constituent, f is 96,496 C (equiv)$^{-1}$, W_0 and W are the weights of water and solution in the electrode compartment after electrolysis, respectively, I is the electric current in amperes, τ is the time of electrolysis in seconds, m and m_F are the molalities of the solutions in the electrode compartment before and after electrolysis, respectively, and M_s is the molecular weight of the solute, $CuSO_4$.

Our values of the cupric transference numbers t_+ are given in Table I at the corresponding molalities m. With one exception, two measurements were made on each solution. The notation t_+ (calcd) refers to values calculated from Equation 5 below. Also given in Table I are the pH's of the Cu equilibrated solutions, the molalities m_s of the stock solution and m_{am}, m_{cm}, and m_c of the anode-middle, cathode-middle, and cathode compartments, respectively, after electrolysis. The number in parentheses after a molality is the number of analytical determinations made on that sample. The initial molality of the solution, m, is the weighted mean of m_s, m_{am}, and m_{cm}, whose weights are the number of analytical determinations made on the sample. The number of Faradays is denoted by q. The molecular weights used for Cu and $CuSO_4$ are 63.54 and 159.60, respectively.

Table I shows that the reproducibility of t_+ for a given solution averages ±0.003, which is about the level of precision expected from the uncertainties in the analytical determinations. The data, except at $0.046m$, are found to be well represented by the semiempirical equation

$$t_+ = 0.4010 - 0.1426m^{1/2} + 0.0186m \qquad (\sigma = 0.005) \tag{5}$$

where σ is the standard deviation, and whose coefficients were evaluated by the method of least squares. The constant term in Equation 5 was fixed at the correct limiting value of 0.401_0, calculated from tabulated ionic conductances (*25*). The data above $0.1m$ were assigned a weight of unity. Since the two most dilute solutions studied appeared to be somewhat in error relative to the rest of the data, these data were assigned a weight of ¼.

Table I. Hittorf Transference Numbers in Copper Equilibrated Aqueous $CuSO_4$ Solutions at 25° C

m	pH (±0.05)	m_s	m_{am}	m_{cm}	m_c	$10^3 q$	t_+	t_- (calcd)
0	...	...	...	...	...	...	0.401[a]	0.401
0.04634_5	3.28	0.04633_6 (3)	0.04634_4 (2)	0.04634_2 (2)	0.03694_7 (2)	0.4257	0.392	0.371
			0.04637_3 (1)	0.04634_9 (2)	0.03666_1 (2)	0.4352	0.389	0.371
0.08350	3.17	0.08347 (4)	...	0.08352 (2)	0.07333 (2)	0.4340	0.357	0.361
			0.08350 (2)	0.08353 (2)	0.07333 (2)	0.4334	0.351	0.361
0.11480	3.18	0.11483 (2)	0.11479 (2)	0.11479 (1)	0.09374 (2)	0.9041	0.360	0.355
			0.11487 (1)	0.11474 (2)	0.10414 (2)	0.4550	0.355	0.355
0.1795_5	3.14	0.1795_5 (3)	0.1795_0 (1)	0.1796_0 (1)	0.1548_0 (2)	1.0353	0.346	0.344
			0.1795_4 (1)	0.1796_0 (1)	0.1537_9 (2)	1.0772	0.349	0.344
0.2775_6	3.02	0.2775_6 (4)	0.2775_2 (2)	0.2775_2 (2)	0.2217_4 (2)	2.305	0.331	0.331
			0.27762 (2)	0.2775_9 (2)	0.2216_2 (2)	2.326	0.334	0.331
0.4260_3	2.98	0.4263_2 (4)	0.4256_3 (2)	0.4257_7 (2)	0.3401_1 (2)	3.486	0.313	0.316
			0.4260_5 (2)	0.4260_8 (2)	0.3417_2 (2)	3.364	0.314	0.316
0.5400_0	2.92	...	0.5400_7 (2)	0.5399_2 (2)	0.4367_5 (2)	4.081	0.308	0.306
0.5441_9	2.86	0.5442_1 (2)	0.5442_5 (1)	0.5440_6 (1)	0.4722_3 (3)	2.869	0.298	0.306
			0.5441_8 (1)	0.5442_1 (1)	0.4706_5 (3)	2.935	0.301	0.306
0.6997_9	2.89	0.6999_9 (4)	0.6991_9 (2)	0.6997_6 (2)	0.6236_2 (3)	2.972	0.302	0.295
			0.6999_5 (1)	0.6999_5 (2)	0.6197_5 (2)	3.120	0.297	0.295
0.8975	2.86	0.8986 (4)	...	0.8954 (2)	0.7030 (2)	7.150	0.278	0.283
			0.8977 (2)	0.8972 (2)	0.7060 (2)	7.306	0.279	0.283
0.9060	2.85	0.9063 (2)	0.9064 (1)	0.9062 (1)	0.7829 (3)	4.712	0.282	0.282
			0.9053 (1)	0.9053 (1)	0.7806 (3)	4.850	0.281	0.282
0.9792	2.76	0.9791 (2)	0.9791 (2)	0.9791 (2)	0.8069 (3)	6.501	0.276	0.278
			0.9792 (2)	0.9793 (2)	0.8106 (3)	6.415	0.275	0.278
1.169_0	2.84	1.168_4 (2)	1.169_7 (1)	1.169_2 (1)	1.033_1 (3)	5.094	0.264	0.269
			1.169_7 (1)	1.168_6 (1)	1.034_5 (3)	5.076	0.267	0.269
1.314_0	...	...	1.313_9 (2)	1.313_9 (2)	1.046_8 (2)	10.03_7	0.269	0.262
			1.313_9 (2)	1.314_2 (2)	1.033_9 (2)	10.43_2	0.269	0.262
1.399_4	2.70	1.399_1 (2)	1.399_4 (2)	1.399_7 (2)	1.171_2 (3)	8.335	0.258	0.258
			1.399_5 (2)	1.399_5 (2)	1.189_8 (3)	7.424	0.260	0.258

[a] Calculated from tabulated ionic conductances (*25*).

Deviations of the data from Equation 5 are random (Figure 1), but are somewhat larger than the deviations between duplicate runs on a given solution, particularly for the two solutions below 0.1*m*. It is interesting to note that the coefficient of the $m^{1/2}$ term in Equation 5 is in fair agreement with the theoretical limiting law value (*9*) of 0.18. We estimate the uncertainty in a "smoothed" transference number, calculated from Equation 5, to be less than ±0.005 above 0.1*m*, and less than ±0.01 in the region between 0.1*m* and infinite dilution.

Our data, the old Hittorf data (*3, 10, 11, 13*), and the moving boundary results of Fritz and Fuget (*6*) are shown for comparison in Figure 1. First, we see that the results of this research are in satisfactory agreement with the moving boundary data. We therefore conclude that our data are free from significant systematic errors. Second, the old Hittorf data are, in general, in fairly good agreement with ours although systematic errors on the order of 0.02–0.03 in t_+ are evident in the data of Hopfgartner (*11*) and of Jahn (*13*). Since there does not appear to be a connection between errors in the old data and the temperature, we conclude that t_+ is nearly independent of temperature (at least within ±0.01 in t_+) in the range, 4-25° C.

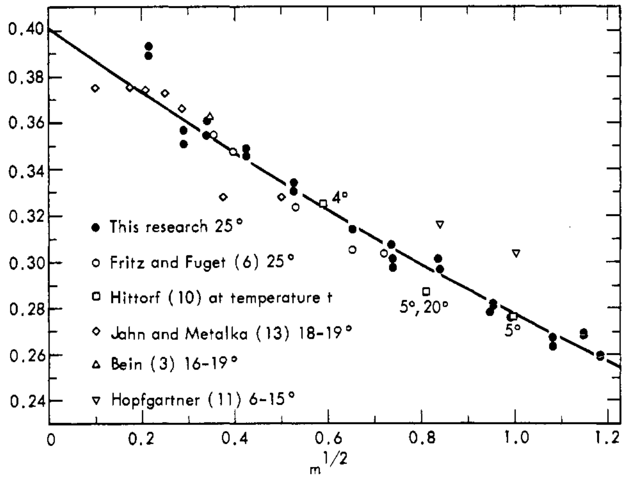

Figure 1. Plot of t_+ of $CuSO_4$ of various authors. All are Hittorf measurements except Fritz and Fuget's, which are moving boundary. The solid line is Equation 5, the least-squares fit of this research. All temperatures are in ° C

It is particularly interesting to note that Hittorf's 1853 data (*10*) appear to be the most accurate of the old data, deviating from ours by no more than 0.01 in t_+ at any concentration. In our opinion, this was a remarkable achievement for an experimentalist working in this field nearly 120 years ago.

APPENDIX

We summarize the results of an extensive unpublished investigation into $CuSO_4$ concentration cells done by D. G. Miller and F. McMurphy in 1959-60. Contrary to the reported experience of others, no Cu electrode system was found whose surface did not rapidly cover over with Cu_2O in $CuSO_4$ solutions. Such electrodes are extremely unreproducible compared to the precision of 10-50 μV required for adequate cell transference numbers. Systems investigated were Cu rod, Cu plated on Pt, saturated 2-phase Cu amalgams, dilute amalgams, and Cu-plated Pt flashed with Hg.

A very smooth series of emf's as a function of concentration was obtained using Hg/Hg_2SO_4 electrodes. However, the appearance of a yellow film of a presumed mercury oxide upon adding $CuSO_4$ solution to the dry Hg/Hg_2SO_4 electrode convinced us that there was a serious systematic error. The known unreliability of the Hg/Hg_2SO_4 electrode at higher pH (*12*) and the substantial disagreement of calculated cell transference numbers with the moving boundary ones of Fritz and Fuget (*6*) provided further evidence of this systematic error.

All measurements with both Cu and Hg_2SO_4 electrodes were done in the absence of air using recrystallized $CuSO_4$. It is possible that equilibrating all solutions with Cu metal, with the associated lowering of the pH, might improve both electrode types. However, there will also be an additional liquid junction potential arising from the extra species created by the equilibration.

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Apparent Molal Volumes of Aqueous Tetraphenyl Arsonium Chloride Solutions at 0°, 25°, and 50° C

FRANK J. MILLERO
Rosenstiel School of Marine and Atmospheric Sciences, The University of Miami, Miami, Fla. 33149

The apparent molal volumes, Φ_V's, of dilute (0.002–0.1*m*) aqueous solutions of tetraphenyl arsonium chloride (Ph_4AsCl) have been determined at 0°, 25°, and 50° C from precision density measurements. The Φ_V's, as a function of $(c)^{1/2}$, approach limiting law behavior at all the temperatures studied. The deviations of the Φ_V's from the limiting law are positive at 0°, and negative at 25° and 50° C. The Φ_V's at infinite dilution have been extrapolated with the aid of the limiting law. The effect of temperature on the Φ_V^0's of the Ph_4AsCl solutions is similar to other common electrolytes, in that $\partial^2\Phi_V^0/\partial T^2 = \partial\Phi_E^0/\partial T$ is negative. The ion-ion and ion-water interactions responsible for the observed behavior of the Φ_V's for Ph_4AsCl solutions are briefly discussed.

The thermodynamic properties of electrolytes with a hydrocarbon portion—e.g., the symmetrical tetraalkylammonium halides, R_4NX's—have been the subject of considerable interest in recent years. The concentration and temperature behavior of the apparent molal volumes, Φ_V's, of organic electrolytes appear to be abnormal compared to common electrolytes like NaCl (*7, 11, 12*). The Φ_V's of organic electrolytes have large negative deviations from the Debye-Hückel limiting law (*1, 3, 7, 11, 12*) and the infinite dilution Φ_V^0's do not appear to go through a maximum as a function temperature (*7, 11, 12*) like the more common electrolytes—e.g., NaCl—(*3, 9*).

This study on the Φ_V's of dilute tetraphenyl arsonium chloride (Ph_4AsCl) solutions was made to provide precise data that may prove useful in interpreting the ion-ion and ion-water interactions of electrolytes with a hydrocarbon portion. The Φ_V^0 of the Ph_4As^+ ion can be used to examine the effect of the aromatic ring on ion-water interactions and compared to the Φ_V^0 results for the R_4N^+ ion (*1, 3, 7, 11, 12*) and the BPh_4^- ion (*8*).