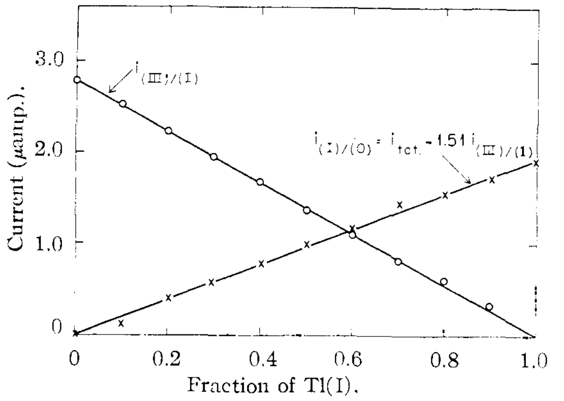

Fig. 2.—Diffusion currents of Tl(III) and Tl(I) in 0.6 *M* HCl; total Tl = 0.332 × 10^{-3} *M*, 25°, no maximum suppressor.

$i_{(III)/(0)}$. By substituting the measured current, $i_{(III)/(I)}$, in the relationship, $i_{(III)/(0)} = \alpha\, i_{(III)/(I)}$ where α = a proportionality constant, the Tl(I) current, $i_{(I)/(0)}$ may be calculated by the expression

$$i_{(I)/(0)} = i_{\text{tot}} - \alpha i_{(III)/(I)} \qquad (1)$$

where i_{tot} = total current corrected for residual current at −0.7 v. *vs.* S.C.E. Figure 2 also shows a plot of $i_{(I)/(0)}$ calculated by equation 1 (using the experimental value α = 1.51) *vs.* fraction of Tl(I). It can be seen that $i_{(I)/(0)}$ is proportional to Tl(I) concentration. At small fractions of Tl(I), $i_{(I)/(0)}$ values were, of course, subject to greater errors because of difficulty of measuring small differences between two relatively large reduction currents. A similar series of measurements with solutions containing a total thallium concentration of 1.00 × 10^{-3} *M* gave essentially similar results.

It can be concluded from these experiments that diffusion current constants for Tl(I) and Tl(III) are independent of the Tl(I)/Tl(III) ratio in Tl(I)–Tl(III) mixtures and hence analysis of such mixtures may be carried out rather easily, by utilizing the linear relationship expressed in equation 1. Certain reducible substances, such as Fe(III) which also produce a constant reduction current in the region 0 to −0.45 v. *vs.* S.C.E. must of course be taken into consideration in analytical applications.

C. Half-wave Potential of Tl(I).—The most precise measurements of the Tl(I)/(0) half-wave potential (*vs.* S.C.E.) reported in the literature appear to be those by Lingane[2] who found $E_{1/2}$ = −0.458 ± 0.003 v. in 0.10 *M* KCl and $E_{1/2}$ = −0.480 v. in 1.0 *M* KCl. The average of three determinations in this Laboratory in 0.10 *M* KCl was $E_{1/2}$ = 0.458 ± 0.003 and a single measurement in 0.1 *M* KCl, 0.005 *M* HCl gave $E_{1/2}$ = −0.462, in reasonable agreement with Lingane's value for 0.1 *M* KCl. In 1.0 *M* HCl, $E_{1/2}$ was found to be −0.491 v., considerably more negative than Lingane's value for 1.0 *M* KCl. This more negative value probably is due, in part, to the fairly large liquid junction potential which exists between 1 *M* HCl and the saturated calomel reference electrode.

Half-wave potentials of the wave appearing in the polarograms of pure Tl(III) solutions were found to be essentially the same[12] as those for pure Tl(I) solution in the same supporting electrolyte. For example, $E_{1/2}$ = −0.463 ± 0.003 and −0.495 ± 0.003 in 0.10 *M* KCl, 0.005 *M* HCl and 1.0 *M* HCl, respectively. Each measurement was based on at least three separate determinations with pure Tl(III) solutions. All waves were tested for reversibility, plotting log $(i - i_{(III)/(I)})/(i_{(III)/(0)} - i)$ *vs.* E_{cor}, and the resulting slopes were found to agree within ±0.004 v. with the expected Nernst slope, −0.059 v. at 25°.

Acknowledgment.—The authors are indebted to Dr. Kurt A. Kraus for helpful criticisms and advice during the course of the work.

(12) This wave is thus associated with the Tl(I) to Tl(0) reduction as pointed out previously by Hughes and Hush (ref. 5).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Transference Numbers in Aqueous Zinc and Cadmium Sulfates[1]

BY ROBERT E. LANG AND CECIL V. KING

RECEIVED FEBRUARY 26, 1954

Transference numbers of zinc and cadmium ions in aqueous solutions of the sulfates at 25° have been determined from the electromotive force of concentration cells with lead amalgam-lead sulfate electrodes. The results for zinc ion agree with those found by Purser and Stokes,[3] and values for cadmium ion are similar.

Transference numbers of the sulfate ion in aqueous zinc and cadmium sulfates were calculated by Wolten and King[2] from the e.m.f. of concentration cells with zinc and cadmium amalgam electrodes. The measurements with zinc sulfate were repeated by Purser and Stokes,[3] who pointed out that the experimental e.m.f. values of Wolten and King were not adequate for the purpose, and that the mathematical treatment and interpretation were improper. The present authors agree with these conclusions, and have made new measurements in order to establish transference numbers in both systems with certainty. The values obtained for zinc ion agree closely with those found by Purser and Stokes, and those for cadmium ion are similar.

Transference numbers of the metal ions were determined directly with the aid of the cells

$$\underset{\text{two phase}}{\text{Pb-Hg}} \mid \text{PbSO}_4(s),\ \text{MSO}_4(m) \mid \text{MSO}_4(\text{ref}),\ \text{PbSO}_4(s) \mid \underset{\text{two phase}}{\text{Pb-Hg}}$$

MSO_4(ref) indicates a constant molality for all

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(1) From a Ph.D. thesis submitted to the Graduate School of New York University by Robert E. Lang.

(2) G. M. Wolten and C. V. King, THIS JOURNAL, **71**, 576 (1949).

(3) E. P. Purser and R. H. Stokes, *ibid.*, **73**, 5650 (1951).

cells, while m is varied over the desired range. The e.m.f. measurements are combined with values for corresponding cells without transference.

Mercury–mercurous sulfate electrodes can, in principle, be used in the same manner, but hydrolysis of the salt limits their application to solutions of sufficient acidity. These electrodes were prepared and employed as a check in the two-molal range. While the precision was poor, the measurements were in complete agreement with the results reported below.

Experimental

The electrode vessels were similar to those described by Bray,[4] but with provision for only one pair of electrodes. The liquid junction was made in the stopcock bore in a vertical section of connecting tubing.

Lead sulfate was prepared as suggested by Bray, by precipitation with zinc sulfate for the zinc cells, with cadmium sulfate for the cadmium cells. Commercial Reagent quality lead sulfate actually gave closely agreeing e.m.f. values.

A 6% lead amalgam was prepared and used essentially as described by Cowperthwaite and LaMer.[5] The amalgam was kept in an atmosphere of purified nitrogen at all times.

All chemicals were of Reagent quality. Water was redistilled in an atmosphere of nitrogen. Nitrogen for deaeration of cell solutions was passed through alkaline pyrogallol, over hot copper gauze, through dilute sulfuric acid and finally through a duplicate of the cell solution.

A stock solution of zinc sulfate (2.191 m) was analyzed for both zinc and sulfate content by standard methods, with agreement to 0.2%. Solutions were prepared by weight dilution; a large amount of the reference solution (0.1003 m) was prepared and its analysis checked. More dilute solutions were made from this. The pH at various dilutions agreed well with values reported in the literature.[6]

Previously dried cadmium sulfate was weighed to make a stock solution (2.400 m) and no other analysis was made. After dilution, all solutions were saturated with lead sulfate and deaerated with nitrogen.

The cells were flushed with nitrogen and filled taking precautions to exclude air. Nitrogen was then bubbled through both solutions for an hour or more, the cells were closed and the junctions made by opening the stopcocks.

The cells were mounted in a water-bath maintained at 25 ± 0.02°. The e.m.f. was measured with a Leeds and Northrup K-1 potentiometer, with 2500 B galvanometer; the shielding method of White[7] was used. In general the e.m.f. came within 0.2 mv. of the steady value in 6 hours, but in some cells a slow drift continued as long as 48 hours. Final readings were constant to ±0.03 mv. for at least 12 hours. All cells were made in triplicate; the maximum divergence in any group was 0.09 mv., the average deviation from the mean less than 0.05 mv. A number of half cells, previously measured against the reference solution, were set up against each other; the steady e.m.f. always came within 0.05 mv. of the expected value.

Results

Average e.m.f. values (E_t) for the zinc sulfate cells are given in Table I. Values labeled E were obtained from the e.m.f. of the cells

$$\text{Pb–Hg} \mid \text{PbSO}_4(\text{s}),\ \text{ZnSO}_4(m) \mid \text{Zn–Hg}$$

as determined by Bray.[4] It is necessary to plot e.m.f. *vs.* log m, interpolate to the molalities of Table I, then subtract the value for 0.1003 m from the others. Since interpolation is difficult, the values above 0.1 m were checked by interpolating activity coefficients from the tables of Robinson and Stokes[8] and inserting in the equation

$$E = -0.0519 \log m\gamma/m\gamma(\text{ref})$$

The agreement is to better than 0.5 mv.

TABLE I

DATA FOR ZINC SULFATE AT 25°

$m(\text{ref}) = 0.1003$

m	E_t, volt	E, volt	$t_{\text{Zn}^{++}}$
2.191	−0.01226	−0.0423	0.187
2.065	− .01194	− .0406	.196
1.933	− .01158	− .0389	.204
1.596	− .01069	− .0347	.224
1.334	− .00997	− .0318	.238
1.036	− .00905	− .0280	.256
0.7710	− .00802	− .0241	.275
.5030	− .00661	− .0188	.301
.2552	− .00387	− .0110	.339
.1003	0	0	.392
.0835	.00117	.0030	.392
.0468	.00439	.0113	.392
.01773	.01011	.0258	.392
.00967	.01392	.0356	.392
.00464	.01908	.0486	.392

Following the procedure of Purser and Stokes,[3] the following equations were found to represent the data, with an average deviation of 0.05 mv. in E_t

$$E_t = 0.392E + 2.42E^2 \quad \text{above } m(\text{ref})$$

$$E_t = 0.392E \quad \text{below } m(\text{ref})$$

Since the transference number is given by dE_t/dE

$$t_{\text{Zn}^{++}} = 0.392 + 4.84E \quad \text{above } m(\text{ref})$$

$$t_{\text{Zn}^{++}} = 0.392 \quad \text{below } m(\text{ref})$$

Values of $t_{\text{Zn}^{++}}$ at the experimental concentrations are included in Table I.

The corresponding data for cadmium sulfate are given in Table II. Values of E, for concentrations below m(ref), were obtained from data of LaMer and Parks[9] on the cells

$$\text{Pb–Hg} \mid \text{PbSO}_4(\text{s}),\ \text{CdSO}_4(m) \mid \text{Cd–Hg}$$

At higher concentrations activity coefficients given by Robinson and Stokes[8] were employed. The data are represented with an average deviation of 0.05 mv. in E_t, by the equations

$$E_t = 0.370E + 2.04E^2 \quad \text{above } m(\text{ref})$$

$$E_t = 0.384E \quad \text{below } m(\text{ref})$$

TABLE II

DATA FOR CADMIUM SULFATE AT 25°

$m(\text{ref}) = 0.0995$

m	E_t, volt	E, volt	$t_{\text{Cd}^{++}}$
2.400	−0.01198	−0.0420	0.199
2.211	− .01154	− .0400	.207
1.961	− .01091	− .0368	.220
1.640	− .01006	− .0334	.234
1.297	− .00905	− .0296	.249
0.975	− .00807	− .0255	.266
.7384	− .00725	− .0221	.280
.5058	− .00610	− .0184	.295
.2361	− .00335	− .0098	.330
.0995	0	0	.370
.05216	.00311	.0080	.384
.01286	.01076	.0284	.384
.004731	.01777	.0463	.384
.001737	.02504	.0652	.384

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[4] U. B. Bray, THIS JOURNAL, **49**, 2372 (1927).

[5] I. A. Cowperthwaite and V. K. LaMer, *ibid.*, **53**, 4333 (1931).

[6] I. M. Kolthoff and T. Kameda, *ibid.*, **53**, 832 (1931).

[7] W. P. White, *ibid.*, **36**, 2011 (1914).

[8] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

[9] V. K. LaMer and W. G. Parks, THIS JOURNAL, **53**, 2040 (1931).

The transference numbers are given by

$$t_{Cd^{++}} = 0.370 + 4.08E \quad \text{above } m(\text{ref})$$
$$t_{Cd^{++}} = 0.384 \quad \text{below } m(\text{ref})$$

Values for the experimental concentrations are given in Table II.

Discussion

Purser and Stokes[3] point out that zinc amalgams deteriorate unless protected from oxygen. Apparently, the measurements of Wolten and King were inaccurate because the solutions were not deaerated and protected. Triplicate cells agreed well since the amalgam was prepared in small lots and was uniform for each set of cells.

Some of the transference numbers found for cadmium ion are plotted *vs.* $\sqrt{m}$ in Fig. 1, with values found by the Hittorf method at 18°, as summarized by Jahn.[10] The temperature difference would affect only the third decimal place.

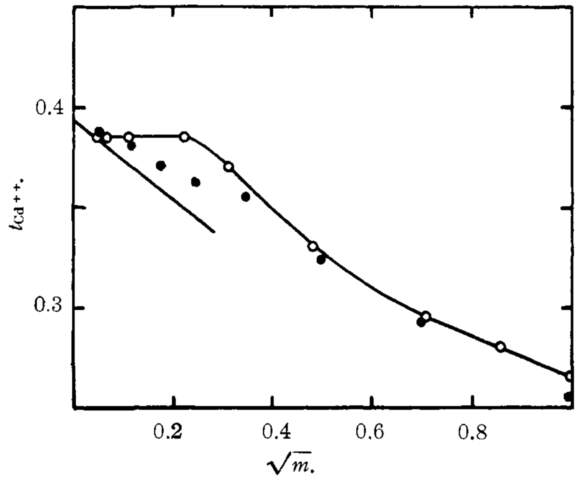

Fig. 1.—Transference numbers in cadmium sulfate: ○, this work, 25°; ●, values summarized by Jahn, 18°; slope of straight line, −0.193.

No data have been found from which the limiting conductance Λ^0 for cadmium sulfate at 25° may be established. At 18°, $\Lambda^0_{CdSO_4}$ is about one unit lower[11] than $\Lambda^0_{ZnSO_4}$, and if the temperature coefficients are the same, $\Lambda^0_{CdSO_4}$ may be taken as 132. Since $\lambda^0_{SO_4^{=}} = 80$, the limiting transference number $t^0_{Cd^{++}}$ should be 0.393 and the limiting slope *vs.* $\sqrt{m}$ should be[12] −0.193. These values are indicated by the straight line of Fig. 1. Corresponding values for zinc ion are[3] 0.398 and −0.184.

It is believed that values of E in the tables are correct to better than 0.5 mv., with the possible exception of one or two points nearest m(ref) in each case. In obtaining the relation between E_t and E, it may be better to use a graphical rather than a least squares method, or in some way give points near m(ref) least weight. The graphical method was used in the case of cadmium sulfate.

Consistency of the data may be shown by plotting E_t *vs.* E below m(ref), E_t/E *vs.* E above m(ref). If E contained irregular errors, the points would not lie near a smooth line. If all errors in E were in the least favorable direction, which is unlikely, t_+ could differ as much as 0.01 at m(ref) and 0.005 or less at other concentrations. It seems more probable that no value of t_+ is in error by more than 0.005. It is, of course, quite certain that t_+ does not become negative at any concentration employed.

Errors of interpolation of the e.m.f. of cells without transference, and use of activity coefficients, could be avoided by including zinc and cadmium electrodes in the cells to measure E directly at each concentration.

[10] H. Jahn, *Z. physik. Chem.*, **58**, 641 (1907).

[11] "Landolt-Börnstein Tabellen," 5th Edition, Vol. II, p. 1080.

[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 1st Edition, Reinhold Publ. Corp., New York, N. Y., 1943, pp. 172, 537.

NEW YORK 3, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF KANSAS]

Mechanism of the Tungstate Catalyzed Reduction of Perchlorate by Stannous Chloride

BY G. P. HAIGHT, JR.[1]

RECEIVED APRIL 16, 1954

The reduction of perchlorate by stannous chloride is catalyzed by the presence of tungstate in concentrated hydrochloric acid. The reaction is zero order with respect to stannous and first order with respect to perchlorate and tungstate. Catalysis is attributed to complex formation between tungstate and perchlorate. This reaction is discussed in terms of information on the catalytic reduction of perchlorate by stannous tin using both tungstate and molybdate as catalyst.

Introduction

The catalytic effect of tungstate on the reduction of perchlorate observed polarographically by Laitinen and Ziegler[2] has been found to be maintained when stannous chloride is substituted for the dropping mercury electrode. This is especially interesting in view of the previously observed catalytic effect of molybdate on the reduction of perchlorate polarographically,[3,4] with stannous ion,[4] and with metallic zinc.[5a,b] To study the tungstate catalysis high concentrations of HCl must be used to prevent precipitation of tungstic acid. Under these conditions molybdate does not catalyze the reduction by stannous chloride since molybdenum is reduced to the trivalent form which is inert.[4] Laitinen and

[1] Department of Chemistry, Swarthmore College, Swarthmore, Penna. Paper presented at the 126th Meeting of the A.C.S., New York, N. Y., September, 1954.

[2] H. A. Laitinen and W. A. Ziegler, THIS JOURNAL, **75**, 3045 (1953).

[3] R. Holtje and R. Geyer, *Z. anorg. Chem*, **246**, 265 (1941).

[4] G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

[5] (a) G. P. Haight, Jr., and W. F. Sager, THIS JOURNAL, **74**, 6056 (1952); (b) G. P. Haight, Jr., *Anal. Chem.*, **25**, 642 (1953).