TABLE II[a]

DERIVATIVES OF MONOPYRIDINE IODINE (I)

Salt	M. p., °C. (uncor.)	Yield, %	Per cent. Iodine as I$^+$ Calcd.	Found	
o-Nitrobenzoate	120–121	36	34.1	33.9	34.0
m-Nitrobenzoate	[b]	55	34.1	34.1	33.8
3,5-Dinitrobenzoate	157dec.	64	30.0	30.0	29.7
α-Naphthoate	109–112d.	48	33.6	33.5	33.5
p-Chlorobenzoate	105–109d.	47	35.1	35.3	35.1
2,4-Dichlorobenzoate[c]	105–113d.	18	32.0	31.6	31.6
p-Bromobenzoate	142–145	62	31.2	30.8	30.9
m-Bromobenzoate	84–93dec.	9	31.2	31.0	30.9
p-Iodobenzoate	152–155d.	58	28.0	27.7	27.7
m-Iodobenzoate	94–96dec.	8	28.0	27.9	27.9
p-Fluorobenzoate	158–162	50	36.8	36.8	36.7
m-Fluorobenzoate	81–84	37	36.8	36.8	36.5
o-Fluorobenzoate[d]	[b]	11	36.8	36.5	36.4
p-Methylbenzoate	118–121d.	60	37.1	37.1	37.0
Acid phthalate[e]	[b]	69	34.4	34.2	34.2
Stearate	64–66	51	25.9	25.9	25.6

[a] The success of the reaction for the synthesis of the iodine salt appears to decrease with decreasing electron withdrawing power of the ring substituents. Moreover, the yield of the desired product seems to depend upon the position of the substituent, decreasing in the order *p* > *m* > *o*. The reaction is unsuccessful when applied to acids which contain *o*-substituents exhibiting weak +I or +T effects, and to acids substituted in any position by groups, such as hydroxy and amino, which exhibit strong +T effects. [b] Decomposes over a wide range. [c] These compounds were prepared by treating the silver salts with a large excess of pyridine and less than the theoretical amount of iodine. If treated under ordinary conditions, a residue was obtained from which the acid could be isolated by extracting with Skellysolve A and removing the excess iodine with mercury. [d] This compound could not be salted out of solution, but the residue remaining after evaporation of the chloroform gave the compound after continuous washing with Skellysolve A and ether. These washings on evaporation yielded crystals identified as the acid. [e] This compound salted out of solution as a heavy, viscous liquid which crystallized on standing in the cold.

tion of sodium carbonate was added until the solution tested basic to litmus. Nitric acid was then added dropwise until the solution tested acid to litmus. Any solid present was filtered off and a hot aqueous solution of an equivalent amount of silver nitrate was added. The silver salt was removed by filtration, washed with distilled water and alcohol, and dried at 70°.

Preparation of Positive Iodine Compounds.—To a suspension of a few grams of the silver salt of the acid in dry chloroform, iodine was added with shaking until the solution remained light orange in color. A slight excess of the coördinating base was then added and the addition of iodine was continued until the solution again remained colored after shaking. The silver iodide was filtered and a volume of Skellysolve A from one to four times the volume of the solution, depending upon the solubility of the compound being prepared, was added. The solution was allowed to stand overnight in the dark and the solid which had precipitated was filtered, washed with ether (or with Skellysolve if the compound was soluble in ether), and dried *in vacuo* over sulfuric acid. The positive iodine compounds are white or pale yellow crystalline solids.

Analysis of Positive Iodine Compounds.—To a 0.05-g. sample of the iodine compound, an excess of potassium iodide solution was added. Five ml. of carbon tetrachloride was then added and the solution acidified with a few drops of acetic acid. The organic acid which separated was retained in the carbon tetrachloride layer and did not interfere with the analysis. Finally, the free iodine in the solution was titrated with a 0.01 *N* sodium thiosulfate solution.

Acknowledgment.—The authors wish to thank the Upjohn Company for their grant during the time this work was carried out.

Summary

Thirty-one new compounds of positive univalent iodine coördinated with pyridine or α- or β-picoline have been prepared.

LAWRENCE, KANSAS RECEIVED SEPTEMBER 15, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Transference Numbers of Zinc and Cadmium Sulfates at 25°, as Functions of the Concentration

BY GERARD M. WOLTEN AND CECIL V. KING

The method of determining transference numbers by means of the ratio of the electromotive forces of concentration cells with transference to those without[1] is thought by some[2] to be capable of great accuracy.

To throw further light on this method and to provide additional data on transference numbers, we have applied this method to solutions of zinc sulfate and cadmium sulfate at 25°.

Experimental

To measure the e. m. f.'s of zinc and cadmium sulfate concentration cells with transference, of the type MHg, MSO$_4$(m'), MSO$_4$(m''), MHg, where MHg indicates an amalgam, we used a cell of the same design as used by Stokes and Levien.[3] A Leeds and Northrup type K-1 potentiometer and a no. 2500B galvanometer, with 8000 to 10,000 ohms in series for suitable damping, were used. To shield against electric leakage and stray currents, the equipotential shielding method of White[4] was used. The thermostat was kept at 25.00 ± 0.02°. All cells reached equilibrium within one hour and stayed constant for at least several hours. Duplicate cells were reproducible within 0.05 mv., each cell being constant within 0.03 mv. or better.

Materials

Zinc, zinc sulfate, and cadmium sulfate were the "C. P. Analysed" reagent grade of the J. T. Baker Chemical Co. C. P. triply distilled mercury was obtained from F. W. Berk & Co. Cadmium was obtained from the Udylite Corp. and by spectrographic analysis shown to be 99.95%

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[1] Harned and Dreby, THIS JOURNAL, **61**, 3113 (1939).

[2] Taylor and Taylor, "Elementary Physical Chemistry," 3rd ed., D. Van Nostrand Co., New York, N. Y., 1942, p. 388.

[3] Stokes and Levien, THIS JOURNAL, **68**, 333 (1946).

[4] White, *ibid.*, **36**, 2011 (1914).

pure. Distilled water was redistilled from a quartz vessel and swept with nitrogen. The concentrations of the zinc sulfate solutions were determined by titration with potassium ferrocyanide, using diphenylamine as internal indicator.[5] The titrations were performed upon weighed samples of the solutions, so that the molalities followed immediately. The solutions of concentrations lower than 0.5 molal were made by weight dilution from the more concentrated ones. The solutions of cadmium sulfate were made by dissolving the required amounts of anhydrous salt in known weights of water, since it is a standard analytical procedure to determine cadmium quantitatively by weighing it as the sulfate.[6] From the works of Puschin,[7] Bijl,[8] Henderson and Stegeman,[9] Bray,[10] Cowperthwaite and LaMer,[11] and LaMer and Parks,[12] it is evident that all of the amalgams used in this work exhibit an unvarying e. m. f. over a wide range of concentrations of the metal in mercury, including the concentrations used here. Since it was thus unnecessary to reproduce the amalgam concentrations exactly for each run, it was found most convenient to prepare the amalgams in small batches, using a fresh one for each determination. This eliminated any problems of proper storage of these materials. The amalgams were made by heating about 35 g. of mercury and enough zinc or cadmium to make 6 or 8% amalgams, respectively. The heating was done in a stream of nitrogen.

Experimental Results

CONCENTRATION CELLS WITH TRANSFERENCE AT 25°

TABLE I

Zinc sulfate, $m' = 2.059$ molal

m''	E. m. f., v.
2.270	0.00200
2.059	.00000
1.640	− .00370
1.333	− .00515
0.9693	− .01050
.4852	− .01940
.1055	− .03052
.05079	− .03827
.05054	− .03834
.01020	− .06310
.005052	− .07769
.001130	− .09300
.0005669	− .09937

TABLE II

Cadmium sulfate. $m' = 1.003$ molal

m''	E. m. f., v.
2.886	0.02009
2.503	.01722
2.013	.01103
1.526	.00693
1.003	.00000
0.5025	− .00960
.09852	− .02295
.04924	− .03755
.009911	− .05601
.004983	− .06543
.001259	− .08129
.0007394	− .08637

The corresponding concentration cells without transference are of the type

$$\text{MHg, MSO}_4(m'),\ \text{PbSO}_4(\text{s}),\ \text{PbHg},\ \text{PbSO}_4(\text{s}),\ \text{MSO}_4(m''),\ \text{MHg}$$

The e. m. f. of such a cell is the difference between the e. m. f.'s of two cells of the type

$$\text{MHg,MSO}_4(m).\ \text{PbSO}_4(\text{s}),\ \text{HgPb}$$

where m first assumes the value m' and then m''. Bray[10] investigated such cells for M = Zn, and LaMer and Parks[12] for M = Cd. From these data, the e. m. f.'s of zinc sulfate and cadmium sulfate concentration cells without transference have been calculated. If one chooses identical concentrations for the reference electrodes of both types of cells, one can then use the well-known relationship $dE_t/dE = t$, to calculate the transference number (t) of the ion with respect to which the terminal electrodes are not reversible, the sulfate ion in this case. E_t denotes the e. m. f. of a cell with and E the e. m. f. of a cell without transference. For the computation of the differential coefficient, we used the method of Rutledge,[13] following the example of Stokes and Levien.[3,14] Unlike graphical methods of differentiating, the method of Rutledge enables one to utilize the full degree of accuracy of the original data. In this case, the gain is slight, but we like to draw attention to the method, which is an intriguing one.

Discussion

The anionic transference numbers of zinc sulfate and of cadmium sulfate are shown graphically in Figs. 1 and 2, where they are compared with the values obtained by Hittorf, Jahn and co-workers.[15]

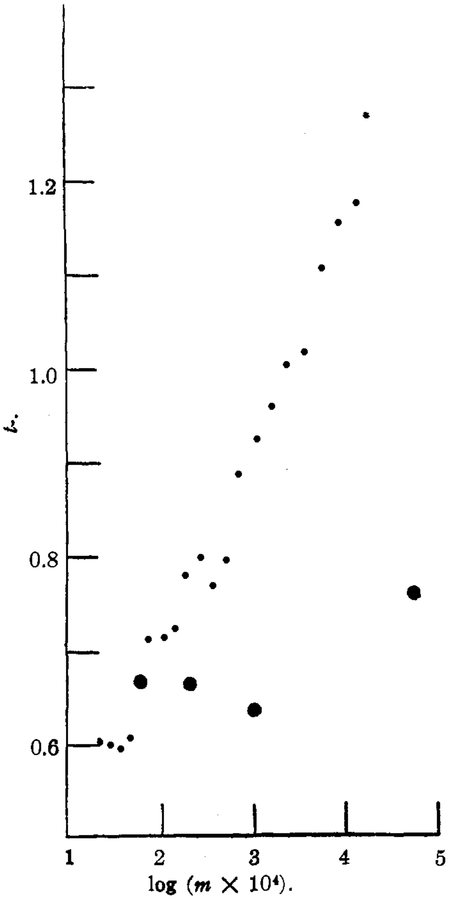

Fig. 1.—Zinc sulfate: small circles. present data; large circles, data of Hittorf. *et al.*

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[5] "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., New York, N. Y., p. 1064 ff.

[6] *Ibid.*, p. 202.

[7] Puschin, *Z. anorg. Chem.*, **36**, 210 (1903).

[8] Bijl, *Z. physik. Chem.*, **41**. 641 (1902).

[9] Henderson and Stegeman, THIS JOURNAL, **40**, 84 (1918).

[10] Bray, *ibid.*, **49**, 2372 (1927).

[11] Cowperthwaite and LaMer, *ibid.*, **53**, 4333 (1931).

[12] LaMer and Parks, *ibid.*, **53**, 2040 (1931).

[13] Rutledge, *Phys. Rev.*, **40**, 262 (1932).

[14] Stokes and Levien, THIS JOURNAL, **68**, 1852 (1946).

[15] Jahn, *Z. physik Chem.*, **33**, 649 (1900).

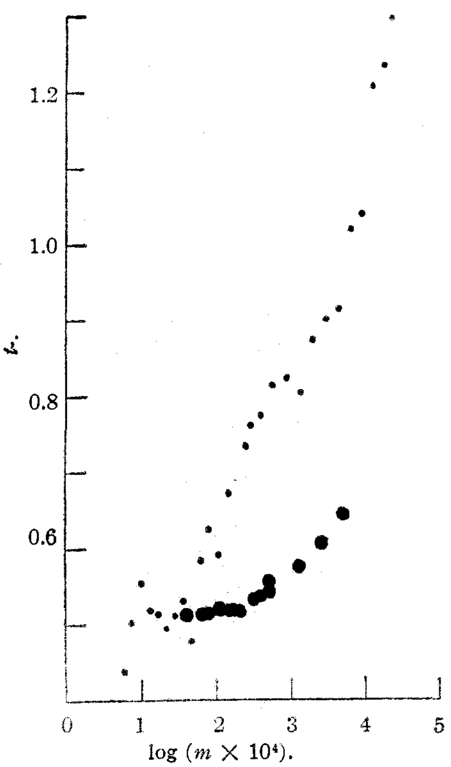

Fig. 2.—Cadmium sulfate: small circles, present data; large circles, data of Redlich and Goldlust, as reported by Jahn.[15]

We have no explanation to offer for the discrepancy. We can, however, point out that the presence of complex-formation, which our results indicate, is strongly supported by the low values of the activity coefficients. According to Masaki and Ikkatai,[16] Bray,[10] and LaMer and Parks,[12] the activity coefficients of both zinc and cadmium sulfate are about 0.08 in a 0.3 molal solution. This is approximately the concentration above which our results indicate negative cationic transference numbers. It has also been shown by McBain and Van Rysselberghe[17] that the cations in solutions of magnesium, zinc and cadmium sulfates form negatively charged complexes in the presence of excess alkali sulfate. The cationic and the anionic transference numbers must necessarily add up to unity. We have determined the anionic transference number. The cationic transference number can be determined in a quite similar manner, by means of the cell

$$\mathrm{PbHg,\ PbSO_4(s).\ MSO_4}(m'),\ \mathrm{MSO_4}(m''),\ \mathrm{PbSO_4(s).\ PbHg}$$

The use of lead amalgam requires the rigid exclusion of air,[10] and a cell must be used which makes this possible. Such a cell vessel differs from the one used in the present investigation. For this reason, measurements on the above cell have not been included in this work, but it is hoped to make such a report in a future communication from this department.

Summary

The transference numbers of zinc and cadmium sulfate have been investigated at 25° by the method of electromotive forces.

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RECEIVED[18] JULY 14, 1948

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(16) Masaki and Ikkatai, *Bull. Chem. Soc. Japan*, **7**, 238-246 (1932).

(17) McBain and Van Rysselberghe, THIS JOURNAL, **52**, 2326 (1930).

(18) Original manuscript received December 18, 1947.

[CONTRIBUTION NO. 57 FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF TENNESSEE]

The Salts of Perrhenic Acid. II. The Iron Family and Manganese[1]

BY WILLIAM T. SMITH, JR., AND GROVER E. MAXWELL

The perrhenates of cobalt, nickel and manganese have been previously prepared and the colors and compositions of these salts reported.[2,3,4]

This paper deals with a more extensive examination of the composition and properties of the perrhenates of these metals in the divalent state as well as the perrhenates of iron in both di- and trivalent states.

Preparation of the Salts.—The carbonate or hydroxide of the metal was treated with a solution of perrhenic acid[5] and the hydrated salt was crystallized from the solution by evaporation at room temperature. All of these salts are deliquescent at the prevailing humidity in Knoxville during summer and were consequently crystallized by evaporation in a vacuum. In winter the crystallizations take place spontaneously in contact with the ambient air. The preparation of ferrous perrhenate was first attempted in an atmosphere of hydrogen. In spite of the precautions, approximately 10% of the iron present was oxidized to the ferric state, and the perrhenate so obtained suddenly became very viscous and black on evaporation at room temperature in a vacuum. This black semi-solid was very soluble in water giving a brown solution which on repeated evaporation gave the black semi-solid again. This solid was very soluble in ether although tests showed that neither the pure ferrous nor ferric perrhenate was

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(1) This paper is based on a thesis presented by Grover E. Maxwell to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the M.S. degree, August 4, 1948.

(2) Briscoe, Robinson and Rudge, *J. Chem. Soc.*, 2211 (1931).

(3) Druce, *ibid.*, 966 (1938).

(4) Wilke-Dorfurt and Gunzert, *Z. anorg. allgem. Chem.*, **215**, 369 (1933).

(5) Smith and Long, THIS JOURNAL, **70**, 354 (1948).