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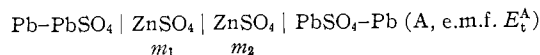
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF MICHIGAN  
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### An Alternative Computation of the Transference Numbers in Zinc Sulfate Solutions

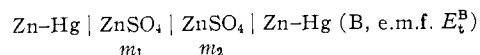
BY R. H. STOKES

RECEIVED FEBRUARY 14, 1955

Lang and King<sup>1</sup> have recently published electromotive force measurements on the cell with transference



from which, in combination with activity coefficient data, they obtained by the method of Stokes and Levien<sup>2</sup> the transference numbers at 25° for the ions over the concentration range  $m_2 = 0.005$  to 2  $M$ . Their data are in satisfactory agreement with those obtained earlier by Purser and Stokes<sup>3</sup> using the cell



The activity coefficient data used in both these researches were those of Bray<sup>4</sup> for solutions below 0.1  $M$  in concentration, and of Stokes and Robinson<sup>5</sup>—above 0.1  $M$ ; the former were obtained from e.m.f. measurements on cells without transference, and the latter from isopiestic vapor pressure measurements. Now both sets of transference numbers exhibit rather sudden changes in the vicinity of 0.1  $M$ , and there is clearly a possibility that this is a spurious effect arising from experimental errors in the activity data. Another possible source of spurious change lies in the fact that both transference number researches employed two separate equations to represent the relation between  $E_t$  and  $E$  ( $E$  = e.m.f. of cell without transference), *viz.*, a linear equation below 0.1  $M$  and a quadratic above 0.1  $M$ . The transference number is given by the differential relation  $t = dE_t/dE$ ; differential coefficients are notoriously sensitive to experimental error near the ends of the range of the equations from which they are obtained, and the region of 0.1  $M$  is subject to this objection. I have now made an alternative computation of the transport numbers, avoiding the use of the activity coefficient data altogether, and employing a single cubic equation to represent the relation between  $E_t$  and  $E$  over the entire range, as follows:

From cell A, we have  $t_{\text{Zn}^{++}} = dE_t^A/dE$ , and from cell B,  $t_{\text{SO}_4^{--}} = 1 - t_{\text{Zn}^{++}} = dE_t^B/dE$ . Hence  $dE = dE_t^A + dE_t^B$ , and by integration between  $m_1$  and  $m_2$

$$E = E_t^A + E_t^B \quad (1)$$

This of course assumes that  $m_1$  and  $m_2$  are the same

- (1) R. E. Lang and C. V. King, *THIS JOURNAL*, **76**, 4716 (1954).
- (2) R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333, 1852 (1946).
- (3) E. P. Purser and R. H. Stokes, *ibid.*, **73**, 5650 (1951).
- (4) U. B. Bray, *ibid.*, **49**, 2372 (1927).
- (5) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

in both cells. By graphical interpolation of suitable deviation functions, values of  $E_t^A$  were obtained corresponding to the e.m.f.'s of cell A for the molalities used in cell B by Purser and Stokes, and values of  $E$  were obtained from equation 1. The cubic equation 2 was then obtained by the method of least squares

$$E_t^B = 0.6281E + 1.257 \times 10^{-3} E^2 + 1.734 \times 10^{-5} E^3 \quad (2)$$

This reproduced the nine experimental  $E_t^B$  values with an average deviation of 0.08 mv. The transport numbers are therefore given by

$$t_{\text{SO}_4^{--}} = 1 - t_{\text{Zn}^{++}} = 0.6281 + 2.514 \times 10^{-3} E + 5.202 \times 10^{-5} E^2 \quad (3)$$

These values are shown in the figure along with those reported by Lang and King and by Purser and Stokes. The value obtained by equation 3 for the most dilute solution (0.373 at 0.0048  $M$ ) is omitted, as it is obtained from a differential coefficient at one extreme of the range of validity of equation 2; that for the most concentrated solution is also suspect, but is included since equation 2 fitted very accurately in this region, and also since the experimental e.m.f.'s in this region are more reliable.

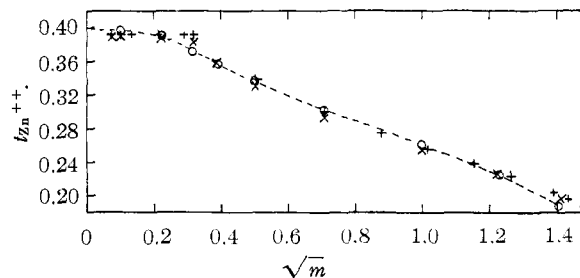


Fig. 1.—Zinc ion transference numbers versus square root of molality:  $\circ$ , present method;  $\times$ , data of Purser and Stokes (cell B);  $+$ , data of Lang and King (cell A).

Over most of the range, the transport numbers from all three methods differ only in the third place, which is as good as can be expected of the Helmholtz method. However, the new calculations reported here give a much smoother curve in the region of 0.1  $M$ , suggesting that the abrupt change found by the earlier methods is in fact largely spurious.

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### The Preparation of Iodopentamminecobalt(III) Salts from Cobalt(II)

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RECEIVED FEBRUARY 18, 1955

Weak acid solutions of iodopentamminecobalt(III) ion react with iodide ion to form iodine and cobalt(II).<sup>1</sup> Because of this reaction iodopentamminecobalt(III) salts cannot be prepared in aqueous solution by the replacement of the water molecule in the aquopentamminecobalt(III) ion by iodide ion. Instead iodopentamminecobalt(III) iodide is prepared by heating aquopentammineco-

- (1) R. G. Yalman, *THIS JOURNAL*, **75**, 1842 (1953).

balt(III) iodide in an oven at 60° for eight hours.<sup>1,2</sup> The product is further purified and converted to the nitrate by grinding it several times with cold saturated ammonium nitrate solutions. This procedure is long and involves the preparation of five different cobalt(III) complexes. The over-all yield based on cobalt(II) is about 25%.

When aquopentamminecobalt(III) iodide is prepared by the neutralization of hydroxopentamminecobalt(III) iodide with acetic acid and the filtrate is allowed to evaporate slowly in an open dish, large crystals of iodopentamminecobalt(III) iodide are formed. In addition to cobalt(II) and iodide ion this solution also contains iodine and ammonia. Subsequent experiments showed that both iodopentamminecobalt(III) and hexamminecobalt(III) chlorides, bromides, and nitrates were formed by the oxidation of cobalt(II) with iodine in ammoniacal solutions containing high concentrations of the corresponding ammonium salts. However if sufficient iodide ion (0.025 *M* at *pH* 8.5 and 0.1 *M* at *pH* 9) was present to prevent the hydrolysis of iodine, only iodopentamminecobalt(III) salts were obtained. The oxidation of cobalt(II) by iodine occurs so much more rapidly than the reduction of iodopentamminecobalt(III) by iodide ion in the ammoniacal solutions that iodopentamminecobalt(III) iodide was obtained in the presence of 2 *M* iodide ion. The mechanisms of these reactions are being investigated at the present time.

Because of their slight solubility<sup>3</sup> iodopentamminecobalt(III) chloride, bromide, iodide and nitrate can be prepared nearly quantitatively from cobalt(II). The slightly soluble sulfate of this series precipitates slowly and is best prepared by treating the chloride salt with cold concentrated sulfuric acid. Similarly the very soluble perchlorate salt is prepared by treating iodopentamminecobalt(III) chloride with cold concentrated perchloric acid.

#### Experimental

In each of the preparations described below the stoichiometric amounts of cobalt(II) and iodine are used and the theoretical yield is ten grams. The final solutions are five molar in the corresponding ammonium salts, except the ammonium chloride solution which is ten molar, and approximately one molar in aqueous ammonia.

**Iodopentamminecobalt(III) Nitrate.**—To a suspension of 3.2 g. of powdered iodine in 40 ml. of a solution containing 20 g. of ammonium nitrate, 7.4 g. of cobalt(II)

nitrate 6-hydrate and 0.5 g. of ammonium iodide, add with stirring 10 ml. of concentrated aqueous ammonia. An apple green precipitate begins to form immediately. After all of the ammonia has been added, continue stirring for 20–30 minutes or until all of the iodine has reacted. Wash the bulky precipitates twice by decantation with 100 ml. of cold water and once with 100 ml. of ethanol and then transfer it to a filter with the aid of ethanol. Any unreacted iodine can be removed by passing ethanol through the product which is finally washed with ether and air-dried. The yield of iodopentamminecobalt(III) nitrate is 9.4 g. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_2$ : Co, 14.91; I, 32.10. Found: Co, 14.89, 14.93; I, 32.06, 32.10.

**Iodopentamminecobalt(III) Chloride.**—This compound is prepared in the same way as the nitrate except that 7 g. of cobalt chloride(II) 6-hydrate, 25 g. of ammonium chloride and 3.7 g. of iodine were used. A 93% yield of a dark green product was obtained. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{Cl}_2$ : Co, 17.24; I, 37.11. Found: Co, 17.22, 17.24; I, 37.06, 37.11.

**Iodopentamminecobalt(III) Bromide.**—In the preparation of this salt 5.5 g. of cobalt(II) chloride 6-hydrate, 20 g. of ammonium bromide and 2.9 g. of iodine were used. The dark green product weighed 9.6 g. and contained no chloride ion. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{Br}_2$ : Co, 13.69; I, 29.46. Found: Co, 13.66, 13.68; I, 29.48, 29.50.

**Iodopentamminecobalt(III) Iodide.**—This compound was made in the same way as the nitrate but 4.6 g. of cobalt(II) chloride, 30 g. of ammonium iodide and 2.4 g. of iodine were used. Although the product has a deep brown cast, both it and the mother liquor were shown to be free of hexamminecobalt(III) iodide. The yield is 9.3 g. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{I}_2$ : Co, 11.24; I, 72.54. Found: Co, 11.20, 11.17; I, 72.57, 72.50.

**Iodopentamminecobalt(III) Sulfate.**—Seven and one-half g. of iodopentamminecobalt(III) chloride in a mortar cooled in ice is ground with 10 ml. of ice-cold concentrated sulfuric acid. The acid is added in small portions while hydrogen chloride is being evolved. After the addition of the acid is complete the paste is mixed for an additional ten minutes and then transferred to a sintered glass filter with the aid of one hundred ml. of ice-cold alcohol. A little decomposition occurs due to local heating. The deep green precipitate is washed on the filter with alcohol until the filtrate is acid free and then with ether and air-dried. The yield is 9.3 g. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{SO}_4$ : Co, 16.07; I, 34.58. Found: Co, 16.09, 16.12; I, 34.59, 34.60.

**Iodopentamminecobalt(III) Perchlorate.**—This compound is made in the same way as the sulfate except that 9.5 g. of iodopentamminecobalt(III) chloride and 10 ml. of perchloric acid are used. The acid free product can be recrystallized by dissolving it quickly in 250 ml. of water at 40–45°, filtering, and allowing the filtrate to drop into an equal volume of ice-cold 50% perchloric acid. After standing for several hours, the lustrous deep green product is filtered, washed free of acid with alcohol, followed by ether and finally air-dried. A yield of 8.5 g. of the readily soluble iodopentamminecobalt(III) perchlorate is obtained. *Anal.* Calcd. for  $[\text{Co}(\text{NH}_3)_5\text{I}](\text{ClO}_4)_2$ : Co, 12.55; I, 27.00. Found: Co, 12.57, 12.59; I, 27.00, 27.04.

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(2) A. Werner, *Ber.*, **41**, 3008 (1908); F. Basolo and R. K. Murmann, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 173.

(3) F. Ephraim, *Ber.*, **56**, 1531 (1923).