mercial Solvents Corporation for supplying the nitroparaffin samples.
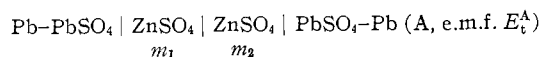
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

An Alternative Computation of the Transference Numbers in Zinc Sulfate Solutions

By R. H. STOKES

RECEIVED FEBRUARY 14, 1955

Lang and King[1] have recently published electromotive force measurements on the cell with transference

$$Pb-PbSO_4 \mid ZnSO_4 \mid ZnSO_4 \mid PbSO_4-Pb \text{ (A, e.m.f. } E_t^A)$$
$$m_1 \qquad m_2$$

from which, in combination with activity coefficient data, they obtained by the method of Stokes and Levien[2] 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[3] using the cell

$$Zn-Hg \mid ZnSO_4 \mid ZnSO_4 \mid Zn-Hg \text{ (B, e.m.f. } E_t^B)$$
$$m_1 \qquad m_2$$
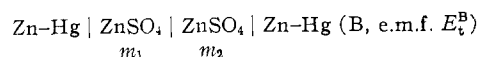
The activity coefficient data used in both these researches were those of Bray[4] for solutions below 0.1 M in concentration, and of Stokes and Robinson[5]—above 0.1 M; the former were obtained from e.m.f. measurements on cells without transference, and the latter from isopiestic vapor pressure measurements. 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 $t_{Zn^{++}} = dE_t^A/dE$, and from cell B, $t_{SO_4^{--}} = 1 - t_{Zn^{++}} = dE_t^B/dE$. Hence $dE = dE_t^A + dE_t^B$, and by integration between m_1 and m_2

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

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

$$t_{SO_4^-} = 1 - t_{Zn^{++}} = 0.6281 + 2.514 \times 10^{-3}E + 5.202 \times 10^{-5}E^2 \quad (3)$$

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.
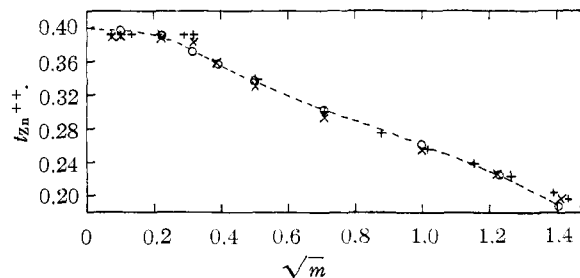

Fig. 1.—Zinc ion transference numbers versus square root of molality: ⊙, present method; X, data of Purser and Stokes (cell B); +, data of Lang and King (cell A).

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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WESTERN AUSTRALIA
NEDLANDS, WESTERN AUSTRALIA

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

By RICHARD G. YALMAN

RECEIVED FEBRUARY 18, 1955

Weak acid solutions of iodopentamminecobalt(III) ion react with iodide ion to form iodine and cobalt(II).[1] 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).