melt at 122°, was prepared from the sample of methacrylic acid and found to melt at 120–121°.

Fraction B1b (b. r., 68–70° at 8.2 mm.) was neutralized with sodium hydroxide and distilled (86° at 22 mm., $n^{20}D$, 1.4087, $d^{20}_4$, 1.0450, and saponification equiv., 80.2). These constants for ethyl α-acetoxypropionate are, respectively: 86° at 22 mm., 1.4085, 1.0441 and 80.1. Further reasons for concluding that this sample was ethyl α-acetoxypropionate are: saponification yielded ethanol, identified as the 3,5-dinitrobenzoate (m. p., 94–95°); acetanilide (m. p., 115°) was obtained by refluxing the sample with aniline; and the temperature at which a 50-50 solution by volume of the sample and *n*-heptane separated into 2 layers was 3° (50-50 solutions of *n*-heptane-ethyl α-acetoxypropionate and *n*-heptane-ethyl α-acetoxyisobutyrate became immiscible at 3° and −20 to −25°, respectively).

It was assumed that ethylene was the gaseous olefin produced in experiments 5A–5C.

**Polymeric Carbomethoxymethyl Acrylate.**—When emulsion polymerized as described previously,[3] 10 g. of the acrylate of methyl glycolate yielded 8.5 g. of soft and pliable polymer that became brittle at 15 to 20°. Mass polymerization occurred readily when a sealed tube of the monomer containing 1% benzoyl peroxide was allowed to stand at room temperature.

The polymer (0.25 g. per 5 ml. solvent) was soluble in acetone, ethyl acetate, methyl lactate, dioxane, nitromethane and ethylene chloride; the last two compounds seemed to have highest solvent power. The polymer was insoluble in toluene, β-butoxyethyl acetate, heptane, ethanol and water.

**Polymeric Carbomethoxymethyl Methacrylate.**—When the emulsion of the polymer was coagulated, the polymer separated as a fine powder that filtered with difficulty. At approximately 65° the polymer agglomerated, yielding a granular product that was easily filtered or decanted. Although only 18.5 g. polymer was obtained from 25 g. monomer, probably the polymerization yield was nearly quantitative, since little or no monomer was volatilized by the distillation of water from the emulsion prior to coagulation.

Mass polymerization in a sealed tube at 63° of monomer containing 0.1% benzoyl peroxide yielded a transparent, colorless casting in a few hours. The polymer was hard at room temperature but softened between 52 and 58°. A hard polymer was obtained also by heating monomer in the absence of benzoyl peroxide at 63° overnight.

The polymer (0.25 g. per 5 ml. solvent) gelled without dissolving in acetone, ethyl acetate, methyl lactate, dioxane, nitromethane, ethylene chloride, and β-butoxyethyl acetate. It swelled slightly in toluene, and was insoluble in heptane, ethanol and water.[16]

## Summary

Several α-carbalkoxyalkyl acrylates and methacrylates were prepared by pyrolyzing the α-acetoxypropionate of methyl glycolate and methyl lactate and the α-acetoxyisobutyrate of methyl glycolate, methyl lactate and ethyl lactate. The relation between ester structure and thermal stability is discussed.

The acrylate and methacrylate of methyl glycolate were polymerized, and certain properties of the polymers determined.

[16] Strain (ref. 3) polymerized carbomethoxymethyl methacrylate at 100° and obtained a soluble polymer. Possibly the increased solubility of his polymer was due to lower molecular weight.

PHILADELPHIA 18, PA. RECEIVED OCTOBER 26, 1945

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

# The Osmotic and Activity Coefficients of Zinc Nitrate, Zinc Perchlorate and Magnesium Perchlorate. Transference Numbers in Zinc Perchlorate Solutions

BY R. H. STOKES AND BARBARA J. LEVIEN

Zinc chloride in aqueous solutions exhibits anomalies which may be ascribed to the formation of intermediate or complex ions. The activity coefficient curve plotted against $\sqrt{m}$ does not fall into the regular sequence of other bivalent metal chlorides,[1] and at high concentrations the cationic transference numbers are negative.[2,3] Similar anomalies have been found to occur with zinc bromide with respect to both the activity coefficient[4] and the transference numbers.[5] With zinc iodide these interfering effects appear to be negligible up to about 0.5 *M*, but at higher concentrations deviations of the same type have been found.[6,7,8]

At low concentrations the activity coefficient of zinc iodide is close to that of magnesium iodide, suggesting that if intermediate and complex ion formation were absent, there would be a parallelism between the activity coefficients of zinc and magnesium salts. This view is supported by the observation that the ionic diameters of these two cations are similar in the crystal state. To test this further, a search has been made for "normal" zinc salts, for which purpose the activity coefficient of zinc nitrate has been determined and compared with the known values for magnesium nitrate,[9] the activity coefficients of zinc and magnesium perchlorates have been measured and compared and transference numbers in zinc perchlorate solutions have been calculated from the e. m. f.'s of cells with transference.

## Experimental

**Preparation of Solutions.**—A weighed quantity of zinc oxide, previously heated to drive off water and carbon dioxide, was dissolved in the calculated amount of a perchloric acid solution whose concentration had been deter-

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[1] R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

[2] G. Scatchard and Tefft, THIS JOURNAL, **52**, 2272 (1930).

[3] A. C. Harris and H. N. Parton, *Trans. Faraday Soc.*, **36**, 1139 (1940).

[4] R. H. Stokes, J. M. Stokes and R. A. Robinson, *ibid.*, **40**, 533 (1944).

[5] H. N. Parton and J. W. Mitchell, *ibid.*, **35**, 758 (1939).

[6] R. H. Stokes, *ibid.*, **41**, 12 (1945).

[7] W. Hittorf, *Pogg. Ann.*, **106**, 513 (1859).

[8] R. G. Bates, THIS JOURNAL, **60**, 2983 (1938).

[9] R. A. Robinson, J. M. Wilson and H. S. Ayling, *ibid.*, **64**, 1469 (1942).

mined by weight titration against sodium carbonate. This gave a stock solution 3 *M* in concentration. A second stock solution, 4.5 *M*, was made in a similar way. This method was also used to prepare a 3 *M* solution of magnesium perchlorate which was duplicated by recrystallizing "anhydrone" several times as the hexahydrate and dissolving in water, to give a solution of which the concentration was found by analysis for magnesium as pyrophosphate. The compositions of the other solutions were calculated from that of the perchloric acid, the solution of the oxides being made in closed flasks to prevent loss of water from the system. The two pairs of solutions gave results in satisfactory agreement with one another. A solution of zinc nitrate was prepared in a similar way from zinc oxide and nitric acid. In all cases reagents of the best analytical quality were used.

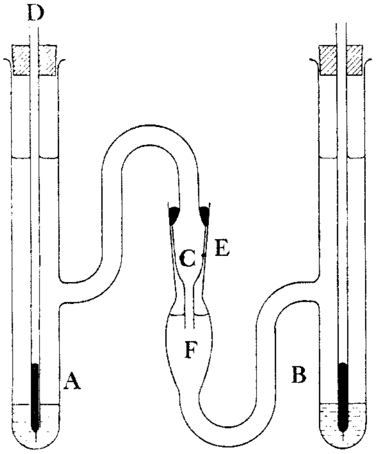

Fig. 1.—Cell with transference for determining transference numbers in zinc perchlorate solutions.

**Measurements.**—The isopiestic measurements were made by the usual method,[10] the experimental results being given in Table I.

TABLE I

ISOPIESTIC SOLUTIONS OF ZINC NITRATE, ZINC PERCHLORATE AND MAGNESIUM PERCHLORATE AT 25°

$m_1$, Molality of zinc nitrate; $m_2$, molality of zinc perchlorate; $m_3$, molality of magnesium perchlorate; $m_4$, molality of potassium chloride; $m_5$, molality of sulfuric acid.

Zinc Nitrate

| $m_1$ | $m_4$ | $m_1$ | $m_4$ | $m_1$ | $m_4$ |
|---|---|---|---|---|---|
| 0.1113 | 0.1576 | 0.1161 | 0.1647 | 0.1421 | 0.2017 |
| .1823 | .2619 | .2037 | .2936 | .2364 | .3441 |
| .3559 | .5359 | .3680 | .5565 | .3693 | .5572 |
| .4520 | .6970 | .5116 | .8011 | .6304 | 1.018 |
| .7307 | 1.209 | .8984 | 1.544 | .9027 | 1.555 |
| .9302 | 1.610 | 1.028 | 1.820 | 1.113 | 2.006 |
| 1.148 | 2.086 | 1.208 | 2.216 | 1.296 | 2.421 |
| 1.546 | 3.018 | 1.730 | 3.477 | 1.774 | 3.589 |
| 1.805 | 3.668 | 1.888 | 3.892 | 2.043 | 4.306 |
| 2.063 | 4.361 | 2.219 | 4.785 | 2.230 | 4.807 |

| $m_1$ | $m_5$ | $m_1$ | $m_5$ | $m_1$ | $m_5$ |
|---|---|---|---|---|---|
| 2.064 | 2.907 | 2.240 | 3.156 | 2.278 | 3.208 |
| 2.392 | 3.364 | 2.871 | 4.038 | 3.369 | 4.735 |
| 4.075 | 5.731 | 4.191 | 5.894 | 4.211 | 5.920 |
| 5.199 | 7.347 | 5.383 | 7.612 | 5.834 | 8.293 |
| 6.310 | 9.003 | 6.439 | 9.194 | | |

Zinc Perchlorate

| $m_2$ | $m_4$ | $m_2$ | $m_4$ | $m_2$ | $m_4$ |
|---|---|---|---|---|---|
| 0.09173 | 0.1335 | 0.1143 | 0.1681 | 0.1219 | 0.1798 |
| .2333 | .3642 | .3022 | .4879 | .3811 | .6377 |
| .4472 | .7720 | .4713 | .8228 | .5770 | 1.052 |
| .6029 | 1.113 | .6184 | 1.153 | .6400 | 1.202 |
| .6549 | 1.239 | .8115 | 1.640 | .8772 | 1.820 |
| .9270 | 1.958 | .9340 | 1.978 | 1.001 | 2.177 |
| 1.018 | 2.226 | 1.069 | 2.383 | 1.153 | 2.651 |
| 1.202 | 2.804 | 1.268 | 3.023 | 1.301 | 3.142 |
| 1.318 | 3.198 | 1.369 | 3.378 | 1.374 | 3.389 |
| 1.446 | 3.639 | 1.528 | 3.949 | 1.660 | 4.449 |
| 1.754 | 4.807 | | | | |

| $m_2$ | $m_5$ | $m_2$ | $m_5$ | $m_2$ | $m_5$ |
|---|---|---|---|---|---|
| 1.668 | 2.961 | 1.837 | 3.304 | 1.881 | 3.393 |
| 2.044 | 3.727 | 2.051 | 3.744 | 2.126 | 3.900 |
| 2.618 | 4.950 | 2.815 | 5.380 | 2.935 | 5.650 |
| 3.042 | 5.895 | 3.173 | 6.186 | 3.284 | 6.445 |
| 3.461 | 6.861 | 3.789 | 7.645 | 3.886 | 7.891 |
| 4.015 | 8.207 | 4.268 | 8.862 | 4.282 | 8.890 |
| 4.311 | 8.966 | | | | |

Magnesium Perchlorate

| $m_3$ | $m_4$ | $m_3$ | $m_4$ | $m_3$ | $m_4$ |
|---|---|---|---|---|---|
| 0.1098 | 0.1624 | 0.1973 | 0.3044 | 0.2285 | 0.3581 |
| .2297 | .3605 | .4136 | .7064 | .4460 | .7729 |
| .5456 | .9879 | .5621 | 1.026 | .5967 | 1.105 |
| .6422 | 1.212 | .7307 | 1.430 | .7849 | 1.569 |
| .8826 | 1.829 | 1.110 | 2.495 | 1.237 | 2.895 |
| 1.392 | 3.410 | 1.404 | 3.459 | 1.468 | 3.673 |
| 1.533 | 3.918 | 1.563 | 4.032 | 1.624 | 4.253 |
| 1.726 | 4.645 | 1.767 | 4.807 | | |

| $m_3$ | $m_5$ | $m_3$ | $m_5$ | $m_3$ | $m_5$ |
|---|---|---|---|---|---|
| 1.789 | 3.178 | 1.968 | 3.523 | 2.001 | 3.587 |
| 2.296 | 4.205 | 2.494 | 4.610 | 2.704 | 5.067 |
| 2.764 | 5.182 | 2.849 | 5.365 | 3.000 | 5.699 |
| 3.468 | 6.747 | 3.470 | 6.772 | 3.619 | 7.122 |
| 3.837 | 7.620 | 4.152 | 8.384 | 4.346 | 8.853 |
| 4.418 | 9.059 | | | | |

For the purpose of making vacuum corrections to the weights, densities of zinc perchlorate solutions were measured at 25° in a simple pycnometer of 20-ml. capacity. The values, given in Table II, should be reliable to about one part in 2000.

The e. m. f.'s of the cell

$$\begin{array}{l|c|c|l} \text{Hg–Zn} & Zn(ClO_4)_2 & Zn(ClO_4)_2 & \text{Zn–Hg} \\ \text{2 phase} & m_1 & m_2 & \text{2 phase} \end{array}$$

were measured at 25° over the concentration range 0.1 to 4 *M*. The cell vessel is shown in Fig. 1.

TABLE II

DENSITIES OF ZINC PERCHLORATE SOLUTIONS AT 25°

| $m$ | $d^{22}_{4}$ | $m$ | $d^{22}_{4}$ | $m$ | $d^{22}_{4}$ |
|---|---|---|---|---|---|
| 0.0962 | 1.0162 | 0.2594 | 1.0478 | 0.4042 | 1.0752 |
| .4563 | 1.0843 | .8178 | 1.1494 | 1.002 | 1.1806 |
| 1.502 | 1.2612 | 2.002 | 1.3357 | 2.498 | 1.4041 |
| 2.999 | 1.4674 | 3.416 | 1.5164 | 3.841 | 1.5636 |
| 3.960 | 1.5760 | | | | |

Two solutions of concentrations $m_1$ and $m_2$ were prepared in tap-funnels by weight-dilution of the main stock. Air was removed by repeated pumping out and admission of hydrogen, the loss of water vapor being determined by reweighing. A 5% zinc amalgam was prepared by heating

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[10] R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

TABLE III

OSMOTIC AND ACTIVITY COEFFICIENTS OF ZINC NITRATE, ZINC PERCHLORATE AND MAGNESIUM PERCHLORATE IN AQUEOUS SOLUTION AT 25°

| $m$ | $Zn(NO_3)_2$ | | $Zn(ClO_4)_2$ | | $Mg(ClO_4)_2$ | |
|---|---|---|---|---|---|---|
| 0.1 | 0.862 | 0.532 | 0.893 | 0.573 | 0.898 | 0.577 |
| .15 | .868 | .507 | .911 | .560 | .917 | .567 |
| .2 | .873 | .490 | .928 | .556 | .935 | .565 |
| .3 | .890 | .475 | .966 | .565 | .974 | .576 |
| .4 | .909 | .470 | 1.010 | .588 | 1.016 | .599 |
| .5 | .934 | .474 | 1.056 | .620 | 1.062 | .632 |
| .6 | .958 | .481 | 1.105 | .661 | 1.108 | .673 |
| .7 | .982 | .490 | 1.157 | .710 | 1.158 | .722 |
| .8 | 1.009 | .503 | 1.212 | .769 | 1.211 | .780 |
| .9 | 1.037 | .519 | 1.269 | .838 | 1.267 | .848 |
| 1.0 | 1.064 | .536 | 1.328 | .916 | 1.323 | .925 |
| 1.2 | 1.120 | .576 | 1.450 | 1.111 | 1.437 | 1.111 |
| 1.4 | 1.180 | .626 | 1.578 | 1.367 | 1.558 | 1.354 |
| 1.6 | 1.238 | .682 | 1.708 | 1.695 | 1.683 | 1.667 |
| 1.8 | 1.296 | .746 | 1.843 | 2.126 | 1.815 | 2.077 |
| 2.0 | 1.355 | .819 | 1.984 | 2.694 | 1.945 | 2.594 |
| 2.5 | 1.506 | 1.047 | 2.363 | 5.11 | 2.306 | 4.78 |
| 3.0 | 1.664 | 1.363 | 2.742 | 9.88 | 2.670 | 9.01 |
| 3.5 | 1.817 | 1.781 | 3.128 | 19.58 | 3.049 | 17.51 |
| 4.0 | 1.960 | 2.313 | 3.506 | 38.9 | 3.411 | 33.9 |
| 4.5 | 2.098 | 3.00 | 3.808[a] | 67.8[a] | 3.679[a] | 56.4[a] |
| 5.0 | 2.238 | 3.90 | .... | .... | .... | .... |
| 5.5 | 2.372 | 5.05 | .... | .... | .... | .... |
| 6.0 | 2.500 | 6.50 | .... | .... | .... | .... |
| 6.5 | 2.614 | 8.25 | .... | .... | .... | .... |

[a] At 4.4 $M$.

A. R. zinc with redistilled mercury, then washing with dilute acid and distilled water. It was dried and placed in an oven at 100° to keep it liquid. In filling the cell, the vessel A was filled with the less dense solution $m_1$ and 2–3 ml. of the warm amalgam run in. The tube C was kept temporarily closed by a cap and the contact rod D was fitted. The solution was exposed only very briefly to the air in the filling operation. After similarly filling vessel B with the stronger solution to the level shown, the two parts were fitted together by the ground joint E, which was sealed with mercury as an extra precaution against leakage from the thermostat. The air space in the bulb F prevented the liquid from coming in contact with the lubricant on the ground joint. The cell was then thermostated at 25 ± 0.01°, and the e. m. f. measured with a Leeds and Northrup type K potentiometer, checked against Eppley standard cells. Equilibrium was reached within an hour and maintained within 0.03 mv. for about a day. As a check on the stability of the liquid junction, the cell was set up with water and potassium dichromate solution in the two sides, and the state of the junction observed visually. It was found to be remarkably stable to shaking and tilting of the cell, and to remain in the tube C for at least twenty-four hours.

A few of the measurements were made in duplicate and gave a reproducibility of 0.03 mv.

The majority of the measurements were made with $m_1$ = 0.30015, but a few were made relative to $m_1$ = 0.1000. The concentration $m_2$ was made in each case as near as possible to a round value, and a slight correction not exceeding 0.2 mv. was applied to the observed e. m. f. in order to bring it to the exact value. The corrections were determined by plotting suitable deviation functions against $m$ and $\sqrt{m}$. The e. m. f.'s, $E_t$, in Table IV have been expressed relative to 0.1 $M$ in order to simplify the subsequent calculations; this involves merely the addition of the e. m. f. of the cell [0.100 $M$/0.30015 $M$] to that of the cell [0.30015 $M/m$] actually measured.

TABLE IV

TRANSFERENCE NUMBERS IN ZINC PERCHLORATE SOLUTION AT 25°

$E_t$ = e. m. f. of cell: Hg-Zn | $Zn(ClO_4)_2$, 0.1 $M$ | $Zn(ClO_4)_2$, $m$ | Zn-Hg; $E$ = e. m. f. of hypothetical cell without transference calculated from activity coefficient data in Table III; Δ = Deviation in mv. of observed $E_t$ from that calculated by the equation: $E_t = 0.59071\ E + 0.4092\ E^2 - 0.398\ E^3 - 0.00002$; $n = dE_t/dE$ = anionic transference number.

| $m$ | $E_t$ | $E$ | Δ | $n_-$ |
|---|---|---|---|---|
| 0.1 | 0 | 0 | −0.02 | 0.591 |
| .15 | .00871 | .01476 | + .08 | .603 |
| .2 | .01519 | .02559 | + .18 | .611 |
| .3 | .02540 | .04182 | − .03 | .623 |
| .4 | .03334 | .05444 | − .05 | .632 |
| .5 | .04004 | .06508 | ± .00 | .639 |
| .6 | .04607 | .07456 | + .06 | .645 |
| .7 | .05189 | .08327 | − .11 | .651 |
| .8 | .05722 | .09147 | − .09 | .656 |
| .9 | .06239 | .09930 | − .11 | .660 |
| 1.0 | .06731 | .10683 | − .03 | .665 |
| 1.1 | .07207 | .11413 | + .07 | .669 |
| 1.2 | .07687 | .12127 | + .06 | .672 |
| 1.3 | .08161 | .12830 | + .06 | .676 |
| 1.4 | .08629 | .13518 | + .04 | .680 |
| 1.5 | .09094 | .14196 | + .01 | .683 |
| 1.6 | .09546 | .14863 | + .05 | .686 |
| 1.7 | .10002 | .15527 | + .05 | .689 |
| 1.8 | .10465 | .16188 | − .02 | .692 |
| 2.0 | .11394 | .17508 | − .14 | .697 |
| 2.5 | .13718 | .20829 | − .01 | .709 |
| 3.0 | .16041 | .24077 | − .04 | .719 |
| 3.5 | .18364 | .27305 | + .04 | .725 |
| 4.0 | .20676 | .30464 | − .10 | .729 |

## Calculation of Results

The osmotic and activity coefficients of these three salts have been evaluated from the osmotic coefficients of Shankman and Gordon[11] for sulfuric acid and Robinson[12] for potassium chloride. The values of $\gamma$ at 0.1 $M$ were obtained by the method of Robinson and Sinclair[11] using the curve for calcium chloride as standard. A similar calculation for magnesium chloride is described elsewhere.[13]

The method of determining transference numbers from the e. m. f.'s of reversible cells with transference ($E_t$) and without transference ($E$), in the form $n = dE_t/dE$, is well known. While it is not capable of as high accuracy as the moving boundary method (owing to the sensitivity of the differential coefficient to slight changes in the observed quantities),[14] it is nevertheless capable of moderately accurate results in cases where the transference number does not vary rapidly with the concentration. In the present case the e. m. f.'s of the cell without transference cannot be measured since there is no electrode reversible to

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(11) V. S. Shankman and A. R. Gordon, *ibid.*, **61**, 2370 (1939).

(12) R. A. Robinson, *Trans. Roy. Soc. New Zealand*, in press.

(13) R. H. Stokes, *Trans. Faraday Soc.*, in press.

(14) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 169.

the perchlorate ion. The e. m. f.'s nevertheless can be calculated from the activity coefficient data by means of the formula

$$E = (3RT/2F)\ \ln\ (m_2\gamma_2/m_1\gamma_1)$$

It will be noted that an error in the value assigned to $\gamma$ at 0.1 $M$ will not affect the calculated e. m. f.'s, since all the values of log $\gamma$ at higher concentrations would be altered by a constant amount. The values of $E$ given in Table IV were obtained in this way from the $\gamma$ values of Table III.

By a least squaring process the equation

$$E_t = 0.59071\,E + 0.4092\,E^2 - 0.398\,E^3 - 0.00002 \quad (1)$$

was found to reproduce the $E_t$ values with an average deviation of 0.05 mv., the differences between $E_t$ (observed) and $E_t$ (calculated) being given in Table IV. It will be noted that the largest, 0.18 mv., occurs in the dilute region where the isopiestic method is least accurate and where, furthermore, the high internal resistance of the cells reduces the accuracy. When it is remembered that the $E$ values have been obtained by an integration process from vapor pressure data, the fit of equation (1) may be considered very fair.

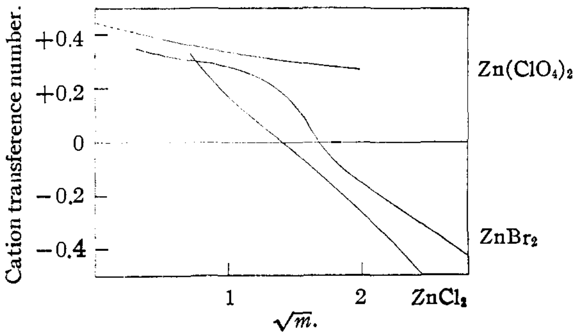

Fig. 2.—Transference numbers of zincp erchlorate, bromide and chloride.

The transference numbers were then evaluated by differentiating (1), giving

$$n_- = 1 - n_+ = \mathrm{d}E_t/\mathrm{d}E = 0.5907 + 0.8184\ E - 1.194\ E^2$$

The values at round concentrations are given in Table IV. They should not be regarded as having an accuracy greater than 0.002.

## Discussion

It is apparent that the transference numbers in zinc perchlorate are quite normal, there being no negative values or sharp changes such as might be expected in the event of complex ion formation. The curve of $n$ against $\sqrt{m}$ extrapolates reasonably well to the value of 0.556 at infinite dilution, obtained from the limiting mobilities of zinc[15] and perchlorate ion.[16] The slope of the curve, however, is much less than that demanded by Onsager's theory, a difficulty which was also found by Longsworth[17] for calcium chloride at much greater dilutions. In Fig. 2 the curve is compared with that for zinc chloride and bromide.

The osmotic coefficient curves of zinc and magnesium perchlorate are seen to lie very close together (Fig. 3); this also applies to the nitrates. Thus we may reasonably claim that the osmotic properties of a normally dissociated zinc salt closely resemble those of the corresponding magnesium salt. Figure 3 also compares the curves for the halide salts, showing a rapidly increasing abnormality as we pass through the series iodide–bromide–chloride.

The activity coefficients, particularly those of the two perchlorates, reach exceedingly high values in the concentrated solutions; this no doubt is due to the high degree of hydration resulting from the small size of the bivalent ions. Attempts to deal quantitatively with this effect have, however, not yet been successful.

We wish to thank Prof. H. S. Harned and Dr. R. A. Robinson for their interest in the course of this work.

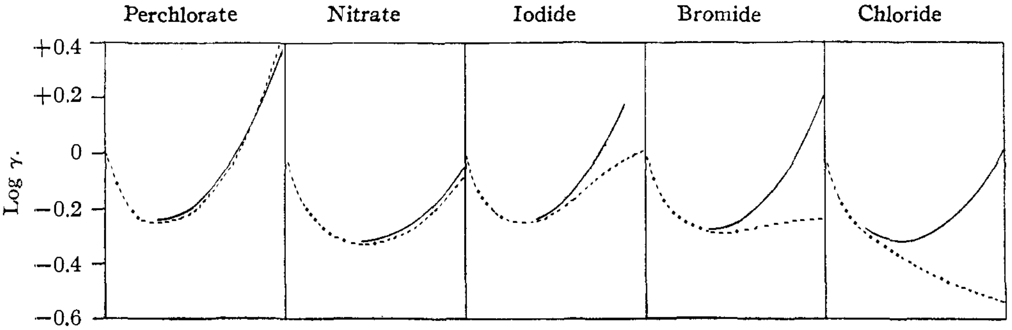

Fig. 3.—Activity coefficients of magnesium and zinc salts: ——— magnesium salts; ------ zinc salts. In each graph the abscissa represents $\sqrt{m}$ from 0 to 1.4.

## Summary

The osmotic and activity coefficients of zinc and magnesium perchlorates and of zinc nitrate have

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[15] Landolt-Börnstein, "Tabellen," Zweiter Ergänz., 1931, p. 1062.

[16] R. A. Robinson and C. W. Davies, *J. Chem. Soc.*, 574 (1937).

[17] L. G. Longsworth, This Journal, **57**, 1185 (1935).

## APPENDIX

WATER ACTIVITIES, OSMOTIC COEFFICIENTS, ACTIVITY COEFFICIENTS, AND RELATIVE MOLAL VAPOR PRESSURE LOWERINGS OF SODIUM AND POTASSIUM CHLORIDE SOLUTIONS AT 25°

| | Sodium chloride | | | | Potassium chloride | | | |
|---|---|---|---|---|---|---|---|---|
| $m$ | $a_W$[a] | $\varphi$ | $1 + \log \gamma$ | $\frac{p^\circ - p}{Mp^\circ}$ | $a_W$ | $\varphi$ | $+ \log \gamma$ | $\frac{p^\circ - p}{Mp^\circ}$ |
| 0.1 | 0.996646 | 0.9324 | 0.8912 | 0.03354 | 0.996668 | 0.9266 | 0.8864 | 0.03332 |
| .2 | .993360 | .9245 | .8661 | .03320 | .993443 | .9130 | .8562 | .03279 |
| .3 | .99009 | .9215 | .8511 | .03303 | .99025 | .9063 | .8373 | .03250 |
| .4 | .98682 | .9203 | .8406 | .03295 | .98709 | .9017 | .8233 | .03228 |
| .5 | .98355 | .9209 | .8332 | .03290 | .98394 | .8989 | .8124 | .03212 |
| .6 | .98025 | .9230 | .8278 | .03292 | .98078 | .8976 | .8038 | .03203 |
| .7 | .97692 | .9257 | .8240 | .03296 | .97763 | .8970 | .7967 | .03196 |
| .8 | .97359 | .9288 | .8211 | .03301 | .97448 | .8970 | .7907 | .03190 |
| .9 | .97023 | .9320 | .8190 | .03308 | .97133 | .8971 | .7854 | .03186 |
| 1.0 | .96686 | .9355 | .8175 | .03314 | .96818 | .8974 | .7809 | .03128 |
| 1.2 | .9601 | .9428 | .8158 | .03325 | .9619 | .8986 | .7733 | .03175 |
| 1.4 | .9532 | .9513 | .8159 | .03343 | .9556 | .9010 | .7676 | .03171 |
| 1.6 | .9461 | .9616 | .8178 | .03369 | .9492 | .9042 | .7634 | .03175 |
| 1.8 | .9389 | .9723 | .8208 | .03394 | .9428 | .9081 | .7603 | .03178 |
| 2.0 | .9316 | .9833 | .8245 | .03420 | .9364 | .9124 | .7580 | .03180 |
| 2.2 | .9242 | .9948 | .8291 | .03445 | .9299 | .9168 | .7564 | .03186 |
| 2.4 | .9166 | 1.0068 | .8344 | .03475 | .9234 | .9214 | .7554 | .03192 |
| 2.6 | .9089 | 1.0192 | .8402 | .03504 | .9169 | .9264 | .7549 | .03198 |
| 2.8 | .9011 | 1.0321 | .8466 | .03532 | .9103 | .9315 | .7548 | .03204 |
| 3.0 | .8932 | 1.0453 | .8535 | .03560 | .9037 | .9367 | .7550 | .03210 |
| 3.2 | .8851 | 1.0587 | .8608 | .03591 | .8971 | .9421 | .7557 | .03216 |
| 3.4 | .8769 | 1.0725 | .8684 | .03621 | .8904 | .9477 | .7567 | .03223 |
| 3.6 | .8686 | 1.0867 | .8766 | .03650 | .8837 | .9531 | .7578 | .03230 |
| 3.8 | .8600 | 1.1013 | .8852 | .03684 | .8770 | .9588 | .7593 | .03237 |
| 4.0 | .8515 | 1.1158 | .8939 | .03713 | .8702 | .9647 | .7610 | .03245 |
| 4.2 | .8428 | 1.1306 | .9029 | .03743 | .8634 | .9707 | .7629 | .03252 |
| 4.4 | .8339 | 1.1456 | .9122 | .03775 | .8566 | .9766 | .7649 | .03259 |
| 4.6 | .8250 | 1.1608 | .9218 | .03804 | .8498 | .9824 | .7670 | .03266 |
| 4.8 | .8160 | 1.1761 | .9315 | .03833 | .8429 | .9883 | .7693 | .03273 |
| 5.0 | .8068 | 1.1916 | .9415 | .03864 | | | | |
| 5.2 | .7976 | 1.2072 | .9517 | .03892 | | | | |
| 5.4 | .7883 | 1.2229 | .9620 | .03920 | | | | |
| 5.6 | .7788 | 1.2389 | .9726 | .03950 | | | | |
| 5.8 | .7693 | 1.2548 | .9833 | .03977 | | | | |
| 6.0 | .7598 | 1.2706 | .9940 | .04003 | | | | |

[a] Vapor pressures in columns 2, 5, 6 and 8 are tabulated relative to $p^\circ$ = 23.756 mm. for pure water at 25°.

been measured by the isopiestic method. By combining the activity coefficient data for zinc perchlorate with the e. m. f.'s of cells with transference, the transference numbers in zinc perchlorate have been calculated. Zinc perchlorate and zinc nitrate resemble the magnesium salts in being normally dissociated; this behavior is in marked contrast with that of the zinc halides.

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