tions in the solubility dependence of Pu(IV) phosphate. The monophosphate plutonium complex has a ratio of hydrogen/phosphate of nearly 3, while for all complexes containing up to five phosphate residues, ratios greater than 2 were obtained.

**Distribution of TTA.**—Table II gives the distribution of TTA between an aqueous phase 0.09 molar in $HClO_4$ of the indicated ionic strength in $NaClO_4$ and 0.50 *M* TTA in benzene. Concentrations of TTA in the aqueous phase were determined by measurement of light absorption at 267 and 292 mμ. A value of 6.3 was used for $K_6$ in equation (11) at an ionic strength of 2.0. A value of 7.6 was estimated for an ionic strength of 6.0.

TABLE II

DISTRIBUTION OF TTA (BENZENE/WATER)

| $\mu$ | 0.59 | 1.09 | 2.09 | 4.09 | 6.09 |
|---|---|---|---|---|---|
| $R$ | 49 | 57 | 76 | 167 | 443 |

TABLE III

SUMMARY OF CONSTANTS

| | Ionic strength *M* $\mu$ | Equilibrium constants $K$ |
|---|---|---|
| $Th^{+4} + NO_3^- = Th(NO_3)^{+++}$ | 5.97 | 2.83 |
| $Th^{+4} + 2NO_3^- = Th(NO_3)_2^{++}$ | 5.97 | 1.41 |
| $Th^{+4} + HF = ThF^{+++} + H^+$ | 0.5 | $5.0 \times 10^4$ |
| $Th^{+4} + 2HF = ThF_2^{++} + 2H^+$ | 0.5 | $2.9 \times 10^7$ |
| $Th^{+4} + Cl^- = ThCl^{+3}$ | 4.0 | 1.30 |
| $Th^{+4} + 2Cl^- = ThCl_2^{++}$ | 4.0 | 0.125 |
| $Th^{+4} + 3Cl^- = ThCl_3^+$ | 4.0 | ~0.037 |
| $Th^{+4} + 4Cl^- = ThCl_4$ | 4.0 | ~0.014 |
| $Th^{+4} + HSO_4^- = ThSO_4^{++} + H^+$ | 2.0 | 159 |
| $Th^{+4} + 2HSO_4^- = Th(SO_4)_2 + 2H^+$ | 2.0 | 2850 |
| $Th^{+4} + 2HSO_4^- = Th(HSO_4SO_4)^+ + H^+$ | 2.0 | ~800 |
| $Th^{+4} + H_3PO_4 = Th(H_3PO_4)^{+4}$ | 2.0 | 78 |
| $Th^{+4} + H_3PO_4 = Th(H_2PO_4)^{+3} + H^+$ | 2.0 | 150 |
| $Th^{+4} + 2H_3PO_4 = Th(H_2PO_4H_3PO_4)^{+3} + H^+$ | 2.0 | 14000 |
| $Th^{+4} + 2H_3PO_4 = Th(H_2PO_4)_2^{++} + 2H^+$ | 2.0 | 8000 |

## Discussion

The change in composition of the organic layer at constant $(TTA)_b$ with changing concentration of complexers in the aqueous phase is very slight and it is reasonable to assume that the activity coefficients for TTA and $ThT_4$ remain very nearly constant. The activity coefficients of the aqueous species may, however, undergo substantial variation if the composition of the solution is extensively changed at constant ionic strength. The activity coefficient for thorium enters into the complexing and extraction equilibria in opposite directions with respect to its effect on the distribution coefficient. Changes in the activity coefficients of a complexing anion and of the corresponding complex may also tend to compensate. A change in the activity coefficient of hydrogen ion, however, which enters into the distribution expression to the fourth power, probably accounts for a significant part of the observed change in distribution with changing complexer concentration. For the chloride and nitrate complex data, in which another salt is substituted for a large part of the initial perchlorate medium, the constants, particularly those beyond the first one, may be seriously affected. Development of satisfactory methods for estimating activities in mixed electrotypes is necessary to permit a more generally significant treatment of the data for higher complex equilibria in the case of such weak association.

SCHENECTADY, N. Y. RECEIVED MAY 21, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA]

# Transference Numbers in Aqueous Solutions of Zinc Sulfate

BY E. P. PURSER AND R. H. STOKES

Transference numbers of zinc sulfate in aqueous solution at 25° have been measured over the concentration range 0.005 to 2.0 molal by the electromotive force method. The results show normal behavior in concentrated solution with no indication of the formation of negatively charged zinc complex ions. At high dilution the slope of the curve $t_+ = f(\sqrt{m})$ approaches the Onsager limiting slope from above.

Data for transference numbers of aqueous solutions of zinc sulfate at 25° were reported by Wolten and King,[1] their results being derived from e.m.f. studies of concentration cells with zinc sulfate electrolyte and two-phase zinc amalgam electrodes, after the method of Stokes and Levien.[2] The measurements extended over the concentration range 0,005 to 2.270 molal.

The results of these workers for concentrated solutions gave negative values for the transference numbers of the cation, indicating the formation of negatively charged complex zinc ions at high concentration. This conclusion is contrary to the findings of Davies[3] in his work on the conductivity of zinc sulfate solutions. His results are consistent only with the formation of ion pairs $(Zn^{++}\text{-}SO_4^{--})$ which should cause no change in the transference numbers.

The present work is a redetermination of the transference numbers of zinc sulfate at 25° by the same method.

## Experimental

Stock solutions of zinc sulfate, 2.0 and 0.1 *M*, were prepared from B.D.H. "Analar" zinc sulfate and double-distilled water. The crystalline salt was checked for purity and the solutions standardized by zinc and sulfate determinations. The solutions for use in the cells were made up as required by weight dilution of the stock solutions with double-distilled water.

Mercury for the amalgam electrodes was first treated by anodic oxidation after the method of Reilly and Rae,[4] then

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[1] Wolten and King, THIS JOURNAL, **71**, 576 (1949).

[2] Stokes and Levien, *ibid.*, **68**, 333 (1946).

[3] Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); Davies, *ibid.*, **29**, 834 (1933).

[4] Reilly and Rae, "Physico-Chemical Methods," 2nd ed., revised, Methuen and Co., Ltd., London, 1933, p. 725.

washed, dried, filtered through chamois leather, and distilled under vacuum. Zinc amalgam was prepared electrolytically; the purified mercury formed the cathode of a cell, the anode being platinum and the electrolyte a concentrated solution of zinc sulfate. The resulting amalgam was found by weight analysis to contain 5.7% zinc. At the experimental temperature this is two-phase.

The concentration cells used were similar to those of Stokes and Levien[4] with the modification that all rubber stoppers were replaced with "Quickfit" ground joints. A water thermostat with mercury–toluene regulator maintained a temperature of 25° with a differential of ±0.005°. A Tinsley type 3184 potentiometer and Tinsley reflecting galvanometer mounted externally were used for the measurement of e.m.f. All joints in electrical wiring were soldered, and contacts made in mercury where possible. The thermostat, potentiometer stand and galvanometer stand were earthed, and all wiring was shielded in lead which was earthed. The solutions for the cells were deaerated by boiling under vacuum at room temperature. This procedure caused no appreciable change in molality. The solutions were then introduced into the cells and the zinc amalgam poured in from a tap funnel while hot. The cells were made up in triplicate and the e.m.f. reached a steady value within an hour or two of placing in the thermostat, the triplicates agreeing with a mean deviation of ±0.05 mv. Over a period of days, however, a slight but steady rise was observed, instead of a drop which might be expected. The rise was accompanied by formation of a white deposit on the surfaces of the electrodes, presumably due to the oxidation of the zinc to form solid zinc oxide.

*p*H measurements on the stock solutions showed that the A.R. zinc sulfate used in their preparation contained free acid. The stock solutions were therefore refluxed for some hours with sufficient A.R. zinc oxide to saturate the solutions exactly. Cells were then made up containing zinc oxide-treated solutions and containing untreated solutions. The initial e.m.f. agreed well within the experimental error, but that of the cell containing treated solutions remained steady for three days. No further trouble was experienced with drift in the e.m.f. until work was done on dilute solutions (less than 0.05 *M*), when the trouble recurred. It was thought that boiling the solutions under vacuum before filling the cells did not de-aerate the solutions sufficiently to stop oxidation of the zinc in dilute solution. The cells were therefore modified to enable hydrogen to be bubbled slowly through the solution in the dilute limb while the cells were in the thermostat and e.m.f. measurements being made. This procedure reduced the extent of the drift in the e.m.f. but did not eliminate it entirely. Solutions of molality 0.005 *M* marked the limit of dilution consistent with reproducibility of the cells.

The densities ($d^{25}{}_4$) of zinc sulfate solutions at various molalities were determined using a 25-ml. pycnometer.

## Calculation of Results

The measured values of $E_t$, the e.m.f. of the cells with transference, are shown for various values of $m$ in Table I. One side of the cell contained solution of molality 0.09836 in all cases.

TABLE I

| $m$ | $E_t$, volt | $E$, volt |
|---|---|---|
| 1.976 | 0.02831 | 0.03985 |
| 1.512 | .02356 | .03412 |
| 0.9942 | .01886 | .02762 |
| .5041 | .01282 | .01944 |
| .2498 | .00736 | .01140 |
| .1528 | .00354 | .00563 |
| .04987 | − .00579 | − .00951 |
| .01005 | − .02108 | − .03446 |
| .004805 | − .02915 | − .04771 |

The third column of Table I gives values of $E$, the e.m.f. of the cell without transference, calculated from the relation

$$E = 0.05915 \log (m\gamma_{\pm}/m_{\text{ref.}}\ \gamma_{\pm\text{ref.}})$$

where $m_{\text{ref.}}$ is the molality of the reference solution $= 0.09836$ and $\gamma_{\pm\text{ref.}}$ is the mean ion activity coefficient of the reference solution. Activity coefficients were obtained from isopiestic data[5] for the solutions of molality greater than 0.1 and from the e.m.f. data of Bray[6] for the solutions of molality less than 0.1. Values required for the experimental molalities were obtained by graphical interpolation.

A plot of $E_t$ as a function of $E$ suggested that positive values of $E_t$ might be expressed by a polynomial equation in $E$, and that negative values of $E_t$ might be expressed as a linear equation in $E$. Least-squaring processes were therefore carried out on the two sets of values giving

$$E_t = 0.6155E + 2.333E^2$$

for the positive values with a mean deviation of ±0.06 mv. and $E_t = 0.6112\ E$ for the negative values with a mean deviation of ±0.02 mv. As $t = \mathrm{d}E_t/\mathrm{d}E$ these equations give

$$t_- = 0.6155 + 4.666E$$

for values of $E$ corresponding to $m > 0.09836$ and

$$t_- = 0.6112$$

for values of $E$ corresponding to $m < 0.09836$.

Table II gives values of $t_+$ calculated from the analytical expressions at round molalities.

TABLE II

| $m$ | $t_+$ | $m$ | $t_+$ | $m$ | $t_+$ |
|---|---|---|---|---|---|
| 2.0 | 0.197 | 0.25 | 0.331 | 0.05 | 0.389 |
| 1.5 | .226 | .15 | .359 | .01 | .389 |
| 1.0 | .255 | .1 | .384 | .005 | .389 |
| 0.5 | .294 | | | | |

The figure gives a plot of $t_+$ against $\sqrt{m}$ together with data from the work of Hittorf and Kümmel[7]

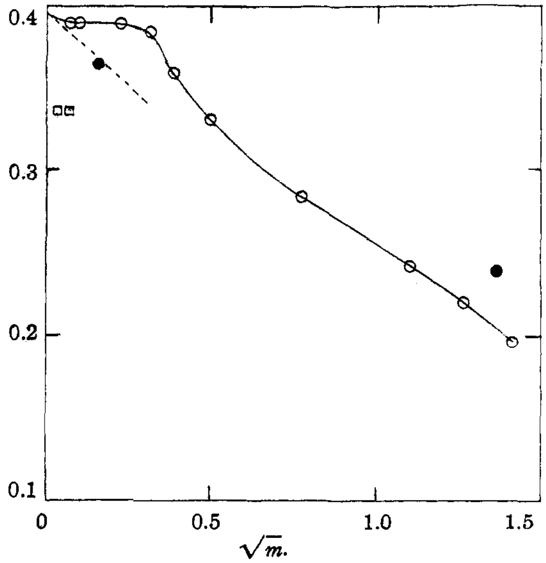

Fig. 1.—Cation transference numbers in zinc sulfate solutions: open circles, present work; filled circles, Hittorf; squares, Kümmel.

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(5) Robinson and Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(6) Harned and Owen, "Physical Chemistry of Electrolytic Solutions," 1st ed. Reinhold Publishing Corp., New York, N. Y., 1943, p. 426.

(7) Hittorf and Kümmel, "Landolt-Börnstein Physikalisch-chemisch Tabellen," Vol. II, Verlag Julius Springer, Berlin, 1933, p. 1104.

presumably carried out at European room temperature.

Table III gives densities of zinc sulfate solutions at selected molalities, supplementing those available in the literature.

TABLE III

| $m$ | 2.003 | 1.512 | 0.5041 | 0.2498 | 0.09836 |
|---|---|---|---|---|---|
| $d^{25}_4$ | 1.2973 | 1.2268 | 1.0772 | 1.0374 | 1.0134 |

## Discussion

The curve of cation transference numbers plotted against $\sqrt{m}$ shows that in concentrated solution the transference numbers follow a normal trend, and there is no evidence to support the existence of negatively charged zinc complex ions. From the Onsager conductivity equation it can be shown that the theoretical limiting slope[8] for zinc sulfate at 25° is $(\mathrm{d}t_+/\mathrm{d}\sqrt{m})_{m\rightarrow 0} = -0.184$. In the figure this gradient is shown dotted, passing through the point $\sqrt{m} = 0$, $t_+ = 0.398$. The gradient of the curve approaches the limiting slope from above as $m \rightarrow 0$.

We have calculated the values of $E$ corresponding to the tabulated values of $E_t$ given by Wolten and King[1] and have plotted $E_t$ as a function of $E$. The experimental points in the present work lie on a smooth curve while the data of Wolten and King are scattered and show a mean deviation from the present values of the order of 5 mv. Their data would be difficult to fit to an analytical expression and it is clear that the calculation of the differential coefficients by the method of Rutledge would be equally inapplicable as this method requires a smooth function.

It would appear that the experimental work of Wolten and King was inaccurate and the mathematical treatment of their experimental data unsound.

NEDLANDS, WESTERN AUSTRALIA RECEIVED MAY 3, 1951

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(8) Reference 6, pp. 162, 172, 151.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

# Organic Compounds of Titanium. II. Association of Organic Titanates in Benzene Solution

BY C. N. CAUGHLAN, H. S. SMITH, WALTER KATZ, WM. HODGSON AND R. W. CROWE

Molecular weight determinations of ethyl, propyl and butyl titanates and monochlorotriethoxytitanium indicate association numbers in dilute benzene solutions to about three. This association is attributed to the fact that the coördination number of titanium is 6, thus allowing additional oxygens to surround the central titanium.

In the course of an investigation to determine the electric moments of some alkyl orthotitanates and related halogen compounds[1] it was necessary to determine molecular weights of these compounds in benzene solution. It was found that although the molecular weight of the solutes approached the calculated molecular weight in very dilute solutions, association apparently took place in more concentrated solutions. This appeared to have little or no effect upon the calculated electric moment since polarizations were calculated at infinite dilution. The existence of the ethyl orthotitanate as a solid and the peculiar manner in which the solid formed suggested the possibility of some abnormal phenomenon. Likewise, the high viscosity and peculiar behavior of the monochlorotriethoxytitanium upon exposure to moist air suggest the possibility of association. The action of the orthotitanates as waterproofing agents described by Speer and Carmody[2] suggests the possibility of association or polymerization. Consequently, a more detailed study has been made of the molecular weights of some of these substances in benzene solution. Ethyl orthotitanate, propyl orthotitanate, butyl orthotitanate and monochlorotriethoxytitanium have been found to be associated in benzene solution.

**Preparation of Materials and Methods of Determining Molecular Weights.**—The ethyl orthotitanate and monochlorotriethoxytitanium were prepared and purified as described by Crowe and Caughlan.[1] Propyl and butyl orthotitanates were prepared and purified essentially by the same method as the ethyl compound. In each case satisfactory purity was indicated by analysis of the compound. The benzene used for the determinations was Merck and Co., Inc., C.P. benzene, thiophene-free. This was kept over sodium until ready for use and then distilled in the absence of moisture. Reproducible results were obtained easily for the three alkyl orthotitanates. Reproducible results were extremely difficult to obtain for the monochlorotriethoxytitanium. Acceptable results were finally obtained by distilling both solute and solvent directly into the apparatus used for the molecular weight determination. Solute and solvent were weighed immediately after collection without opening to the air. Any adjusting necessary was carried out in a dry-box in which phosphorus pentoxide and sulfuric acid reduced the moisture content to a minimum.

Molecular weights were determined by the Beckmann freezing point-lowering method, assuming the solutions dilute enough to be essentially ideal in behavior.

**Results.**—The results are indicated in Figs. 1, 2 and 3 in which association number, *i.e.*, the apparent molecular weight divided by the molecular weight of an unassociated molecule, is plotted against the mole fraction solute. Figure 4 indicates the effect of small amounts of water upon the association of monochlorotriethoxytitanium. The addition of water was accomplished by adding drops of benzene saturated with water. The amounts of water can be considered only approximate in this case since they were calculated from the solubility of water in benzene, *i.e.*, 0.057 weight per cent. at 20°.[3]

**Discussion.**—The association of these orthotitanates appears to be due to the fact that titan-

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(1) R. W. Crowe and C. N. Caughlan, THIS JOURNAL, 72, 1694 (1950).

(2) R. J. Speer and D. R. Carmody, "Tetraalkyl Orthotitanates, New Water-proofing Agents," presented at A. C. S. Meeting, Atlantic City, N. J., 1949.

(3) "International Critical Tables," Vol. III, First Edition, McGraw-Hill Book Co., Inc., New York, N.Y., 1928, p. 389.