range are reminiscent of the tungsten bronzes except for the more restricted range of color.

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The Osmotic and Activity Coefficients of Aqueous Solutions of Thorium Chloride at 25°

BY R. A. ROBINSON

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Isopiestic vapor pressure measurements have been made on solutions of thorium chloride at 25°. The results are not claimed to be of high accuracy but they are of some interest in that they add to our very meager knowledge of 1:4 and 4:1 electrolytes, thorium nitrate and potassium ferrocyanide being the only two electrolytes already studied.

Thorium chloride was prepared by crystallization of a commercial sample which analysis showed to be considerably basic and to which therefore was added slightly more than the requisite amount of hydrochloric acid to give the correct Th:Cl ratio. After three recrystallizations the solution gave the correct Th:Cl ratio on analysis. Table I gives the results of the isopiestic measurements, using sodium chloride as reference salt. Table II gives the calculated osmotic and activity coefficients, the latter being expressed relative to the arbitrary value of 0.350 at 0.05 *M*.

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS OF THORIUM CHLORIDE AND SODIUM CHLORIDE

$ThCl_4$	NaCl	$ThCl_4$	NaCl
0.05252	0.1029	0.7864	2.356
.1286	.2584	.8805	2.755
.1584	.3241	.9983	3.249
.2137	.4551	1.112	3.752
.3009	.6833	1.223	4.199
.3699	.8813	1.368	4.803
.5025	1.288	5.372	1.495
.6152	1.682	5.818	1.590
.6712	1.892	6.156	1.663

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF THORIUM CHLORIDE AT 25°

m	φ	γ	m	φ	γ
0.05	0.731	(0.350)	0.7	1.129	0.327
.1	.736	.292	.8	1.214	.364
.2	.776	.257	.9	1.302	.409
.3	.840	.253	1.0	1.390	.463
.4	.906	.261	1.2	1.536	.583
.5	.974	.275	1.4	1.665	.729
.6	1.048	.297	1.6	1.847	.966

I suspect that, as in the case of uranyl nitrate,[1] the osmotic coefficient is very sensitive to any departure from the exact Th:Cl ratio. Moreover, there is a possibility of this being promoted by loss of hydrogen chloride, formed by hydrolysis, during the evacuation of the desiccator. Thus, in an attempt to extend the range of measurement beyond 1.6 *M* $ThCl_4$, using sulfuric acid as reference electrolyte, I failed to get any consistent results at these high concentrations. For this reason, I do not claim high accuracy for the data in Table II. I think, however, that they are accurate enough to show that thorium chloride has higher osmotic coefficients than thorium nitrate, as has been found with the chlorides and nitrates of lower valency metals.

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Solid Solutions Treatment of Calorimetric Purity Data

BY S. V. R. MASTRANGELO AND R. W. DORNTE

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The application of calorimetry to the absolute determination of purity, in the absence of solid solution formation, is well established.[1-4] Although methods are available[4,5] for detecting solid solutions, no quantitative treatment for these data exists. We have derived a solid solutions treatment for calorimetric melting point data which provides a method for calculating T_0, the melting point of pure major component, and X_2, the total mole fraction of minor component. This treatment is based on analysis of the curvature of the plot of the equilibrium temperature, T_γ, *vs.* $1/\gamma$, the reciprocal of the fraction melted. The occurrence of solid solutions, although rare at low temperatures, is relatively great at high temperatures.

The Lewis and Randall[6] differential equation for solid solutions

$$\frac{\mathrm{d}T}{\mathrm{d}X_2} = \left(\frac{k}{k'} - 1\right)\frac{RT^2}{H_1 - H'} \qquad (1)$$

on integration yields

$$T_0 - T_M = \frac{RT_0^2}{\Delta H_F} X_2''(1 - K) \qquad (2)$$

where T_0 is the melting point of pure major component, T_M is the melting point of a sample containing a total mole fraction X_2'' of minor component whose distribution equilibrium between the solid and liquid phases is expressed by $K = k/k'$, the Henry's law constant, ΔH_F is the heat of fusion of pure major component, and R is the gas constant.

Let X_2' and X_2 be the instantaneous mole fraction of minor component dissolved in the solid and liquid phases, respectively, at any equilibrium temperature, T_γ, corresponding to a fraction of sample, γ, melted in the calorimeter, and let n_2', n_2 and n_0 be

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