

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°

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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 <sub>4</sub>	NaCl	ThCl <sub>4</sub>	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°

<i>m</i>	$\phi$	$\gamma$	<i>m</i>	$\phi$	$\gamma$
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,<sup>1</sup> the osmotic coefficient is very sensitive to any departure from the exact Th:Cl ratio. Moreover,

(1) R. A. Robinson and C. K. Lim, *J. Chem. Soc.*, 1810 (1951).

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<sub>4</sub>, 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

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The application of calorimetry to the absolute determination of purity, in the absence of solid solution formation, is well established.<sup>1-4</sup> Although methods are available<sup>4,5</sup> 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*<sub>0</sub>, the melting point of pure major component, and *X*<sub>2</sub>, the total mole fraction of minor component. This treatment is based on analysis of the curvature of the plot of the equilibrium temperature, *T*<sub>γ</sub>, vs. 1/γ, 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<sup>6</sup> differential equation for solid solutions

$$\frac{dT}{dX_2} = \left( \frac{k}{k'} - 1 \right) \frac{RT^2}{H_1 - H'} \quad (1)$$

on integration yields

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

where *T*<sub>0</sub> is the melting point of pure major component, *T*<sub>M</sub> is the melting point of a sample containing a total mole fraction *X*<sub>2</sub>'' of minor component whose distribution equilibrium between the solid and liquid phases is expressed by *K* = *k*/*k'*, the Henry's law constant, Δ*H*<sub>F</sub> is the heat of fusion of pure major component, and *R* is the gas constant.

Let *X*<sub>2</sub>' and *X*<sub>2</sub> be the instantaneous mole fraction of minor component dissolved in the solid and liquid phases, respectively, at any equilibrium temperature, *T*<sub>γ</sub>, corresponding to a fraction of sample, γ, melted in the calorimeter, and let *n*<sub>2</sub>', *n*<sub>2</sub> and *n*<sub>0</sub> be

(1) H. L. Johnston and W. F. Giauque, *THIS JOURNAL*, **51**, 3194 (1929).

(2) J. G. Aston, H. L. Fink, J. W. Tooke and M. R. Cines, *Ind. Eng. Chem.*, **19**, 218 (1947).

(3) A. C. Werner and S. V. R. Mastrangelo, *THIS JOURNAL*, **75**, 5244 (1953).

(4) D. D. Tunnicliff and Henry Stone, *Anal. Chem.*, **27**, 73 (1955).

(5) J. G. Aston, M. R. Cines and H. L. Fink, *THIS JOURNAL*, **69**, 1532 (1947).

(6) G. N. Lewis and M. Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 238.

the instantaneous moles of minor component in the solid and liquid phases and the total moles of sample, respectively. In the region of partial melting, the identity shown by equation 3 is applicable.

$$K \equiv \frac{X_2'}{X_2} = \left( \frac{n_2'}{n_0(1-\gamma)} \right) \left( \frac{n_0\gamma}{n_2} \right) \quad (3)$$

Since the total moles of minor component,  $n_2''$ , is constant and  $n_2'' = n_2 + n_2'$ , equation 4 follows from equation 3.

$$K = \frac{(n_2'' - n_2)\gamma}{n_2(1-\gamma)} \quad (4)$$

Solving for  $n_2$  equation 5 is obtained

$$N_2 = \frac{n_2''\gamma}{K + \gamma(1-K)} \quad (5)$$

The instantaneous concentration of minor component in the liquid phase is given by equation 6.

$$X_2 = \frac{n_2}{n_0\gamma} = \frac{n_2''}{n_0} \frac{1}{K + \gamma(1-K)} \quad (6)$$

where  $n_2''/n_0 = X_2''$ , and  $\gamma$  is the fraction melted at the corresponding equilibrium temperature  $T_\gamma$ . This form is then substituted in equation 2 with a rearrangement of terms to yield equation 7, the form of the melting point equation suitable for plotting calorimetric data when solid solutions occur.

$$T_\gamma = T_0 - \frac{RT_0^2}{\Delta H_F} X_2'' \frac{1}{\frac{K}{1-K} + \gamma} \quad (7)$$

Equation 7 may be compared with equation 8, the ordinary equation used for plotting calorimetric data in the absence of solid solutions.

$$T_\gamma = T_0 - \frac{RT_0^2 X_2''}{\Delta H_F \gamma} \quad (8)$$

The  $K/(1-K)$  term in equation 7 corrects the upward curvature of the ordinary plot of  $T_\gamma$  vs.  $1/\gamma$  and yields a straight line for the case,  $0 < K < 1$ . For the determination of  $K$ , values of  $T_{1.00}$ ,  $T_{0.50}$ , and  $T_{0.25}$  are read off the ordinary curve at reciprocal fractions melted of 1.00, 2.00 and 4.00, respectively. These values are then substituted in equation 9 (derived from equation 7 by solving for  $K$  at the indicated values of  $T_\gamma$ ).

$$K = \left( \frac{2}{3} \right) \left\{ \frac{T_{1.00} - T_{0.50} - \frac{1}{2}}{T_{0.50} - T_{0.25} - \frac{1}{2}} \right\} \quad (9)$$

after determining  $K$ , equation 7 is used to replot the data for better extrapolation and interpolation of values of  $T_{1.00}$ ,  $T_{0.50}$ , and  $T_{0.25}$ , and for recalculation of  $K$  by equation 9. Equations 10 and 11 are then used for calculating  $T_0$  and  $X_2$ .

$$T_0 = T_{1.00} + (T_{1.00} - T_{0.50}) \frac{1+K}{1-K} \quad (10)$$

$$X_2 = \frac{\Delta H_F}{RT_0^2} (T_{1.00} - T_{0.50}) \frac{(1+K)}{(1-K)^2} \quad (11)$$

This treatment was applied to data taken from a curve of equilibrium temperature vs. reciprocal fraction melted given by Aston and Fink<sup>5</sup> for a mixture of 95.4% 2,2-dimethylbutane and 4.6% 2,3-dimethylbutane, known definitely to form solid solutions.<sup>7,8</sup> The purity, estimated from the  $T_\gamma$  vs.

(7) H. L. Fink, M. R. Cines, F. E. Frey and J. G. Aston, *THIS JOURNAL*, **69**, 1501 (1947).

(8) J. W. Tooke and J. G. Aston, *ibid.*, **67**, 2275 (1945).

$1/\gamma$  plot, calculated by Aston and Fink, was 99.78 mole %, and  $T_0$ , estimated from this plot in the usual way, was about  $-104.85^\circ$  instead of  $-98.86^\circ$ .<sup>7</sup> By applying the treatment outlined above,  $K$  was found to be 0.675,  $T_0$  was calculated as  $-98.86^\circ$  and  $X_2''$  as 4.6 mole %, in excellent agreement with the theoretical values.

As an independent check on this treatment, equation 7 was used to calculate the solidus temperature of this mixture by setting  $\gamma = 0$  and allowing  $K = 0.675$ ,  $T_0 = -98.86^\circ$  and  $X_2 = 0.046$  as calculated from our treatment of the melting data. The calculated solidus temperature was  $-109.2^\circ$ ; the observed value<sup>6</sup> for this mixture was  $-109.4^\circ$ . Agreement to a few tenths of a degree for this calculation is good.

NOTE ADDED IN PROOF.—The treatment outlined above is for one minor component. A general treatment for two or more minor components does not exist because of the uncertainty in the number of unknown parameters (distribution coefficients and concentrations), and the variability of their relative magnitudes. However, the probability of having more than one minor component in a calorimetric sample which has undergone extensive fractional distillations or crystallizations is relatively rare. Also, replotting the data as suggested above assures the absence of more than one minor component (with different distribution coefficients), when a straight line is obtained for  $T_\gamma$  versus  $1/[K/(1-K)] + \gamma$  over the entire range of the experiment. More than one minor component whose distribution coefficients are the same is, of course, allowable.

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### Deuterium Exchange between Trichloroethylene and Water. Infrared Spectral Data for Trichloroethylene-d

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Base-catalyzed deuterium exchange reactions between water and  $\text{CCl}_3\text{H}$ ,<sup>1-3</sup>  $\text{CCl}_2\text{BrH}$ ,<sup>4</sup>  $\text{CClBr}_2\text{H}$ ,<sup>4</sup>  $\text{CClBrH}_2$ <sup>5</sup> and  $\text{C}_2\text{Cl}_3\text{H}$ <sup>6</sup> have been noted.

The study<sup>3</sup> of the  $\text{CCl}_3\text{H}$ -water exchange offers support for the halocarbanion mechanism; the base-catalyzed exchange of  $\text{CCl}_3\text{D}$  with  $\text{CBr}_3\text{H}$ <sup>7</sup> is a related example. The only datum reported<sup>6</sup> in the trichloroethylene exchange is that some deuteration resulted when  $\text{C}_2\text{Cl}_3\text{H}$  was heated with  $\text{Ca}(\text{OD})_2$  in  $\text{D}_2\text{O}$ . Measurements on the exchange rate of  $\text{C}_2\text{Cl}_3\text{H}$  with  $\text{NaOD}$  in  $\text{D}_2\text{O}$  and on the reverse exchange of  $\text{C}_2\text{Cl}_3\text{D}$  with  $\text{NaOH}$  are reported here.

Purified  $\text{C}_2\text{Cl}_3\text{H}$  ( $n^{25}_D$  1.4741) was refluxed with sodium deuteroxide (ca. 6 N NaOD) at  $81-84^\circ$ . The phases were separated and the trichloroethylene weighed, washed, distilled and analyzed for deu-

(1) Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

(2) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

(3) J. Hine, R. Peek and B. Oakes, *THIS JOURNAL*, **76**, 827 (1954).

(4) R. H. Sherman and R. B. Bernstein, *ibid.*, **73**, 1376 (1951).

(5) R. B. Bernstein, unpublished data.

(6) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950).

(7) G. P. Semeluk and R. B. Bernstein, *THIS JOURNAL*, **72**, 4830 (1950).