

THE ENTHALPY AND ENTROPY OF FORMATION OF THALLIUM(I) CHLORIDE COMPLEX (TlCl) IN AQUEOUS SOLUTION AT 25°

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[Manuscript received October 14, 1968]

The results of three studies¹⁻³ of the thermodynamics of formation of TlCl complex in aqueous solution at 25° are listed as the first three entries in Table 1. The Bell and George¹ figures are derived from measurements of the solubility of TlIO₃ in KCl at 0°, 25°, and 40° using the Davies⁴ equation for ionic activity coefficients at ionic strengths less than 0.1m. Anderson² uses solubility measurements on thallium(I) chloride in mixtures of NaCl and NaClO₄ at 1m total ionic strength, and 5°, 25°, and 45°. He assumes that activity coefficients are constant in the constant ionic strength mixture, and that the Debye-Hückel equation containing a distance parameter is adequate at an ionic strength of 0.016 mole l.⁻¹.

TABLE 1
THERMODYNAMIC FUNCTIONS OF FORMATION OF TlCl AT 25° IN AQUEOUS SOLUTION

K (l. mole ⁻¹)	ΔG° (kcal mole ⁻¹)	ΔH° (kcal mole ⁻¹)	ΔS° (cal mole ⁻¹ deg ⁻¹)	Reference
4.8	-0.93	-1.43	-1.7	1
4.8	-0.93	+0.1	+3.5	2
3.1	-0.67	-1.31	-2.1	3
4.2	-0.85	-1.6 ± 0.5	-2.5 ± 1.7	this work
4.8	-0.93	-1.4 ± 0.5	-1.6 ± 1.7	this work

(These figures presumably supersede earlier figures given by Anderson and Dodgen⁵ which were more positive for ΔH° and ΔS°.) Nair and Nancollas³ use conductivity measurements on thallium(I) chloride at 25° and 40° assuming the Davies⁴ equation for activity coefficients. (These authors give ΔS° as -1.8 cal mole⁻¹ deg⁻¹ and no figure for ΔH°. The listed values are calculated from their equilibrium constants.) Thus the listed enthalpy and entropy figures are all obtained from the temperature variation of equilibrium constants, one set at only two temperatures. Since the Anderson figures differ appreciably from the others and since the precision of the temperature coefficient method has often been questioned⁶ we here report a direct calorimetric determination of ΔH°.

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¹ Bell, R. P., and George, J. H. B., *Trans. Faraday Soc.*, 1953, **49**, 619.

² Anderson, E. L., University Microfilms, Ann Arbor, Mich., Publication No. 14222.

³ Nair, V. S. K., and Nancollas, G. H., *J. chem. Soc.*, 1957, 318.

⁴ Davies, C. W., *J. chem. Soc.*, 1938, 2093.

⁵ Anderson, E. L., and Dodgen, H. W., Amer. chem. Soc., 123rd Meeting, 1953, Abstracts 20P.

⁶ See comments by Rowlinson, J. S., by Rossotti, F. J. C., and by Prue, J. E., in *Discuss. Faraday Soc.*, 1957, **24**, 121, 127, 129.

Experimental

Apparatus and Materials

The calorimeter has been described previously⁷ and was recalibrated by measuring the 100-fold dilution of about 10 cm³ of 3.00m sodium chloride at 25°. Results were 345 and 363 cal mole⁻¹ compared with the literature⁸ value of 353 cal mole⁻¹ at the same concentrations. A.R. chemicals were used throughout.

Measurements and Results

The directly measured quantity was the heat of the 100-fold dilution of about 10 cm³ of about 0.4m KCl in a solution of thallium(I) perchlorate to give 1 l. of solution containing, formally, about 0.05 moles of TlClO₄ and 0.004 moles of KCl. The low concentrations, which limit the precision of the measurements, are dictated by the low solubility product of thallium(I) chloride.⁹ Heat changes of the order of 1 cal were observed and, since there was no detectable heat change in similar experiments in which TlClO₄ was replaced by HClO₄, all of this is attributed to formation of the complex TlCl. Table 2 gives the heat absorbed, *Q*, for the five measurements made, together with the formal concentrations of KCl and TlClO₄ after mixing.

Discussion

Calculation of ΔH from the *Q* values of Table 2 requires the assumption of values for the association constant *K* and the ionic activity coefficient of free ions.

TABLE 2
HEAT ABSORBED

10 ² [TlClO ₄] (final)	10 ² [KCl] (final)	<i>Q</i> (cal)	10 ⁴ × Moles TlCl	ΔH (kcal mole ⁻¹)
4.52	0.352	-0.78	3.81	-2.0
4.52	0.350	-0.71	3.79	-1.9
4.51	0.349	-0.90	3.77	-2.4
4.50	0.375	-0.47	4.05	-1.2
4.50	0.336	-0.45	3.65	-1.2
				av. -1.7 ± 0.5

In calculating entries in the last two columns of Table 2 we use $K = 4.2$ l. mole⁻¹ and the Guggenheim specific interaction activity coefficient expression with $\beta_{\text{Tl,Cl}} = -0.02$ l. mole⁻¹. We have shown^{9,10} that these values fit a wide range of solubility data. The uncertainty given for the average value of ΔH is the standard error and this is consistent with our estimated precision. This value of ΔH is appropriate to the ionic strength of the measurements. Correction¹¹ to zero ionic strength gives the figure for ΔH^0 and the corresponding figure for ΔS^0 in the fourth entry in Table 1. The last entry in Table 1 gives figures for ΔH^0 and ΔS^0 calculated from the experimental observations assuming the Bell and George¹ figure for *K* and using their activity coefficient assumption. This entry shows that our direct measurements are consistent with the temperature variation measurements of Bell and George and that

⁷ Anderson, D. W., Malcolm, G. N., and Parton, H. N., *J. phys. Chem.*, 1960, **64**, 494.

⁸ "Selected Values of Chemical Thermodynamic Properties." Natn. Bur. Stand. Circ. No. 500, 1952.

⁹ Macaskill, J. B., and Panekhurst, M. H., *Aust. J. Chem.*, 1966, **19**, 915.

¹⁰ Khoo, K. H., and Panekhurst, M. H., *Aust. J. Chem.*, 1967, **20**, 2633.

¹¹ Austin, J. M., Matheson, R. A., and Parton, H. N., in "The Structure of Electrolytic Solutions." (Ed. W. J. Hamer.) p. 365. (John Wiley: New York 1959.)

the positive values for ΔH^0 and ΔS^0 given by Anderson² are incorrect. The ΔH^0 and ΔS^0 figures are, of course, dependent on the assumptions about K and activity coefficients. We do not wish to discuss this further here.

Acknowledgments

We acknowledge financial support from the Research Grants Committee of the New Zealand University Grants Committee.