The Standard Enthalpy of Formation of Silver Iodate

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A value for the standard enthalpy of formation of silver iodate, $\Delta H_f°[AgIO_3,c]_{298} = -166.24 \pm 0.7$ kJ mol^{-1}, was found using an isoperibol solution/reaction calorimeter.

Previous measurements (*6, 7*) of the standard enthalpy of formation of silver iodate, -169.9 ± 0.4 and -174.1 kJ mol^{-1}, apparently differ by more than the estimated limits of error. Since a precise value was required as an ancillary datum in connection with a systematic calorimetric investigation of a series of polyhalides in this Laboratory, a redetermination was undertaken.

Experimental Section

Materials. Calorimetric solutions of KIO_3, 0.020 M, were prepared by dissolving the appropriate quantity of powdered dried (24 h, 120 °C) KIO_3 (B.D.H., Analar quality reagent) in water saturated with silver iodate (solubility ca. 0.05 g dm^{-3} at ambient temperatures (*2*)). The solution was stored in the dark before use. Silver nitrate (B.D.H., Analar quality reagent) was finely powdered and dried (24 h, 100 °C) before loading into ampoules.

Calorimetric Equipment and Procedure. A commercial instrument (L.K.B. 8700-1 Precision Calorimetry System) was used, with a 100-cm^3 reaction vessel maintained at 25.00 ± 0.01 °C. Satisfactory checks against systematic errors were made by test calorimetric runs on the neutralization of tris(hydroxymethyl)aminomethane ("THAM") in excess HCl, 0.100 M, a reaction for which definitive data are available (*4*).

Crystalline $AgNO_3$ contained in an ampoule was broken into the calorimetric liquid. The reaction is summarized by the equation: $AgNO_3,c + (p + 1)KIO_3, mH_2O$ (saturated $AgIO_3$) $\rightarrow$ $AgIO_3,c + [KNO_3 + pKIO_3]mH_2O$(saturated $AgIO_3$)ΔH_R. It is assumed that the presaturation of the calorimetric liquid with $AgIO_3$ ensured that product $AgIO_3$ was quantitatively precipitated, presumably in its standard state. The relevant thermochemical equation is:

$$\Delta H_f°[AgIO_3,c] = \Delta H_f°[KIO_3, 3000H_2O] + \Delta H_f°[AgNO_3,c] - \Delta H_f°[KNO_3, 3000H_2O] + \Delta H_R$$

Whence, using the value for ΔH_R reported in Table I, and the following ancillary data: $\Delta H_f°[KIO_3, 3000H_2O] = -472.00 \pm 0.5$, (*1, 3*); $\Delta H_f°[AgNO_3,c] = -124.4 \pm 0.1$, (*9*); $\Delta H_f°[KNO_3, 3000H_2O] = -459.7 \pm 0.5$ (*8, 3*) (all values in kJ mol^{-1}; confidence limits estimated, where not stated explicitly, as ten times the last reported figure), we derive

$$\Delta H_f°[AgIO_3,c] = -166.24 \pm 0.7 \text{ kJ mol}^{-1}$$

Although this value is apparently more in agreement with that of Shidlovskii and Voskresenskii, rather than that of Stern et al., recalculation of the published values using more recent ancillary data, and making allowance for the dissolution of a small amount (ca. 1%) of silver iodate (*2, 5*) reverses this conclusion. Results are shown in Table II, together with the published values. The Russian measurements involved the use of crystalline samples of both iodic acid and silver nitrate in the calorimeter. The former is notoriously difficult to prepare in a pure and completely dry condition and this may account for the difference in results.

Table I. Enthalpy Data for the Reaction of Silver Nitrate with Aqueous Potassium Iodate

w,[a] g	Dilution, n	$-\Delta H_R$, kJ mol^{-1}
0.29572	3191	29.605
0.31843	2964	29.436
0.31317	3013	29.363
0.31662	2981	29.403
0.31385	3007	29.532
0.29916	3155	29.581
0.30057	3140	29.638
0.31152	3029	29.620
0.31413	3004	29.535
0.30500	3094	29.683
	Mean: -29.540 ± 0.077[b]	

[a] Masses of silver nitrate, corrected to vacuo. [b] 95% confidence limits, based on Students' *t* distribution with nine degrees of freedom.

Table II. Standard Enthalpy of Formation of Silver Iodate, kJ mol^{-1}; Recalculated Values in Parentheses

Shidlovskii and Voskresenskii (*6*)	Stern et al. (*7*)	This work
-169.9 ± 0.4	-174.1	
(-163.7)	(-165.11)[a]	-166.24 ± 0.7

[a] Includes heat of solution correction for ca. 1% dissolved $AgIO_3$.

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