values have been used with the estimated entropies of the acid and its ions to calculate provisional values of the free energies.

The Heat of the Reaction of Thiosulfate with Triiodide

By H. W. Zimmermann and W. M. Latimer

The heat of the reaction of thiosulfate with triiodide was redetermined in order to obtain a more reliable estimate of the potential of the thiosulfate–tetrathionate couple.

Calorimeter.—The calorimeter was that described by Latimer and Zimmermann.[1]

Materials.—C. p. chemicals were used without further purification. Analysis showed that the sodium thiosulfate was at least 99.8% $Na_2S_2O_3\cdot5H_2O$.
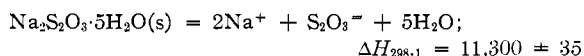
Table I

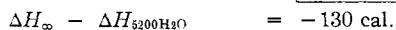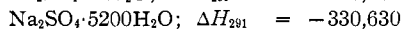HEAT OF SOLUTION OF $Na_2S_2O_3\cdot5H_2O$ AT 25°

No.	$Na_2S_2O_3\cdot5H_2O$ moles	q, cal.	ΔH, cal.
1	0.00930	−105.11	11,302 ± 60
2	.00968	−109.21	11,282 ± 60
3	.00883	− 99.93	11,317 ± 60
		Average ΔH	11,300 ± 35

Total volume in each case 870 cc.

$$Na_2S_2O_3\cdot5H_2O(s) = 2Na^+ + S_2O_3^{=} + 5H_2O;$$
$$\Delta H_{298.1} = 11,300 \pm 35$$
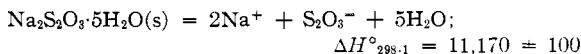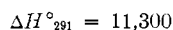
We estimate the heat of dilution by assuming that thiosulfate behaves like sulfate at these concentrations. Bichowsky and Rossini[2] give the heats of formation of sodium sulfate solutions at 18°
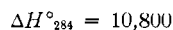
$$Na_2SO_4\cdot\infty H_2O; \quad \Delta H_{291} = -330,760$$
$$Na_2SO_4\cdot5200H_2O; \quad \Delta H_{291} = -330,630$$
$$\Delta H_\infty - \Delta H_{5200H_2O} = -130 \text{ cal.}$$
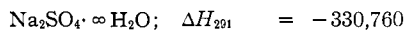
Applying this correction we find

$$Na_2S_2O_3\cdot5H_2O(s) = 2Na^+ + S_2O_3^{=} + 5H_2O;$$
$$\Delta H°_{298.1} = 11,170 \pm 100$$

Thomsen[3] reported for this reaction

$$\Delta H°_{291} = 11,300$$

while Berthelot[4] found

$$\Delta H°_{284} = 10,800$$

(1) W. M. Latimer and H. W. Zimmermann, This Journal, **61**, 1550 (1939).

(2) Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Pub. Corp., New York, 1936.

(3) Julius Thomsen, "Thermochemische Untersuchungen," J. A. Barth, Leipzig, 1882, Vols. I, II.

(4) Berthelot, *Ann. chim. phys.*, [6] **17**, 462 (1889).

Table II shows the heats measured when this salt was dissolved in dilute triiodide solutions.
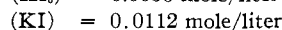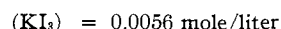
Table II

$$2Na_2S_2O_3\cdot5H_2O(s) + I_3^- = S_4O_6^{=} + 4Na^+ + 3I^- + 5H_2O$$

No.	Initial solution $Na_2S_2O_3\cdot5H_2O$, moles	I_3^-, moles	Excess I_3^-, moles	q, cal.	ΔH, cal./mole $S_2O_3^{=}$
2	0.008730	0.00481	0.00089	−59.99	6873 ± 70
3	.009001	.00481	.00062	64.06	7117 ± 70
4	.008773	.00481	.00085	61.30	6987 ± 70
5	.008710	.00478	.00086	60.68	6966 ± 70
6	.009534	.00506	.00058	66.61	6987 ± 70
				Average ΔH	6986 ± 30

Total volume in each case 870 cc.

In correcting this result to infinite dilution both initial and final solutions should be considered. On the average we may write the concentrations of initial solution:

$$(KI_3) = 0.0056 \text{ mole/liter}$$
$$(KI) = 0.0112 \text{ mole/liter}$$

final solution

$$(Na_2S_4O_6) = 0.0052 \text{ mole/liter}$$
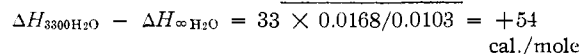$$(KI_3) = 0.00045 \text{ mole/liter}$$
$$(KI) = 0.0164 \text{ mole/liter}$$
$$(NaI) = 0.0103 \text{ mole/liter}$$
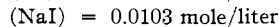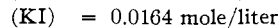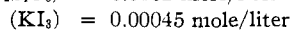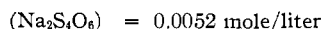
The average amount of $Na_2S_2O_3\cdot5H_2O$ used was 0.0103 mole/liter.

If we consider the initial solution to be made up of 0.0056 + 0.0112 = 0.0168 mole/liter of potassium iodide the heat of dilution will be a trifle high. In the list of Bichowsky and Rossini[2] we find

$$KI\cdot3300H_2O \quad \Delta H_{291} = -73,607$$
$$KI\cdot\infty H_2O \qquad\qquad\qquad -73,640$$
$$\Delta H_{3300H_2O} - \Delta H_{\infty H_2O} = 33 \times 0.0168/0.0103 = +54$$
$$\text{cal./mole}$$

The final solution we assume to contain only

$$0.00045 + 0.01635 + 0.0103 + 2 \times 0.00515 = 0.0324$$
$$\text{mole/liter NaI}$$

The substitution of sodium iodide for potassium iodide and potassium triiodide will make the correction a little high while this substitution for

$0.5Na_2S_2O_4$ tends to give a lower result. Again we find from Bichowsky and Rossini
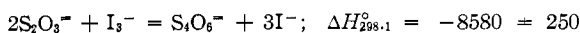
$$NaI \cdot \infty H_2O \qquad \Delta H_{291} = -70,849$$
$$NaI \cdot 1500H_2O \qquad\qquad -70,805$$
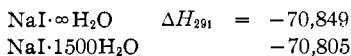
$$\Delta H_{\infty H_2O} - \Delta H_{1500H_2O} = -44 \times 0.0324/0.0103 =$$
$$-160 \text{ cal./mole}$$

Applying these corrections to our experimental result and then doubling we find for the reaction
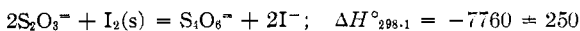
$$2Na_2S_2O_3 \cdot 5H_2O(s) + I_3^- = S_4O_6^- + 4Na^+ + 3I^- +$$
$$10H_2O; \quad \Delta H^\circ_{298.1} = 13,760 \pm 200$$
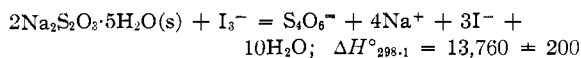
and combining this with the heat of solution

$$2S_2O_3^- + I_3^- = S_4O_6^- + 3I^-; \quad \Delta H^0_{298.1} = -8580 \pm 250$$

The heat of formation of I_3^- (aq) listed by Bichowsky and Rossini, $\Delta H_{291} = -12,140$, does not agree with the experimental data given in the second section of their book. $\Delta H = -12,550$ seems a more probable value for this quantity. Using this figure we find
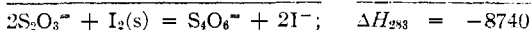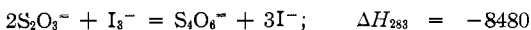
$$I_2(s) + I^- = I_3^-; \quad \Delta H_{291} = 820$$
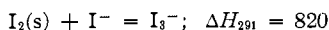
and, neglecting the small temperature difference

$$2S_2O_3^- + I_2(s) = S_4O_6^- + 2I^-; \quad \Delta H^\circ_{298.1} = -7760 \pm 250$$

Thomsen found for this reaction

$$\Delta H_{291} = -7954$$

Berthelot reported

|			
$2S_2O_3^- + I_3^- = S_4O_6^- + 3I^-;$	ΔH_{283}	=	-8480
$I_2(s) + I^- = I_3^-;$			-260
$2S_2O_3^- + I_2(s) = S_4O_6^- + 2I^-;$	ΔH_{283}	=	-8740

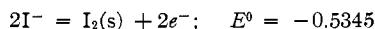Obviously he made a mistake in sign in the second reaction and his result should read

$$\Delta H_{283} = -8220$$

Potential of the Thiosulfate–Tetrathionate Couple.—The entropies of $S_2O_3^-$ and $S_4O_6^-$ are probably about 8 and 35, respectively. These estimates seem reasonable in comparison with the entropies of SO_3^-, SO_4^-, and HSO_3^-, i. e., 3, 4.4, and 32.6, respectively, as given by Latimer.[5]
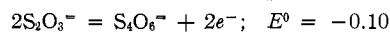
Taking the entropies of $I_2(s)$, 27.9, and of I^-, 25.3, also from Latimer, we find

$2S_2O_3^- + I_2(s) = S_4O_6^- + 2I^-;$	$\Delta S^\circ_{298.1}$	=	42
	$\Delta F^\circ_{298.1}$	=	$-20,200$
	E^0	=	0.44
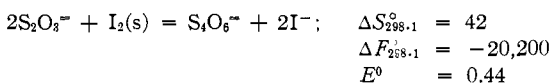
Combining with the potential of the $I^- - I_2$ couple

$$2I^- = I_2(s) + 2e^-; \quad E^0 = -0.5345$$

we find

$$2S_2O_3^- = S_4O_6^- + 2e^-; \quad E^0 = -0.10$$

Summary

The heat of oxidation of thiosulfate by triiodide has been measured. This determination, with the estimated entropies of thiosulfate and tetrathionate, leads to an approximate value for the potential of the thiosulfate–tetrathionate couple.

(5) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

BERKELEY, CALIFORNIA   RECEIVED MARCH 20, 1939

Specific Heats and Heats of Fusion and Transition of Carbon Tetrabromide

BY K. J. FREDERICK AND J. H. HILDEBRAND

The subject of intermolecular forces and solubility has directed our attention particularly to a detailed study of the tetrahalides, for these substances are fine examples of molecules having widely differing volumes and intermolecular fields but with a common highly symmetrical structure. However, in many cases the evaluation of solubility data has been unsatisfactory on account of lack of accurate knowledge of specific heats and heats of fusion. This paper presents the results of determinations of the specific heats and heat of fusion of carbon tetrabromide, whose polymorphic nature, like that of carbon tetrachloride, makes it particularly interesting. The method of mixtures employed in this work

enabled us to determine the heat of the solid transition.

A thorough examination of the literature reveals only meager information concerning carbon tetrabromide. The phase diagram has been studied carefully by Roozeboom and others[1] and they have established definitely the fact that there are two solid forms of carbon tetrabromide with a temperature of transition within the range of 46.6 to 46.9°. There exists also a high pressure modification which need not concern us here. The heat of decomposition of carbon tetrabromide into bromine, hexabromoethane,

(1) B. Roozeboom, "Heterogene Gleichgewichte," Vol. I, 1901, p. 127; W. Wahl, Proc. Roy. Soc. (London), A87, 152 (1913). Phil. Trans., A212, 117 (1913).