two opposed bromate groups would interfere with each other, their interatomic distance being only 2.10 Å. This behavior would give rise to a type of randomness in which all bromate groups in the same column had the same orientation but might differ in orientation from other columns isolated from it by the intervening chains of hydrated neodymium ions.

This type of randomness is suggested by the intensity relationships. The fact that $I_{(03.8)}$ is observed to be greater than $I_{(02.8)}$ demands that z for bromine differ from 0.75 by more than 0.015. This comparison cannot be accounted for by errors in the oxygen parameter, since at the angle at which this reflection occurs the scattering power of oxygen is too small. If the bromine z-parameter is adjusted to give agreement with this comparison the calculated intensity of (50.1) becomes greater than those of many reflections readily observed. However, the reflection (50.1) has never been observed on any photographs. Deviations from z-bromine = 0.75 lead to similar discrepancies for many planes. If the type of randomness suggested above is postulated and introduced into the intensity calculations, these discrepancies disappear. This evidence makes it probable that randomness of this reasonable type exists in the crystal.

Tables II and III give calculated intensities for the polar and for the completely random structure. Table III gives also intensities calculated assuming one-third of the bromate groups to be

oriented in one direction and two-thirds in the opposite direction.

The positive result of the pyroelectric experiment and the fact that it would seem that the best agreement between calculated and observed intensities is obtained with only partial randomness suggest that the orientation of bromate groups in one column may influence that in adjacent columns to some extent, and that consequently the randomness is not complete.

Summary

The structure of $Nd(BrO_3)_3 \cdot 9H_2O$ has been determined, and it has been found that the nine water molecules are coördinated about the rare earth ion, six at the corners of a trigonal prism and three out from the prism faces. The Nd–OH_2 distance has been found to be the same within the limits of error for all water molecules and equal to 2.50 ± 0.05 Å.

The symmetry of the isolated $Nd(OH_2)_9^{+++}$ group is approximately that of D_{3h}. The space group determination gives the point group symmetry at the Nd ion C_{3v}.

The Br–O separation in the bromate group has been determined to be 1.74 ± 0.07 Å., lending support to the interatomic distance reported by Hamilton, 1.78 Å., which is considerably larger than earlier published values.

The existence of randomness in the crystal structure is suggested and discussed.

The Thermodynamics of Hyponitrous Acid

BY WENDELL M. LATIMER AND HERBERT W. ZIMMERMANN

The heat of formation of hyponitrous acid given by Berthelot[1] indicates that the potential of the N_2–$H_2N_2O_2$ couple in acid solution is about equal to that of the fluorine couple. Since experimentally the reduction of hyponitrous acid to nitrogen is very difficult in water solution, it seemed desirable to redetermine the heat of formation of the acid and its ions.

The Calorimeter.—The calorimeter was essentially that described by Pitzer.[2] The main object in its construction was that it should permit accurate measurement of small

amounts of heat so that dilute solutions could be employed which would minimize the correction to infinite dilution.

The reaction vessel was a 1-liter Dewar jar to which was fitted an evacuated glass stopper. A tube of small diameter through the center of this stopper accommodated the stirrer, the leads to heating coil and resistance thermometer. The material which was to react with the solution in the calorimeter was placed in a thin-walled glass bulb, sealed to the end of the stirrer, and could be broken against the bottom of the vessel.

The heater consisted of 102.30 ohms of no. 40 manganin wire with leads of no. 24 copper wire. Approximately 100 ohms of no. 40 wire, with leads of no. 24 manganin, formed the thermometer. The latter was enclosed in the upper part, and the heater in the lower, of a closely

(1) Berthelot, *Ann. chim. phys.*, [6] **18**, 571 (1889).

(2) K. S. Pitzer, THIS JOURNAL, **59**, 2365 (1937).

wound spiral of glass tubing which took the place of the silver cylinder used by Pitzer.

Only glass and paraffin were exposed to the solution in the calorimeter. Even so, solutions of bromine were found to react with paraffin, but with the dilute solutions employed the reaction was only barely noticeable and the resulting heat effect was automatically eliminated from the result in the extrapolation of the temperature.

Resistance changes of the thermometer, accurate to $\Delta R = 10^{-5}$ ohm, were measured by means of a Wheatstone bridge using a measuring current of 0.004 ampere. The energy dissipated by the heater was determined to 0.03% by means of a potentiometer and an electric switch operated by a time signal from the university observatory. The signal also furnished the timing for temperature readings which were taken at one-minute intervals.

The precision of the results obtained was limited mainly by the accuracy with which the temperature drift could be determined. In order to make this drift as small and uniform as possible, the stirrer was driven by a synchronized motor at the lowest practical speed. The central tube through the stopper of the calorimeter was made to extend well above the latter so that the entire stopper could be immersed in the water of the thermostat which was controlled to within 0.003 at 25°.

The heats measured in this calorimeter were reliable, under favorable circumstances, to 0.3 cal. However, the necessity of extrapolating over long periods of time increased this uncertainty considerably. The limits of accuracy given with each experimental result are based upon an estimate of the reliability of the extrapolation.

Preparation of Silver Hyponitrite.—The most convenient method of preparation of hyponitrous acid was found to be the reduction of nitrite by sodium amalgam as described by Divers.[3] Silver hyponitrite was precipitated from the solution and purified by dissolving twice in cold dilute sulfuric acid and reprecipitating, after filtration, by sodium carbonate. The product was of a brilliant yellow color. Analysis of this solid gave 78.05% silver against the theoretical 78.24%. Hyponitrous acid solutions were prepared by treating an excess of the silver salt with hydrochloric acid at 0°. The concentrations of the acid were determined by precipitating the silver salt and weighing as metallic silver.
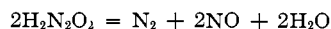
Stability of Hyponitrous Acid Solutions.—

Hyponitrous acid decomposes mainly according to the reaction

$$H_2N_2O_2 = H_2O + N_2O$$
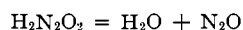
If this is the only reaction taking place, we should expect the percentage of hyponitrous acid decomposed in a given time to be independent of the concentration. A series of experiments disclosed, however, that at 25° a 0.1 M solution was practically completely decomposed in one hour while a 0.01 or 0.001 M solution did not change noticeably in two hours. The decomposition of the 0.1 M solution was quite slow at first but became faster as time went on.

(3) E. Divers, J. Chem. Soc., **75**, 95 (1899).

Partington and Shaw[4] found that in acid solution hyponitrous acid decomposes to some extent into nitrogen and nitric oxide
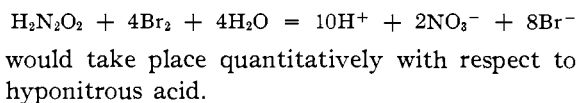
$$2H_2N_2O_2 = N_2 + 2NO + 2H_2O$$

Nitric oxide with the oxygen of the air would form nitrous acid. Thus, if we can assume a fairly rapid reaction

$$H_2N_2O_2 + 2HNO_2 = 4NO + 2H_2O$$
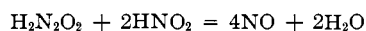
we have a possible explanation of our observations.

Our experiments showed that a 0.001 M solution of hyponitrous acid is sufficiently stable for our calorimetric determinations.

Reaction of Hyponitrous Acid with Bromine.—The reaction of hyponitrous acid with bromine has been examined by several investigators.[5-7] In all cases somewhat less than 4 molecules of bromine were found to be consumed per molecule of hyponitrous acid. In view of these reports it was necessary to determine under what conditions the reaction

$$H_2N_2O_2 + 4Br_2 + 4H_2O = 10H^+ + 2NO_3^- + 8Br^-$$

would take place quantitatively with respect to hyponitrous acid.

For the sake of brevity the details of the large number of experiments will be omitted and merely the results given. The reaction velocity decreases with increasing hydrogen-ion concentration and is comparatively slow in 0.1 M H$^+$. The reaction is rapid in alkaline solution with the formation of nitrite but the oxidation to nitrate is slow. The most favorable condition for the oxidation was found to be with liquid bromine without the addition of either acid or alkali. With a 0.001 M solution of hyponitrous acid and excess bromine 3.98 moles of bromine per mole of hyponitrous acid were used up in one hour and the reaction was at least 99% complete in forty minutes.

Determination of the Heat of Reaction.—In the calorimetric experiments liquid bromine from a sealed glass bulb was added to solutions usually of about 0.001 mole of hyponitrous acid per liter. The contribution of the reaction to the temperature drift could not be determined after forty minutes. Repeatedly the drift of temperature was observed for much longer periods of time but never could any further heat of reaction be observed.

(4) Partington and Shaw, J. Chem. Soc., 2071 (1931).

(5) Berthelot and Ogiers, Ann. chim. phys., [6] **4**, 239 (1885).
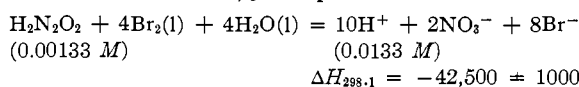
(6) Maquenne, ibid., [6] **18**, 560 (1889).

(7) Kirschner. Z. anorg. Chem., **16**, 434 (1898).

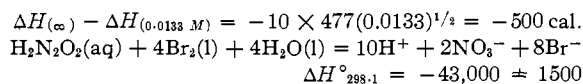Table I shows the results of these experiments together with the amounts of reagents used.

TABLE I

Total volume in each case 870 cc.

No.	$H_2N_2O_2$, moles	Br_2, moles	Excess Br_2, moles	q, cal., obsd.	$-\Delta H$, cal.
4	0.001980	0.02700	0.01908	87.8	39,500
6	.000919	.00891	.00524	39.9	40,600
7	.000994	.01177	.00780	45.4	41,800
9	.001012	.00922	.00518	45.4	42,300
10	.000954	.00486	.00104	41.5	42,900
11	.001009	.00548	.00145	45.8	44,600
12	.000964	.00592	.00106	40.4	41,300
13	.001029	.00488	.00076	45.1	43,400
14	.001031	.00455	.00043	43.1	41,600
15	.001671	.00730	.00061	71.8	42,800

Average ΔH $-42,100$
                         $\pm 1,000$

The heat of solution of bromine in solutions containing 0.01 mole of nitric acid and 0.008 mole of potassium bromide per liter was found to be -500 ± 200 cal. per mole. On the basis of this figure the heat of solution of the excess bromine was deducted from q given in Table I and ΔH calculated from the remainder. Assuming that the reaction was 99% complete we write

$$H_2N_2O_2 + 4Br_2(l) + 4H_2O(l) = 10H^+ + 2NO_3^- + 8Br^-$$
(0.00133 M)   (0.0133 M)
$$\Delta H_{298.1} = -42,500 \pm 1000$$

Correcting to infinite dilution we may neglect the heat of dilution of hyponitrous acid and assume that the Debye–Hückel law holds for the final solution

$$\Delta H_{(\infty)} - \Delta H_{(0.0133\ M)} = -10 \times 477(0.0133)^{1/2} = -500\ \text{cal.}$$
$$H_2N_2O_2(aq) + 4Br_2(l) + 4H_2O(l) = 10H^+ + 2NO_3^- + 8Br^-$$
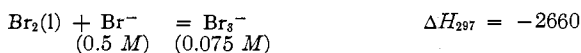$$\Delta H°_{298.1} = -43,000 \pm 1500$$

The temperature extrapolation was made difficult in these experiments by the rather vigorous stirring which was found necessary to bring about solution of the bromine. It is felt, however, that the result is certainly accurate within the stated limits.

Comparison with Berthelot's Result.—Berthelot[1] allowed twice the theoretical quantity of a potassium tribromide solution to react with solid calcium hyponitrite and found
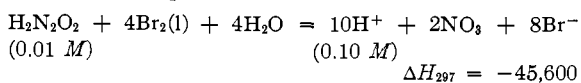
$$CaN_2O_2·4H_2O(s) +$$
$$4Br_3^- = 8H^+ + Ca^{++} + 2NO_3^- + 12Br^-$$
(0.075 M)   (0.08 M)   (0.55 M)
$$\Delta H_{297} = -41,400$$
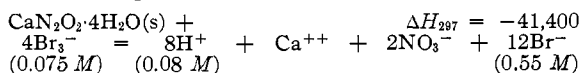
For his tribromide solution he had found

$$Br_2(l) + Br^- = Br_3^-   \Delta H_{297} = -2660$$
(0.5 M)   (0.075 M)

He also dissolved the calcium salt in 0.5 M hydrochloric acid and observed

$$CaN_2O_2·4H_2O(s) + 2H^+ = H_2N_2O_2 + Ca^{++} + 4H_2O$$
(0.5 M)   (0.02 M)
$$\Delta H_{297} = -6410$$
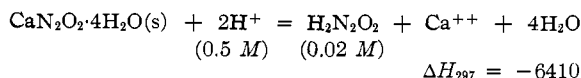
From these figures he calculated

$$H_2N_2O_2 + 4Br_2(l) + 4H_2O = 10H^+ + 2NO_3 + 8Br^-$$
(0.01 M)   (0.10 M)
$$\Delta H_{297} = -45,600$$

In similar experiments with strontium hyponitrite he found for the same reaction

$$\Delta H_{297} = -46,400$$

The discrepancy between these results and ours becomes even greater if we consider heats of dilution and the probability that some of Berthelot's hyponitrous acid decomposed into water and nitrous oxide. We see, however, that Berthelot's results depend very greatly upon the heat of formation of his tribromide solution.

The values listed by Bichowsky and Rossini[8] for the heat of solution of bromine vary from $+900$ to -1240 cal./mole. Our value for this heat, corrected for the formation of 10% Br_3^-, is -400 ± 200 cal. From equilibrium measurements Linhart[9] calculated

$$Br_2(aq) + Br^- = Br_3^-   \Delta H_{298.1} = -1290$$

With our result for the heat of solution of bromine this would lead to

$$Br_2(l) + Br^- = Br_3^-   \Delta H_{298.1} = 1700$$

It seems rather probable that Berthelot's heat for this reaction is high. A value only 400 cal. smaller than his would place his result for the oxidation of hyponitrous acid within the limits of our result.

The Heat of Ionization of Hyponitrous Acid.—The heat of neutralization of hyponitrous acid was determined by adding 13.22-cc. portions of 6.58 N sodium hydroxide to 857 cc. of hyponitrous acid
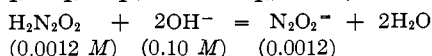
TABLE II

No.	Mole per liter		Calories			$-\Delta H$
	$H_2N_2O_2$	NaOH	q_1	q_2	q_3	
1	0.001206	0.10	31.5	15.1	16.4	15,600
2	.001195	.10	31.2	15.1	16.1	15,500

Average ΔH $-15,500$
                         ± 350

q_1 is the heat evolved when 13.22 cc. of NaOH soln. was added to 857 cc. of $H_2N_2O_2$ soln.

q_2 is the heat evolved when 13.22 cc. of NaOH soln. was added to 857 cc. of water

$q_3 = q_1 - q_2$; $-\Delta H = q_3/0.870$ ($H_2N_2O_2$)

$$H_2N_2O_2 + 2OH^- = N_2O_2^- + 2H_2O$$
(0.0012 M)   (0.10 M)   (0.0012)
$$\Delta H_{298.1} = -15,550 \pm 350$$

(8) Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Pub. Corp., New York, N. Y., 1936.
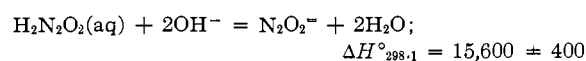(9) Linhart, THIS JOURNAL, 40, 158 (1618).

solution. Experiments in connection with the ionization constants showed that the decomposition of hyponitrous acid in complete and rapid neutralization is negligible, while an alkaline solution of $N_2O_2^-$ decomposes much less readily than a solution of the acid.

The heat of dilution of the sodium hydroxide solution was determined in separate experiments. Results are shown in Table II.

Correcting to infinite volume we neglect the small change in concentration of OH^- and the heat of dilution of hyponitrous acid and assume the Debye–Hückel law for sodium hyponitrite

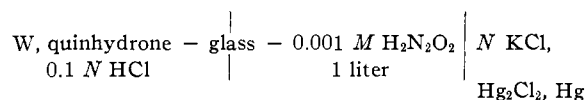$$\Delta H_{(\infty)} - \Delta H_{(0.0012\ M)} = -2480\ (0.0012)^{1/2} = -80\ \text{cal.}$$

Hence

$$H_2N_2O_2(aq) + 2OH^- = N_2O_2^- + 2H_2O;$$
$$\Delta H^\circ{}_{298.1} = 15{,}600 \pm 400$$

Since the heat of ionization of water is 26,700 cal.,[2] we write

$$H_2N_2O_2(aq) = 2H^+ + N_2O_2^-;\quad \Delta H^\circ{}_{298.1} = 11{,}100 \pm 400$$
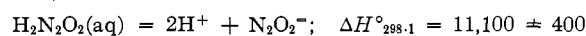
The Ionization Constants of Hyponitrous Acid.—A value for the first constant was obtained by measuring the potential of the cell

W, quinhydrone − glass − 0.001 M $H_2N_2O_2$ | N KCl,
0.1 N HCl | 1 liter |
                                         Hg_2Cl_2, Hg

during the titration at $25°$, with 0.1 N sodium hydroxide. To convert the potentials measured into pH the cell was calibrated repeatedly against a series of Sørensen phosphate buffers.

The potentials were determined within 1 mv. by means of a potentiometer circuit put at the writer's disposal by Messrs. Morse and Preston of this Laboratory.

In these titrations an increasingly rapid drift of the pH was observed as the concentration of $HN_2O_2^-$ was built up, indicating a rapid decomposition

$$HN_2O_2^- = N_2O + OH^-$$
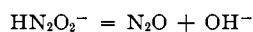
Fortunately this decomposition was not rapid enough to distort the results obtained when the entire titration was completed within three to four minutes.
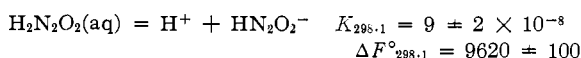
At the point of inflection of the pH curve

$$K' = \frac{a_{(H^+)}\,a_{(HN_2O_2^-)}}{a_{(H_2N_2O_2)}} = a_{(H^+)};\quad \log\frac{1}{a_{(H^+)}} = p\text{H}$$

We observed

$$K' = 10^{-7.05},\ 10^{-7.10},\ 10^{-7.00}$$

and write

$$H_2N_2O_2(aq) = H^+ + HN_2O_2^-\quad K_{298.1} = 9 \pm 2 \times 10^{-8}$$
$$\Delta F^\circ{}_{298.1} = 9620 \pm 100$$

For the determination of the second ionization constant we prepared a 0.00960 M solution of sodium hyponitrite by neutralizing, in the cold, a freshly prepared solution of hyponitrous acid. One drop of a solution of Alizarin Yellow R was added at the same time both to 20-cc. buffer portions and an equal volume of sodium hyponitrite solution in a series of selected test-tubes. Comparison placed the pH of the latter solution between 11.36 and 11.89. The buffer solutions were Sørensen glycocoll–sodium hydroxide mixtures, as given by Clark.[10]

In a second experiment the interval between pH 11.36 and 11.89 was filled with four more buffer solutions and the pH of a 0.00952 M sodium hyponitrite solution determined as 11.4 ± 0.1.

From this result we calculate

$$HN_2O_2^- = N_2O_2^- + H^+;\quad K_{298.1} = 1.00 \pm 0.25 \times 10^{-11}$$
$$\Delta F^\circ{}_{298.1} = 15{,}020 \pm 150$$
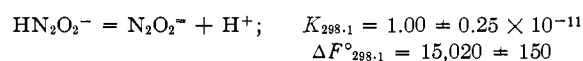
Latimer[11] gave 52 as an estimate of the entropy of $H_2N_2O_2(aq)$. Using this value the entropy of $N_2O_2^-$ is 6.6, which seems reasonable in comparison with 4.4 ± 1.0 for SO_4^-.[12] If these values are correct, the entropy of $HN_2O_2^-$ should be approximately 34.

From the thermal data tabulated by Bichowsky and Rossini[8] the following values of the heats of formation are obtained, $NO_3^- - 49{,}190$ cal., Br^- 128,670 cal., and H_2O (l) $- 68{,}370$ cal. Using the entropy values[11] $H_2(g)$ 31.23, $N_2(g)$ 45.79 and $O_2(g)$ 49.03 e. u., we may then calculate

$$H_2(g) + N_2(g) + O_2(g) = H_2N_2O_2\ (aq)$$
$$\Delta H^\circ{}_{298.15} = -11{,}300 \pm 1500$$
$$\Delta S^\circ{}_{298.15} = -74$$
$$\Delta F^\circ{}_{298.15} = 11{,}000 \pm 2000$$
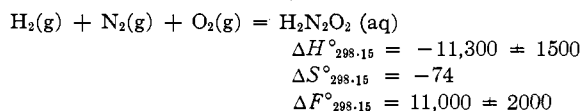
Table III summarizes the thermal data for the acid and its ions.

TABLE III

ΔH°, ΔS° AND ΔF° AT 298.15°K. FOR HYPONITROUS ACID AND ITS IONS

	$H_2N_2O_2$ (aq)	$HN_2O_2^-$	$N_2O_2^-$
$\Delta H^\circ{}_{298.15}$	$-11{,}300 \pm 1500$	$-7{,}000 \pm 2000$	-200 ± 1500
$\Delta F^\circ{}_{298.15}$	$11{,}000 \pm 2000$	$20{,}400 \pm 2000$	$35{,}400 \pm 2000$
$S^\circ{}_{298.15}$	52	34	6.6

Summary

The heat of oxidation by bromine, the heat of neutralization, and both ionization constants of hyponitrous acid have been determined. These

(10) W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, Md., 1928.

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

(12) Latimer, Pitzer and Smith, THIS JOURNAL, **60**, 1829 (1938).

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

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

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% $Na_2S_2O_3 \cdot 5H_2O$.
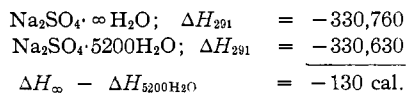
TABLE I

HEAT OF SOLUTION OF $Na_2S_2O_3 \cdot 5H_2O$ AT 25°

No.	$Na_2S_2O_3 \cdot 5H_2O$ 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.

$$Na_2S_2O_3 \cdot 5H_2O(s) = 2Na^+ + S_2O_3^- + 5H_2O;$$
$$\Delta H_{298 \cdot 1} = 11,300 \pm 35$$
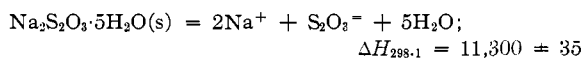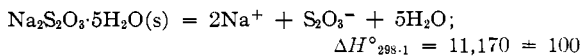
We estimate the heat of dilution by assuming that thiosulfate behaves like sulfate at these concentrations. Bichowsky and Rossini[2] give the heats of formation of sodium sulfate solutions at 18°

$$Na_2SO_4 \cdot \infty H_2O; \quad \Delta H_{291} = -330,760$$
$$Na_2SO_4 \cdot 5200H_2O; \quad \Delta H_{291} = -330,630$$
$$\Delta H_\infty - \Delta H_{5200H_2O} = -130 \text{ cal.}$$

Applying this correction we find

$$Na_2S_2O_3 \cdot 5H_2O(s) = 2Na^+ + S_2O_3^- + 5H_2O;$$
$$\Delta H°_{298 \cdot 1} = 11,170 \pm 100$$

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).

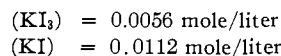Table II shows the heats measured when this salt was dissolved in dilute triiodide solutions.

TABLE II

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

	Initial solution				
No.	$Na_2S_2O_3 \cdot 5H_2O$, 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

$$(Na_2S_4O_6) = 0.0052 \text{ mole/liter}$$
$$(KI_3) = 0.00045 \text{ mole/liter}$$
$$(KI) = 0.0164 \text{ mole/liter}$$
$$(NaI) = 0.0103 \text{ mole/liter}$$
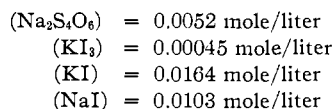
The average amount of $Na_2S_2O_3 \cdot 5H_2O$ used was 0.0103 mole/liter.

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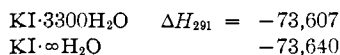
$$KI \cdot 3300H_2O \quad \Delta H_{291} = -73,607$$
$$KI \cdot \infty H_2O \quad -73,640$$
$$\Delta H_{3300H_2O} - \Delta H_{\infty H_2O} = 33 \times 0.0168/0.0103 = +54$$
$$\text{cal./mole}$$

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