Since all of the ordinary lead chloride concerned had been very carefully purified and sublimed in quartz, the 18 individual determinations yielded a significant result for the atomic weight of ordinary lead, namely, 207.217.

CAMBRIDGE, MASSACHUSETTS

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

THE HEAT OF SOLUTION OF SULFUR DIOXIDE[1]

BY ANGIE G. STILES WITH W. A. FELSING

RECEIVED MARCH 16, 1926 PUBLISHED JUNE 5, 1926

Object of the Investigation

The object of this investigation was the direct determination of the total heat of solution of sulfur dioxide in water at various concentrations of sulfurous acid produced. From the data obtained the heat of solution of sulfurous acid solution can be calculated for the concentration range investigated. The data on the total heat of solution, as found recorded in the literature, are not concordant and only one direct determination of the heat of dilution was found recorded. Since, in an investigation in progress in this Laboratory, accurate data of the heat of solution were essential, it was decided to measure directly the heat values.

The Existing Data

The data on the total heat of solution are mostly older data and are not concordant. The values of $-\Delta H$, the total heat of solution per mole of sulfur dioxide dissolved range from 9130 to 6680 calories for concentrations of sulfurous acid produced, expressed by the ratio "moles of H_2O/mole of SO_2" from 6630 to 93. No regularity between $-\Delta H$ and concentration of sulfurous acid solution produced nor agreement between the different investigators[2] is observable.

The Experimental Procedure

The heat of solution of sulfur dioxide was measured directly by passing the gas into distilled water, measuring the temperature rise, and determining the concentration of the sulfurous acid produced.

The details of the calorimeter and accessories are given in Fig. 1.

The calorimeter consisted of a highly evacuated, silvered Dewar flask fitted with a closely fitting, hard rubber cover. Through this cover are fitted, except in case of very

---

[1] Constructed from a thesis submitted by Angie G. Stiles in partial fulfilment of the requirement for the degree of Master of Arts at the University of Texas.

[2] The investigators who have made direct determinations are Thomsen ["Thermochemische Untersuchungen," J. A. Barth, Leipzig, **1882,** Vol. II, pp. 249 and 250] and Berthelot [*Ann. chim. phys.*, [VI] **1,** 74 (1884)]. Bichowsky [THIS JOURNAL, **44,** 130 (1922)] has used a datum by Thomsen and one by Mathias [*Compt. rend.*, **106,** 1148 (1888)] as well as some vapor-pressure data on sulfurous acid solutions by Linder [*Monatsh.*, **33,** 654 (1912)].

concentrated solutions, a 2° Beckmann thermometer T, which was read to 0.001°, a bell-shaped glass stirrer B, an inlet tube leading up into the bell of the stirrer, and outlet tube, Y, for conducting off any sulfur dioxide gas, and a heating coil, C, of platinum, with copper current leads. Fine copper leads, not shown in the figure, were provided for the measurement of the voltage drop across the heating coil. An opening H, closed with a stopper during a determination, is provided for the introduction of the tube P, which allows a sample to be drawn into the weight buret O. The stirrer B is carried by a shellac-coated brass bearing; the lubricant used prevents all but a mere trace of sulfur dioxide from escaping into the room.

The *water equivalent* was determined in the usual manner; the heating current was so adjusted that the time of calibration was the same (or practically the same) as the time of a regular heat of solution determination. The average of six determinations was 38.66 calories (the maximum deviation from the mean was 0.6 calorie or 1.5%).

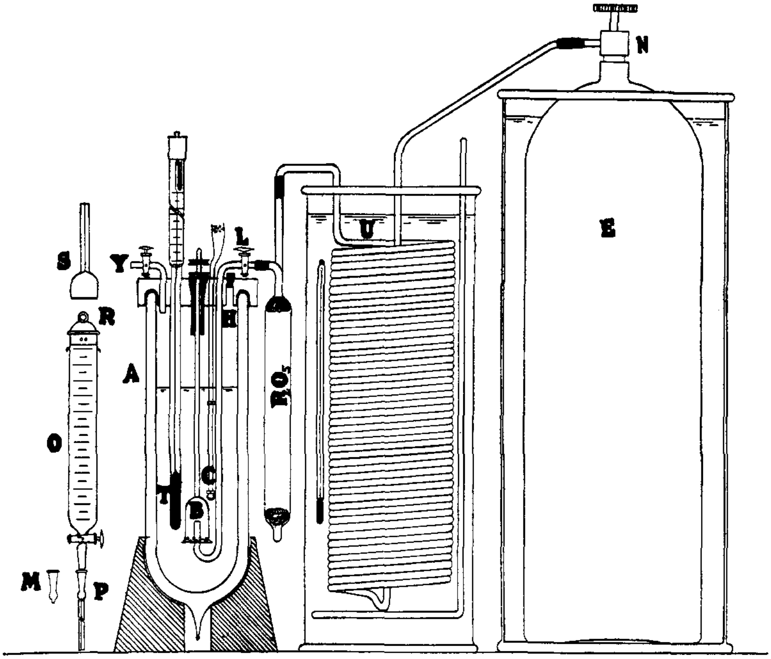

Fig. 1.—Apparatus.

Since (1) the time of calibration was made, by trial, the same in length as the time of an actual determination, (2) the surrounding temperature conditions remained essentially the same, (3) the stirring rate was held constant, and (4) the Dewar flask was highly evacuated and silvered, no radiation corrections were applied in the regular determinations. Also, no temperature corrections were applied for any water evaporated by the excess of sulfur dioxide passing through, because practically all of the gas introduced was dissolved. Only mere traces of sulfur dioxide were detectable at Y, the outlet of the calorimeter; its rate of introduction was governed by the stopcock L.

A regular determination of the heat of solution was carried out as follows.

After the requisite amount of boiled-out, distilled water had been weighed into the calorimeter, the thermometer properly adjusted, and the whole system brought to room temperature (about 25°), a slow stream of sulfur dioxide was passed from the cylinder E (in a water-bath), through the copper coil U and through the phosphorus pentoxide tube into the calorimeter underneath the bell of the stirrer B. After a desired amount of sulfur dioxide had been dissolved, during regular, vigorous stirring, the valve of N and the stopcock L were closed. The maximum rise in temperature, with continued stirring, was carefully noted. The stopper of the opening H was then removed, the tube P inserted well down into the solution, and the tip of the dry weight buret O inserted into the ground junction of P. With the auxiliary extension stopper S in place, a sample was drawn up into O. The stopcock of O was then closed, the extension S removed, and the stopper R replaced. The buret was then withdrawn, the tip wiped quickly, and closed with the cover M. The buret was then weighed. The tip of the buret was then placed down into an excess of standard iodine solution, and a sample was allowed to flow in *under* the iodine solution. Any material adhering to the tip of the buret, after withdrawal, was washed down into the iodine solution, the tip wiped, the cover M replaced, and the weight of buret again determined. The difference in weights gave immediately the weight of sample of sulfurous acid solution. Duplicate analyses for sulfurous acid content were always made.

The excess iodine was then titrated with standard thiosulfate solution, using starch as an indicator and a faint pink as the end-point. This "excess of iodine" method for sulfur dioxide is recommended by Ferguson[3] and the specification of the faint pink as the end-point of titration is due to Washburn.[4]

The Data

The data are listed in Table I. The order of presentation in the table is *not* the order of experimental trial; the tabular order is made according to the increasing concentration of sulfurous acid produced. The column headings make the table self-explanatory.

These data were plotted on very large cross-section paper: log (moles of H_2O/moles of SO_2) = log "N" against $-\Delta H$(cals./mole). A "best" line was drawn through these experimental points; this line is a straight line, and fits the data as well as the accuracy of the determination allows. The average deviation of the experimental points from this straight line

---

[3] Ferguson, THIS JOURNAL, **39**, 366 (1917).

[4] Washburn, *ibid.*, **30**, 42 (1908).

TABLE I

EXPERIMENTAL DATA ON THE TOTAL HEAT OF SOLUTION OF SULFUR DIOXIDE

No.	Δt (°C.)	SO_2, g.	H_2O, g.	$\frac{\text{Moles of } H_2O}{\text{moles of } SO_2}$	$-\Delta H$ (obs.) Cals./mole	$-\Delta H$ (calcd. by Eq. 1) Cals./mole
1	0.180	0.2712	163.28	2140.9	8587	8592
2	.260	.3936	160.12	1446.6	8412	8405
3	.279	.4435	170.07	1363.6	8412	8376
4	.447	.7448	172.59	824.01	8122	8134
5	.553	.9233	170.40	656.27	8021	8025
6	.568	.9572	173.49	644.51	8065	8016
7	.615	1.0365	172.72	592.55	8015	7976
8	.632	1.0630	170.00	568.58	7947	7956
9	.658	1.0973	168.18	545.01	7946	7936
10	.678	0.9271	129.62	497.17	7884	7893
11	.800	1.2631	155.11	436.67	7862	7830
12	.920	1.4840	156.32	374.57	7744	7756
13	.947	1.6411	170.83	370.15	7745	7750
14	1.080	1.8860	170.83	322.10	7685	7684
15	1.097	1.9410	173.22	317.34	7671	7676
16	1.422	2.5120	168.67	238.76	7519	7539
17	1.476	2.6240	168.92	228.90	7480	7519
18	1.768	3.1480	167.59	189.30	7421	7428
19	1.830	3.3074	170.15	182.94	7401	7412
20	3.420	6.3901	168.50	93.76	7103	7091
21	4.190	7.9602	168.76	75.29	6994	6986

relation is 0.2%; the maximum deviation (No. 6) is 0.6%. The relation obtained is

$$-\Delta H(\text{cals./mole}) = 4911.6 + 1105.26 \log_{10} \text{"N"} \qquad (1)$$

The last column of the table presents the values of $-\Delta H$ calculated by this relation for the experimental values of N.

The rate of change of the total heat of solution per mole of sulfur dioxide at any concentration point is given by

$$d(-\Delta H)/dN = 479.92\ (1/N) \qquad (2)$$

Berthelot[5] cites a value for the *heat of dilution* of a certain sulfurous acid solution at 12.9°. He diluted a solution containing 84 g. per liter of *solution* with five times its volume of water. The measured heat effect was equivalent to 560 calories when a solution of sufficient volume to contain 1 mole of sulfur dioxide, at a concentration of 84 g. of sulfur dioxide per liter of *solution*, is diluted with five times its volume of water.

A density datum on his concentrated solution not being available, the mole-ratios, **N,** could only be approximated, at 41 and 253. Integrating Equation 2 between the limits of **N** of 41 and 253, there is obtained as the *heat of dilution* the value 873.5. This value is considerably higher than Berthelot's single experimental value of 560 calories, made at 12.9°.

[5] Berthelot, *Ann. chim. phys.*, [VI] **1,** 74 (1884).

Summary

The total heat of solution of sulfur dioxide has been determined at 25° (very nearly) for a number of concentrations of sulfurous acid produced.

The relation between $-\Delta H$(cals./mole of sulfur dioxide) and **N**(moles of water/mole sulfur dioxide) is given by the equation $-\Delta H = 4911.6 + 1105.26 \log_{10} \mathbf{N}$, which reproduces the experimental data on an average to within 0.2%; the agreement is much closer in most cases, and the relation is considered accurate to better than 1 part in 400 at 25°.

Austin, Texas

[Contribution from the Chemical Laboratory, University of Maine]

THE SYSTEM: SODIUM IODIDE-ACETONE-WATER

By Rudolph Macy and Edgar W. Thomas[1]

Received March 23, 1926 Published June 5, 1926

The purification of sodium iodide by precipitation of the double compound, $NaI.3CH_3COCH_3$, was first proposed by Shipsey and Werner.[2] This method has since been extensively employed in place of the former practice of precipitating the double compound with sodium bisulfite, $NaHSO_3.CH_3COCH_3$. Purification by means of sodium iodide has also been applied to methylethyl ketone,[3] the double compound having been assigned the formula $NaI.CH_3COC_2H_5$.

Several statements in the original article by Shipsey and Werner in regard to the conditions necessary for obtaining large yields of crystals of the sodium iodide compound made it seem advisable to investigate the solubility relationships of sodium iodide in acetone and in mixtures of acetone and water. The solubility of sodium iodide in acetone has been measured up to the boiling point of the saturated solution, and the ternary system with water has been studied at 25°.

The sodium iodide was recrystallized from the Merck product and kept dry in an oven at 105° until used. Two samples of acetone were employed, one obtained from Merck and the other from the Eastman Kodak Co. They were dried over copper sulfate and redistilled, using a 60 cm. fractionating column and a calibrated Anschütz thermometer. Both samples boiled at 56.3° (765 mm.).

Equilibrium between sodium iodide and solution was obtained by stirring the salt with solvent at constant temperature in a tube fitted with a mercury seal. Samples of the saturated solutions were obtained by pressure through a tube fitted with a muslin filter; the samples were forced over from the solubility apparatus into a weighed bottle with a calibrated stem,

---

[1] Some of the data reported in this paper were originally obtained by E. W. Thomas, and submitted in a thesis for the Bachelor's degree at the University of Maine in June, 1925.

[2] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[3] Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).