ACTA CHEMICA SCANDINAVICA 17 (1963) 1917–1924

The Heats of Solution and Oxidation of Sulfur Dioxide

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The heat of formation of sulfuric acid has been determined from measurements of the heat of oxidation of a water solution of SO_2 by elemental bromine and the heat of solution of gaseous SO_2 in water. Literature data on heats of formation of SO_2, HBr, and H_2O and heats of dilution of H_2SO_4 have been used. For the reaction

$$H_2(g) + S(rh) + 2\ O_2(g) + 2500\ H_2O(liq) \rightarrow H_2SO_4,\ 2500\ H_2O$$

the obtained result is -214.33 ± 0.15 kcal.mole^{-1} which is 0.27 kcal.mole^{-1} different from that obtained by combustion experiments, -214.01 ± 0.05 kcal.mole^{-1}.

An accurate value for the heat of formation of sulfuric acid is necessary for determination of the thermochemical and thermodynamic properties of sulfur-containing compounds. The heat of combustion of rhombic sulfur to produce an aqueous solution of sulfuric acid has been determined recently [1-5] by means of rotating-bomb calorimetric techniques; the results indicate that the value given by Rossini, Wagman *et al.*[6] is high by about 600 calories.

The heat of formation of gaseous sulfur dioxide was determined by Eckman and Rossini [7] to be -70.96 ± 0.05 kcal/mole; this value is believed to be accurate within the assigned uncertainty. An examination of the existing data on the heat of solution of sulfur dioxide [8-11] indicated the possibility of systematic errors and it was therefore decided to make a separate determination over the range of concentrations pertinent to these experiments.

In order to complete the data from rhombic sulfur to aqueous sulfuric acid it was necessary to measure the heat of oxidation of aqueous sulfur dioxide to sulfuric acid. The method used in this investigation was to introduce a known quantity of liquid bromine into a solution containing a slight excess of sulfur dioxide and to measure the energy evolved by this process. The heats of dilution of sulfuric acid have been carefully determined in a recent investigation.[12]

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* Sponsored by the *Swedish Natural Science Research Council* and the *Swedish Technical Research Council.*

HEAT OF OXIDATION OF AQUEOUS SULFUR DIOXIDE

Materials

Bromine. The bromine was taken from a fresh ampoule of reagentgrade material. Traces of water were removed by extraction with concentrated sulfuric acid. A small quantity of potassium bromide was added and the bromine was distilled in a closed system at reduced pressure. The first fourth of the distillate was selaed off and put aside; about half of the remaining material was distilled and sealed into ampoules containing about 5 ml each. Thin-walled spherical sample bulbs, having a diameter of 6—8 mm and a 1/2 mm capillary stem, were prepared from soft glass; the base of each bulb was heated and drawn in so that the resulting volume was 0.1 to 0.3 ml. The bromine was introduced by means of a capillary pipet; the bulb was heated to vaporize some of the bromine and was then immediately sealed off. The quantity of bromine was determined from the increase in mass of the sample bulb.

Sulfur dioxide. The sulfur dioxide solution was prepared by passing the gas into a 3-liter, amber-glass flask of freshly-boiled distilled water. A slight excess of sulfur dioxide was added and the excess was removed by bubbling nitrogen gas through the solution. The sulfur dioxide solution was removed from the flask by means of a siphon; water-saturated nitrogen, at a pressure slightly greater than atmospheric, filled the space above the solution in the flask. The concentration of the sulfur dioxide was determined by adding a measured volume of the solution to an excess of 0.1 N standard iodine (in potassium iodide) and titrating the excess with 0.05 N sodium thiosulfate. It was found that a dilute solution of sulfur dioxide (approximately 0.03 M), if carefully prepared and protected from contact with oxygen, could be kept for at least a week with no significant change in composition.

Hydrobromic acid and sulfuric acid. The aqueous hydrobromic acid was prepared by distillation of a portion of a 40 % reagent-grade solution. The sulfuric acid solution was prepared by dilution of concentrated reagent-grade acid. The concentrations of these solutions were determined by titration with 0.1 N standard alkali using bromothymol blue as the indicator; weight burets were used for all titrations. The concentration of the hydrobromic acid solution was 9.912 M; the concentration of the sulfuric acid was 3.491 M.

Apparatus and procedure

The 100 ml glass calorimeter was similar to that described by Sunner and Wadsö [13] except that the sample bulb was enclosed in an enlarged section of the tubular stirrer shaft and was crushed by depressing a glass rod within the shaft. The sample-containing section was open on both sides and was arranged such that there would be a flow of solution through the section during rotation of the shaft. The bottom of the vessel was hemispherical; the stirrer consisted of a glass paddle, the bottom of which conformed to and was situated about 5 mm above the bottom of the vessel. Two thin-glass thimbles, about 5 cm long and 5 mm diameter were sealed to the top and projected into the vessel; one thimble contained the thermistor and the other a 44.867 Ω manganin heating coil. Both the thermistor and the heating coil were immersed in paraffin oil to insure good thermal contact. The leads to the thermistor and to the heating coil passed through an epoxy-resin seal at the top of each thimble. The calorimeter was sealed to the jacket cover with epoxy-resin. The heater and thermistor leads were soldered to a ceramic connector which was sealed into the cover. This system was designed for use with a vacuum jacket; in these experiments, however, the jacket contained air at atomspheric pressure. The entire assembly was lowered into the thermostat and the calorimeter was stirred at 600 rpm by means of a synchronous motor.

Temperatures were determined by means of a thermistor in a Wheatstone D. C. bridge circuit. This particular thermistor had a resistance of 2160.2 Ω at 25.00°C and $\Delta R/\Delta T$ was -80.8 Ω/°C at 25°C. Comparison with a Beckmann thermometer showed no measurable change in its resistance at 25°C during this investigation. The galvanometer was used only as a null instrument; a chronometer was used to determine the time at which the resistance of the thermistor reached certain predetermined values.

Calibration of the calorimetric system was accomplished by introducing a known amount of electrical energy into the system and measuring the corresponding change in the resistance of the thermistor. The quantity of electrical energy was determined from measurements of the time and magnitude of an electric current which was passed through a calorimeter heating coil assuming the resistance of the latter to be constant. The magnitude of the current was determined on a Rubicon Type-B potentiometer from the potential drop across a 10.001 Ω standard resistor in series with the calorimeter heating coil. A double-throw snap switch, operated by a lever which simultaneously started a chronometer, switched the current from a 44.8 Ω "dummy" resistor into the calorimeter heater. A second depression of the lever simultaneously interrupted the current and stopped the chronometer. The error in timing by this procedure was estimated to be approximately ± 0.02 seconds. The fact that a significant change in the magnitude of the electric current did not significantly affect the energy equivalent of a given calorimetric system was taken as evidence that, for all practical purposes, the resistance of the calorimeter heater remained constant. Measurements of the resistance of the heating coil showed that it was constant within ± 0.001 Ω during this investigation. The energy equivalent of a given calorimetric system E° was obtained as the ratio of the quantity of electrical energy to the change in temperature as expressed in units of $\log R_i/R_f$ where R_i and R_f are the initail and final resistances, respectively, of the thermistor. Where the heat capacity of the actual calorimetric system differed significantly from that of the "standard" or calibrated system, a correction, ΔE, was applied to obtain E_a, the energy equivalent of the actual calorimetric system. The thermostat was controlled at 25°C within ± 0.001°C by means of a contact thermometer and an electronic relay using an off-on system.

The calorimeter was charged with 100 ml of solution using a pipet which was filled by means of a siphon; the stirrer together with the sample and crushing rod was introduced, the calorimeter jacket was sealed and the assembly was lowered into the thermostat. The calorimeter was then pre-heated to a point such that, following the reaction, the final temperature would be approximately 25°C. Calorimeter temperatures were observed during a "fore" rating period by recording the times at which the thermistor resistance reached certain predetermined values. 10 min after thermal equilibrium was reached the sample bulb was crushed and the reaction took place. Temperature observations were made until 10 min after thermal equilibrium was reestablished.

The equilibration time of the calorimeter was approximately 1 min. The thermal leakage modulus was 0.0072°C/°C min^{-1}. The stirring energy was 0.10 cal/min. The heat capacity of the calorimetric system was 116.2 cal/°C. The values of R_i and R_f were determined graphically by the method of Dickinson.[14]

The concentrations of the sulfur dioxide in the initial and final solutions were determined in each case by adding a 20-ml portion of the solution to an excess of standard iodine solution and titrating the excess with 0.05 N sodium thiosulfate. The total acidities were also determined in each case on separate samples by flushing out the greater part of the sulfur dioxide with nitrogen, oxidizing the remainder with iodine, and titrating the resulting solution with 0.1 N standard alkali. A correction calculated from the required quantity of the iodine solution was applied for the hydrobromic and sulfuric acids formed by oxidation of the sulfur dioxide.

All energy measurements were made in terms of the absolute joule; for conversion to the conventional thermochemical calorie, one calorie was taken as equivalent to 4.1840 joules. All molecular weights were taken from the 1957 Table of Atomic Weights.[15]

THE HEAT OF SOLUTION OF SULFUR DIOXIDE

The experiments on the heat of solution of sulfur dioxide were carried out in a different calorimeter system. The calorimeter consisted of a 500 ml. Dewar-type glass vessel attached to a standard taper joint. The brass calorimeter head was constructed to fit tightly over the glass taper; the gas-inlet and exit tubes, the calorimeter heater, the thermometer fitting and the bearings for the stirrer shaft were attached to the calorimeter head. The glass stirrer was attached to a tubular stainless-steel shaft which passed through an o-ring seal and was supported by ball-bearings in the calorimeter head. The heater consisted of a 102.7 Ω manganin heating coil sealed between two thin-walled, concentric glass cylinders; the heater leads were enclosed in glass tubes sealed to the calorimeter head.

The gas inlet tube consisted of a coarse capillary which projected below the surface of the liquid to a point about 1 cm above the screw-type stirrer. The capillary gas-outlet tube opened in the vapor space in the upper part of the calorimeter. A 25 Ω glass-sheathed platinum resistance thermometer was attached through a rubber stopper in the calorimeter head and was clamped in place by a threaded brass fitting. The calorimeter was completely immersed in a thermostat at approximately 25.0°C and regulated to ± 0.001°C. The stirring rate was approximately 500 rpm. The heat capacity of the water-filled system was 555.32 cal/°C, the stirring energy was 0.415 cal/min and the thermal leakage modulus was 0.0008°C/min per degree of variation from the temperature of the thermostat.

Calorimeter temperatures were determined to ± 0.00005°C from the resistance of the platinum thermometer as measured on a G-2 Mueller bridge in conjunction with a high-sensitivity galvanometer. The calorimetric system was calibrated by the introduction of a measured quantity of electrical energy [16] and determination of the ratio of the quantity of energy to the corrected temperature rise [17] of the system. In those experiments involving relatively small changes in temperature it was possible to calibrate the actual calorimetric system immediately prior to the calorimetric experiment. For the other experiments it was necessary to calibrate a carefully reproduced system over approximately the same temperature interval as in the calorimetric experiment.

The calorimeter was filled by weighing in 498.5 g of water at about 23.5°C. The calorimeter head was attached, the thermometer inserted and the assembly placed in a water-filled thermostat at 25.0°C which was controlled within ± 0.001°C. The calorimeter was then preheated to the desired initial temperature which was chosen such that the final temperature in each case would be approximately equal to 25°C. Oxygen was removed from the system by flushing with water-saturated nitrogen. After an initial rating period a stream of dry sulfur dioxide gas was introduced; when the calorimeter temperature approached 25°C the flow of sulfur dioxide was discontinued and the gas remaining in the inlet tube was carried into the calorimeter by momentarily introducing a stream of water-saturated nitrogen. This was necessary to prevent the rise of the solution in the inlet tube. The inlet and exit tubes were closed immediately after the introduction of the sulfur dioxide which effectively sealed the calorimeter. Calorimeter temperatures were observed at 1-minute intervals throughout the experiment including a ten-minute initial rating period and were continued for a ten-minute period after a steady state was reached following the reaction period.

A sample of the solution was drawn into a previously weighed and evacuated weight-buret which was closed at the top by means of a stopcock attached to the buret with a glass-taper joint. Air was then let into the buret, the joint was removed, the buret caps quickly attached and the filled buret was weighed. The sulfur dioxide solution was then slowly transferred into a weighed quantity of standard iodine solution (previously cooled to −10°C) by means of a tube attached to the buret, which projected beneath the surface of the iodine solution. Additional iodine solution was added when necessary to maintain an excess of iodine in the titration flask until all of the sulfur dioxide solution had been introduced. The trace of solution remaining in the buret and in the connecting tube was then washed into the titration flask and the excess of iodine determined by titration with 0.05 N sodium thiosulfate solution.

The calculated weight of sulfur dioxide was subtracted from the weight of solution in order to obtain the weight of water in the sample and the fraction of the total calorimeter solution.

RESULTS AND DISCUSSION

The results of the electrical calibration experiments on the system used for measurement of the heat of reaction of bromine with aqueous sulfur dioxide are given in Table 1. Log R_i/R_f was obtained from R_i and R_f, the graphically obtained initial and final resistance values, respectively, of the thermistor, i is the electric current through the calorimeter heating coil, t is the time of flow of the heating current, and E_s is the energy equivalent of the standard calorimeter system, obtained as joules per unit of log R_i/R_f.

The results of the experiments on the heat of reaction of liquid bromine with aqueous sulfur dioxide are given in Table 2 in which E_a is the energy

Table 1. Electrical calibration [a] for system $Br_2(liq) + SO_2(aq)$.

Expt. No.	log R_i/R_f	i amp.	t sec.	E_s j/log R_i/R_f
1	0.0128448	0.147704	399.85	30 471
2	0.0133062	0.147559	415.50	30 505
3	0.0129861	0.147449	405.87	30 487
4	0.0126822	0.147246	379.30	30 475
5	0.0128855	0.147068	404.70	30 478
6	0.0129150	0.147129	405.10	30 464
		Mean		30 480
		Standard deviation of the mean		± 5.9

[a] The resistance of the calorimeter heater is 44.867 Ω; the electrical energy is thus equal to 44.867 i^2t joules.

equivalent of the actual calorimetric system (corrected for the heat capacities of the glass bulb and the bromine), $q_{(obs)}$ is the energy evolved in the process and $q_{(dil)}$ is a correction applied to correct the individual results to refer to a final solution of a given concentration. The results correspond to the process:

$$Br_2(liq) + [1.591\ SO_2 + 2926\ H_2O] = [2\ HBr + H_2SO_4 + 0.591\ SO_2 + 2924\ H_2O]\quad \Delta H(25°C) = -54.31 \pm 0.09\ \text{kcal/mole}. \tag{1}$$

Table 2. Heat of reaction of $Br_2(liq) + SO_2(aq)$.

Expt. No.	Log R_i/R_f	E_a	Br_2 mmole	$q_{(dil)}$ j	$-\Delta H(25°C)$ kj/mole
1	0.0122631	30 492	1.64844	+ 0.29	227.01
2	0.0140726	30 492	1.88475	+ 0.04	227.69
3	0.0131287	30 491	1.75981	+ 0.13	227.55
4	0.0182816	30 495	2.45636	− 0.25	226.86
5	0.0151789	30 493	2.03491	+ 0.17	227.54
6	0.0133227	30 491	1.79466	0.00	226.35
7	0.0124462	30 491	1.66665	+ 0.08	227.75
			Mean		227.25
			Standard deviation of the mean		±0.31

Eqn. (1) may be combined with heats of dilution of sulfuric acid, sulfur dioxide, and hydrobromic acid to obtain the following process:

$$Br_2(liq) + 2(SO_2\cdot 1250\ H_2O) + 2\ H_2O(liq) = [(H_2SO_4\cdot 2500\ H_2O) + 2\ (HBr\cdot 1250H_2O) + (SO_2\cdot 2500\ H_2O)] \tag{2}$$

$$\Delta H(25°C) = -53.41 \pm 0.09\ \text{kcal/mole}.$$

The data used for calculation of the heats of dilution of sulfuric acid and hydrobromic acid were taken from the literature.[6] The data obtained in the present investigation on the heat of solution of sulfur dioxide were used to calculate the heats of dilution of sulfur dioxide.

The results of the experiments on the heat of addition of aqueous sulfuric acid to an aqueous solution of sulfur dioxide are given in Table 3. In this case,

Table 3. Results of the experiments on the heat of addition of aqueous sulfuric acid to aqueous sulfur dioxide.

Expt. No.	Log R_i/R_f	E_a	$q_{(dil)}$ j	H_2SO_4 mmole	$-\Delta H(25°C)$ kj/mole
1	0.0004325	30 562	+ 0.13	1.330	10.04
2	0.0005141	30 681	+ 1.63	1.639	10.62
3	0.0004068	30 482	− 0.25	1.234	9.85
4	0.0004182	30 439	− 0.21	1.242	10.08
5	0.0004120	30 246	− 0.17	1.255	9.79
6	0.0004271	30 709	+ 0.13	1.327	9.98
7	0.0004710	30 876	+ 0.88	1.527	10.10
8	0.0004709	30 529	+ 0.75	1.485	10.19
		Mean			10.08
		Standard deviation of the mean			±0.11

since the increase in the calorimeter temperature amounted to only a few hundredths of a degree, it was possible to calibrate the actual calorimetric system immediately prior to the addition of the acid; it was not necessary, therefore, to make a correction for the heat capacity of the sample or to duplicate the system exactly between experiments. The results have been corrected with $q_{(dil)}$ to make all experiments correspond to a final solution of a given concentration. The results given in Table 3 may be represented by the process:

$$[H_2SO_4 + 16\ H_2O] + [0.729\ SO_2 + 4012\ H_2O] = [H_2SO_4 + 0.729\ SO_2 + 4028\ H_2O]$$
$$\Delta H(25°C) = -2.41 \pm 0.05\ \text{kcal/mole.} \quad (3)$$

The heat of mixing of aqueous sulfuric acid with aqueous sulfur dioxide has been obtained by correction of eqn. (3) with the appropriate heats of dilution and corresponds to the process:

$$H_2SO_4{\cdot}2500\ H_2O + SO_2{\cdot}2500\ H_2O = [H_2SO_4{\cdot}2500\ H_2O + SO_2{\cdot}2500\ H_2O]$$
$$\Delta H(25°C) = 0.75 \pm 0.05\ \text{kcal/mole.} \quad (4)$$

The results of the experiments on the heat of addition of aqueous hydrobromic acid to an aqueous sulfuric acid-sulfur dioxide solution are given in Table 4. The results may be represented by the process:

$$[HBr + 5.59\ H_2O] + [0.547\ H_2SO_4 + 0.264\ SO_2 + 1466.8\ H_2O] = [HBr + 0.547\ H_2SO_4 + 0.264\ SO_2 + 1472.4\ H_2O] \quad (5)$$
$$\Delta H(25°C) = -1.59 \pm 0.02\ \text{kcal/mole.}$$

The heat of mixing of the aqueous hydrobromic acid with the sulfuric acid-sulfur dioxide solution was obtained by correction of eqn. (5) with the appropriate heats of dilution and corresponds to the process:

$$2(HBr{\cdot}1250\ H_2O) + [H_2SO_4{\cdot}2500\ H_2O + SO_2{\cdot}2500\ H_2O] = [2(HBr{\cdot}1250\ H_2O) + H_2SO_4{\cdot}2500\ H_2O + SO_2{\cdot}2500\ H_2O] \quad (6)$$
$$\Delta H(25°C) = 0.65 \pm 0.02\ \text{kcal/mole HBr.}$$

Table 4. Results of the experiments on the heat of addition of aqueous hydrobromic acid to a sulfur dioxide solution containing sulfuric acid.

Expt. No.	Log R_i/R_f	E_a	$q_{(dil)}$ j	HBr(aq) mmole	$-\Delta H$(25°C) kj/mole
1	0.0007896	30 772	-0.02	3.576	6.79
2	0.0008819	30 793	$+0.08$	4.095	6.65
3	0.0008086	30 397	0.00	3.693	6.66
4	0.0009330	30 224	$+0.11$	4.204	6.73
5	0.0007071	30 389	-0.07	3.306	6.48
6	0.0009271	30 396	$+0.09$	4.187	6.75
7	0.0007654	30 383	-0.02	3.567	6.52
8	0.0007768	30 584	-0.08	3.562	6.66
			Mean		6.66
			Standard deviation of the mean		± 0.04

Eqns. (2), (4), and (6) may be combined to give eqn. (7) which corresponds to eqn. (1) after correction for heats of dilution and mixing:

$$\mathrm{Br_2(liq) + SO_2 \cdot 2500\ H_2O + 2\ H_2O(liq) = H_2SO_4 \cdot 2500\ H_2O + 2(HBr \cdot 1250\ H_2O)} \quad \Delta H(25°\mathrm{C}) = -55.47 \pm 0.11\ \mathrm{kcal/mole.} \tag{7}$$

Eqn. (7) may be combined with the heats of formation of aqueous sulfur dioxide [6] (Ref.[6] and this work) and of aqueous hydrobromic acid [6] to obtain the heat of formation of aqueous sulfuric acid:

$$\mathrm{S(rh) + 2\ O_2(g) + H_2(g) + aq = H_2SO_4 \cdot 2500\ H_2O}$$
$$\Delta H(25°\mathrm{C}) = -214.33 \pm 0.15\ \mathrm{kcal/mole.}$$

The results of the experiments on the heat of solution of sulfur dioxide are given in Table 5 where ΔR_c is the corrected temperature rise of the calorimetric system as measured on the platinum resistance thermometer and E_a is the energy equivalent of the actual calorimetric system.

The heat of formation of $H_2SO_4 \cdot 115\ H_2O$ was determined to be -212.20 ± 0.05 kcal/mole from independent rotating-bomb calorimetric determinations.[4,5]

The heat of dilution from $1-115\ H_2O$ to $1-2500\ H_2O$ has been calculated to be -1.81 kcal/mole giving -214.01 kcal/mole for the heat of formation of $H_2SO_4 \cdot 2500\ H_2O$. The value of -214.28 kcal/mole obtained in the present investigation would indicate a discrepancy of 0.27 kcal/mole which is slightly greater than the sum of the assigned single uncertainties of the measurements. This would indicate a possible error in the heat of formation of aqueous sulfur dioxide or aqueous hydrobromic acid.

The heat of oxidation of aqueous sulfur dioxide with gaseous chlorine has been determined in a recent investigation.[18] The difference between the values obtained for the heats of oxidation of sulfur dioxide using bromine and that obtained using chlorine should be a measure of the internal consistency between the accepted values for the heats of formation of hydrogen bromide and hydrogen chloride. Additional evidence for this consistency may be obtained from a similar comparison between heats of oxidation of arsenious oxide.

Table 5. Results of the experiments on the heat of solution of gaseous sulfur dioxide in water.

Expt. No.	ΔR_c ohm	E_a j/ohm	SO_2 mmole	H_2O/SO_2	$-\Delta H(25°C)$ kcal/mole
1	0.156151	23 067	114.83	241	7.497
2	0.070044	23 053	48.654	569	7.932
3	0.056993	23 064	38.968	710	8.062
4	0.044885	23 019	30.084	920	8.208
5	0.030301	23 067	19.752	1401	8.457
6	0.022992	23 068	14.608	1894	8.678
7	0.018242	23 021	11.327	2443	8.861
8	0.012827	23 033	7.699	3594	9.172
9	0.011846	23 086	7.057	3921	9.262
10	0.011272	23 075	6.633	4172	9.372

The heat of oxidation of arsenious oxide with bromine has been determined,[19] and an investigation on the heat of oxidation with chlorine is in progress.[20]

The authors plan to give a more comprehensive discussion of these data in a later publication.

Acknowledgements. The assistance of Dr. Ingemar Wadsö for his help and suggestions and the assistance of Miss S. Kristoffersson and Miss Anna DeKonschin in performing the experiments is gratefully acknowledged. Part of this investigation has been supported by a special grant from the *Swedish Technical Research Council.*

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Received April 16, 1963.