

Lawrence Berkeley National Laboratory

Recent Work

Title

CHEMICAL THERMODYNAMICS OF AQUEOUS THIOSULFATE AND BROMATE IONS

Permalink

<https://escholarship.org/uc/item/98r2488q>

Author

Mel, Howard Charles.

Publication Date

1953-09-01

UCRL 2330

UNCLASSIFIED

UNIVERSITY OF
CALIFORNIA

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. 7405-eng-48

CHEMICAL THERMODYNAMICS OF AQUEOUS THIOSULFATE AND BROMATE IONS

Howard Charles Mel

(Thesis)

September, 1953

Berkeley, California

CHEMICAL THERMODYNAMICS OF AQUEOUS THIOSULFATE AND BROMATE IONS

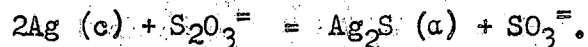
Howard Charles Mel
Radiation Laboratory and Department of Chemistry and Chemical Engineering
University of California, Berkeley, California

September, 1953

ABSTRACT

Part I. Thiosulfate Thermodynamics

In an effort to clear up gross inconsistencies in the thermodynamic data for $S_2O_3^{=}$ ion, the equilibrium constant has been determined as a function of temperature for the new reaction:



A calorimetric heat of oxidation of $S_2O_3^{=}$ with Br_3^{-} has also been measured. From these sources, the thermodynamic properties have been calculated for $S_2O_3^{=}$ at $298.16^\circ K$ with the results: $\Delta H_f^\circ = -154.0$ kcal./mole, $\Delta F_f^\circ = -122.4$ kcal./mole, $S^\circ = 14.1$ e.u. Discussion is given, particularly from the standpoint of the theories of aqueous entropies.

Part II. Bromate Thermodynamics

Discrepancies in thermodynamic data for BrO_3^{-} ion were felt to be primarily due to an inaccurate value for the heat of formation. This quantity has been redetermined from a calorimetric study of the reduction of BrO_3^{-} with I^{-} and the reduction with Br^{-} . Combining these heats with other heat and entropy data, we have the results for BrO_3^{-} at $298.16^\circ K$: $\Delta H_f^\circ = -18.3$ kcal./mole and $\Delta F_f^\circ = 2.1$ kcal./mole. These values have been discussed with respect to other experimental data.

Part I: THIOSULFATE THERMODYNAMICS.

TABLE OF CONTENTS - I
Thiosulfate Thermodynamics

Chapter 1.	<u>Introduction</u>	Page 9
Chapter 2.	<u>Construction and Calibration of Apparatus for Equilibrium Studies.</u>	11
	A. Air Bath	11
	B. Oil Bath	11
	B-1. Oil	11
	B-2. Bath and Heaters	12
	B-3. Stirring	12
	B-4. Temperature Regulation	14
	B-5. Proportional Controller	15
	B-6. Control Resistance Thermometer	15
	C. Calibration of Resistance Thermometer L.N. 55366	17
	C-1. Glass Hypsometer	18
	C-2. Sulfur Boiling Point Apparatus	18
	D. Sulfite Delivery Apparatus	20
Chapter 3.	<u>Equilibrium Studies: $\text{Ca}_2\text{S}_2\text{O}_3$</u>	22
	A. Calcium Sulfite Hydrate	22
	B. Preparation of CaS_2O_3 Solutions	23
	C. Equilibrium Experiments: CaS_2O_3	24
	D. Discussion	25
Chapter 4.	<u>Other Equilibria: The Reaction of $\text{Ag}(c)$ with S_2O_3^-</u>	26
	A. General Analytical Procedure	27
	A-1. Sulfite and Thiosulfate	27
	A-2. Standard Solutions	29
	A-3. Blank Correction	29
	A-4. Preparation of Reagents	30

(a) $\text{Na}_2\text{S}_2\text{O}_3$ Solutions	Page 30
(b) Na_2SO_3 Solutions	30
(c) Ag	30
(d) Ag_2O	31
B. Equilibrium Sets A--E at 122.5°	32
B-1. Introduction	32
B-2. Set A.	33
B-3. Set B.	34
B-4. Sulfite Oxidation in Air	36
B-5. Set C.	37
B-6. Set D.	41
B-7. Set E.	45
C. Equilibrium Sets at Other Temperatures	50
C-1. Set F (195°)	50
C-2. Set G (25°)	54
D. Summary of Equilibrium Results	57
D-1. Correction of K_c at 195°	57
D-2. Influence of Side Reactions	60
E. Extrapolation of K_c Values to Infinite Dilution	60
Chapter 5. <u>Oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ with Br_3^-</u>	69
A. Introduction	69
B. Preparation of Reagents	71
B-1. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(\text{c})$ and its Reagent Solution	71
B-2. Other Reagents	72
C. Calorimetric Procedure	73
D. The Heat of Oxidation of $\text{S}_2\text{O}_3^{2-}$ by Br_3^-	74

Chapter 6. <u>Calculations, Conclusions, Discussion</u>	Page	81
A. Calculation of Heat of Reaction from Equilibrium Data		81
A-1. Heat Capacity Change		81
A-2. Calculation of ΔH_f° for $S_2O_3^\ominus$		82
B. Selection of "Best" Values for Thermodynamic Properties of $S_2O_3^\ominus$ at 298.16° K		84
B-1. SO_3^\ominus Thermodynamic Properties		86
C. Previous Studies		87
C-1. Bichowsky's Study		87
C-2. Ballezo and Kaufmann's Study		89
D. Sulfur Potential Diagram		90
E. Discussion of Entropy of $S_2O_3^\ominus$		91
Chapter 7. <u>References</u>		95

TABLE OF CONTENTS

Figures

Figure 1a	Oil Bath (top view)	Page	13
1b	Helical Stirrer B		13
2	Control Resistance Thermometer		16
3a	Glass Hypsometer		19
3b	Sulfur Boiling Point Apparatus		19
4	Sulfite Delivery Apparatus		21
5a	Extrapolation of K_c to Infinite Dilution at 122.5°C (Extended Debye-Huckel method)		66
5b	Extrapolation of K_c to Infinite Dilution at 122.5°C (Simple $\log K_c$ vs. $\sqrt{\mu}$)		66
6	-4.575 $\log K_o$ vs. 1/T for reaction: $2\text{Ag}(c) + \text{S}_2\text{O}_3^{=} = \text{Ag}_2\text{S}(a) + \text{SO}_3^{=}$		83

TABLE OF CONTENTS

Tables

Table 4-1	Equilibrium Measurements Set B	Page	35
4-2	Oxidation of $\text{SO}_3^=$ by Air		37
4-3	Equilibrium Measurements Set C		39
4-4	Equilibrium Measurements Set D		43
4-5	Equilibrium Measurements Set E - (122.5°C)		47
4-6	Equilibrium Measurements Set F - (195°)		52
4-7	Equilibrium Measurements Set G - (25°)		55
4-8	Summary of Equilibrium Results		59
4-9	The Dielectric Constant of Water		61
4-10	Quantities in Equations (4-17) and (4-18)		67
4-11	K_0 Values as a Function of Temperature		67
5-1	Composition of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(c)$		71
5-2	The Heat of Oxidation of $\text{S}_2\text{O}_3^=$ with Br_3^- (Part 1.)		74
5-3	Bromine Species in Calorimetric Solution		76
5-4	K_d as a Function of Ionic Strength		77
5-5	Sulfate and Bisulfate Formation (See Eq. (5-1).)		78
5-6	The Heat of Oxidation of $\text{S}_2\text{O}_3^=$ with Br_3^- (Part 2.)		79
6-1	"Best" Values for Thermodynamic Properties of $\text{S}_2\text{O}_3^=$ at 298.16°K		86
6-2	Sulfur Potential Diagram		91

I. Thiosulfate Thermodynamics

Chapter 1

Introduction

Aqueous solutions of thiosulfate are among the commonest and most important of analytical reagents, and yet the experimentally determined thermodynamic properties of thiosulfate ion show widely divergent values, and values that cannot be reconciled with what one would consider a reasonable entropy. For example, Bichowsky¹ reported from his study of the equilibrium of aqueous calcium thiosulfate with calcium sulfite and sulfur, ΔF_f° at 298° K = -125.11 kcal./mole for $S_2O_3^{=}$ ion. In attempting to calculate ΔH_f° from his experimental calorimetric data and/or from a Σ plot of his heat capacity and equilibrium data, values are obtained from approximately -145 to -157 kcal./mole. The large uncertainties arise on the one hand from important undetermined dilution corrections and on the other hand from a large scatter of the points in the Σ plot. Some of this work is more critically examined in Chapter 6-C.

Bichowsky and Rossini² calculate from the calorimetric data of Thompsen³ and Berthelot⁴ values for the heat of formation of aqueous $Na_2S_2O_3$, whence for $S_2O_3^{=}$, $\Delta H_f^\circ = -145.9, -147.2$ and -149.1 kcal./mole respectively. Recently Ballozo and Kaufmann⁵ made determinations near room temperature of the equilibrium constant for the reaction studied by Bichowsky.¹ They plotted $\log K$ vs. $1/T$ using their data and also the high temperature data of Bichowsky. From this plot they calculated a reaction heat, whence for $S_2O_3^{=}$, $\Delta H_f^\circ = -164.7$ kcal./mole.

Combining this value for ΔH_f° with the above free energy, one obtains $S_{298}^\circ = -13$ e.u.; on the other hand, using $\Delta H_f^\circ = -145.5$ kcal./mole (the value adopted by Bichowsky and Rossini²) one calculates $S_{298}^\circ = 52$ e.u. for thiosulfate ion. These may be compared with the value $S_{298.16}^\circ = 4.1$ e.u.⁶ for $SO_4^{=}$, an ion somewhat smaller in size with the same overall charge. The Bureau of Standards⁶ has adopted $\Delta F_f^\circ = -127.2$ kcal./mole, $\Delta H_f^\circ = -154$ kcal./mole and $S^\circ = 29$ e.u. for $S_2O_3^{=}$, which are apparently compromise values not based on additional experimental data.

It was with the hope of resolving these large discrepancies and obtaining a standard heat and free energy of formation for $S_2O_3^{=}$, consistent with a reasonable entropy that this investigation was undertaken. A knowledge of the entropy of thiosulfate ion is also of interest for its own sake; entropy data for ions of this type are practically nonexistent.

Unless otherwise specifically noted, all calculations will be made using thermodynamic data tabulated by the Bureau of Standards⁶ with one exception. Thermodynamic properties for $SO_3^{=}$ are taken from Latimer⁷ for reasons which will be explained in Chapter 6.

Chapter 2

Construction and Calibration of Apparatus for Equilibrium Studies

Since much of the apparatus was assembled during the course of the experiments as the need for it was felt, not all the equipment described here was used for all the experiments. Nevertheless, I prefer to describe it all here and then later refer to the various items in this section that are applicable to each specific equilibrium study.

A. Air Bath

The early equilibrium work was done in an air bath which was simply a modified 110 Volt 6 amp. drying oven manufactured by the National Appliance Company, Portland, Oregon. Originally a small a.c. blower was connected to blow air in at the bottom and recycle it by removing it at the top, with insulated conducting pipes to minimize heat losses. The blower turned out to be unsuitable for continuous long term operation, however, so it was replaced with a fan inside the oven, motor-driven by a shaft from outside. It was also necessary to replace the bi-metallic regulator with an electronic relay to operate the heating coil. After the early studies, it was decided to abandon this arrangement altogether in favor of an oil bath with higher heat capacity and better temperature regulation.

B. Oil Bath

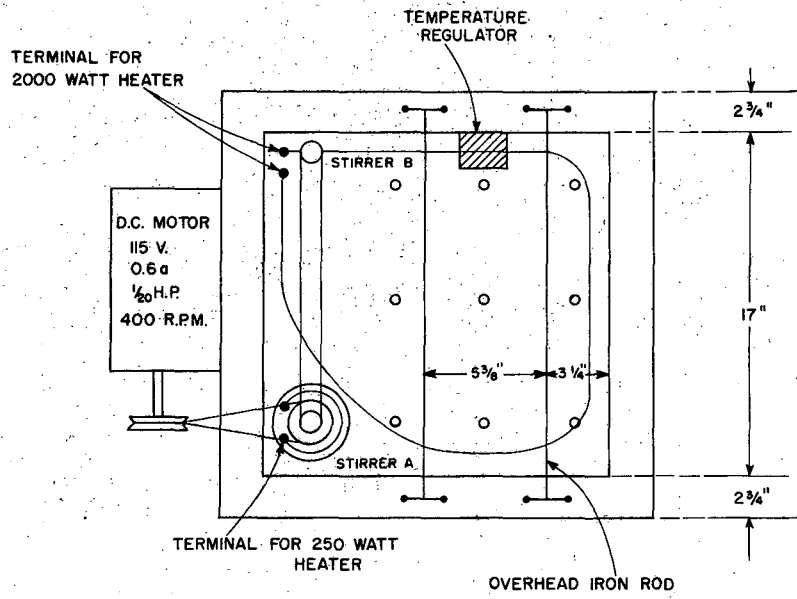
To replace the air bath, an oil bath was set up for heating the equilibrium tubes.

B-1. Oil—The oil chosen was Aeroshell 120, SAE 60, an aviation lubrication oil manufactured by the Shell Oil Company. Its principal virtue is that it is a relatively inexpensive oil suitable for use between approximately 100° and 250°C. At lower temperatures it becomes too viscous for proper stirring. Its disadvantage, however, is that,

upon prolonged heating at high temperatures, it tends to smoke, thicken and tar, causing erratic stirring and temperature regulation, (even if additional Phenyl- α -Naphthylamine inhibitor is added.) At 122.5° it must be replaced in two to six months, but at 195°C it has proved no longer usable after three weeks, if good temperature control is to be maintained. For short term or intermittent operation, even at temperatures up to 250°, it is reported satisfactory and able to maintain constant temperature to $\pm .005^\circ$.⁸

B-2. Bath and Heaters. (See Figure 1-A.) The bath itself is a silver-soldered cubic monel metal box, with wood and silk floss insulating walls and provided with a three-section varnished beaver-board top. The holes in the top are to provide access for temperature sampling at various points throughout the bath, and are normally corked. The principal heating is from a 2000 watt "Calrod" heater held about two inches above the bottom of the box. The power level from a constant voltage "Sola" transformer is adjusted by a series variac to maintain a temperature 5° to 10° below the regulated bath temperature, if left continuously on. The remaining power is supplied by a 250 watt "Calrod" heater inside the well of stirrer A and controlled by the temperature regulating device. The sealed pyrex equilibrium tubes are placed in iron pipes which are suspended in the bath by wires from the overhead iron rods.

B-3. Stirring. Stirrer A is a conventional well-type stirrer, which by itself gives circulating currents with some tendency to support fixed temperature differentials throughout the bath. Stirrer B, however is a singly wound helix on a vertical one-half inch shaft (patterned after the idea of the new "Shell-Brown" stirrer) which gives violent, turbulent stirring. (See Figure 1-B) It was made by cutting out

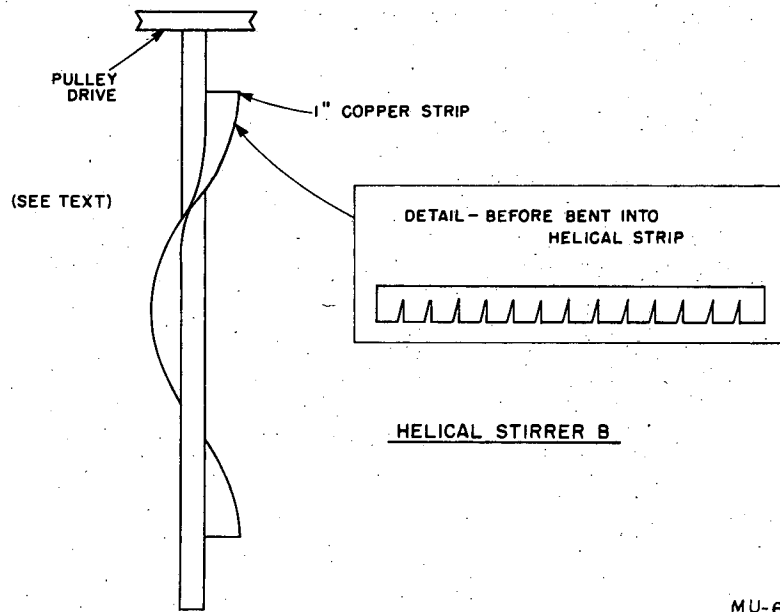


(SEE TEXT FOR DETAILS)

OIL BATH (TOP VIEW)

MU-6121

Fig. 1-A



MU-6122

Fig. 1-B

small notches from one side of a one-inch strip of copper, and then bending the strip around the rod in helical form with the notched side next to the rod, then silver-soldering in place. It has proved very rugged and effective in stirring action. The two stirrers are ganged with pulley and belt to oppose each other, i.e., each tending to "pump" downward.

An important factor in the stirring of an oil bath such as this is likely to be slippage of the belt driving the stirrer. Although the bath is covered, enough oil fumes are present, along with the normal wearing and stretching of a leather belt, to reduce the friction considerably. Consequently, the belt must be frequently wiped free of oil, and sometimes shortened. The obvious answer to this, of course, is a positive chain and sprocket drive or equivalent.

B-4. Temperature Regulation. The "control" power applied to the 250 watt "Calrod" heater was initially controlled by the mercury regulator and electronic relay used for the air bath. For long term operation at such temperatures (120° or higher), the mercury regulator proved less than ideal due to evaporation of the mercury and to scum formation on the surface of the mercury where electrical contact is made, even though oil fumes are excluded by a cover. This would necessitate resetting the temperature control rather frequently, which is inconvenient because of the time lag for temperature readjustment in the large amount of oil (about 20 gallons). For this reason, and also because of the temperature oscillations inherent with any strictly "off-on" type of regulator, it was decided to assemble a resistance thermometer controlled, proportional temperature controller. (One of the main factors in the heating time lag, with its attendant effect on

bath temperature regulation, is again the condition of the oil. The first effect of oil decomposition is usually formation of an insulating crust of decomposition products around the large "Calrod" heater.)

B-5. Proportional Controller. The circuit diagram for this controller, designed by Professors R. E. Powell and W. D. Gwinn, has been given elsewhere.⁸ Briefly, its operation is as follows: A resistance thermometer acts as part of an a.c. bridge as a control element, providing an accessible temperature range of about 0° to 300°C. Any unbalance between the thermometer and the rest of the bridge is amplified and then combined at the grid of a 2D21 thyatron, with another fixed signal 90° out of phase, thus operating the thyatron for a longer or shorter period of time. The 2D21 feeds into the primary of a 500 watt saturable reactor, the secondary of which operates the 250 watt heater, with more heating current produced the greater the unbalance at the bridge.

The only departure from this circuit diagram is in the bridge circuit, where the a.c. bridge was built with the variable resistances covering the range 0 to 190 ohms to balance the 55 ohm platinum control resistance thermometer substituted for the 100 ohm thermometer shown in the circuit diagram. Weltner⁸ states that such a circuit can keep constant temperature in an oil bath at 250° to $\pm .005^\circ$ over a two-hour period.

B-6. Control Resistance Thermometer. (See Figure 2 for constructional details.) The copper part at the bottom is used to contain the sensing element in order to minimize any time-temperature lag. Platinum wire (99.9+% pure, soft temper) was wound in a lathe on a piece of piano wire to form a tightly coiled "spring", the piano wire then being dissolved out in a 150° bath of concentrated nitric and sulfuric acids. After washing and spreading the "spring" slightly

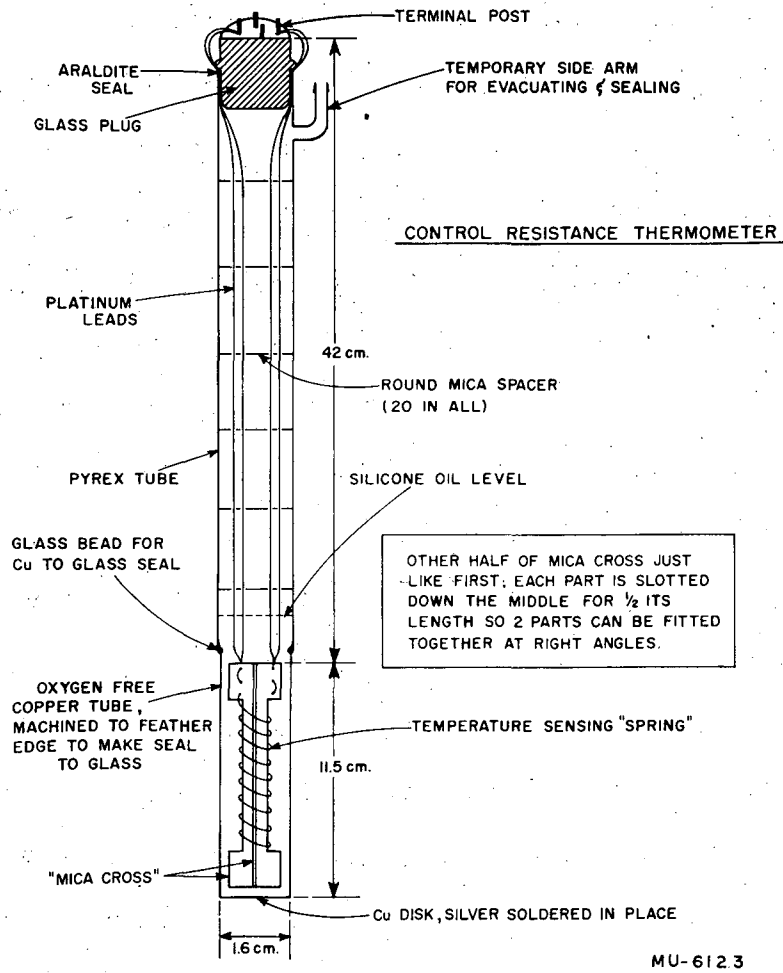


Fig. 2

to avoid shorting turns of the wire, it is bifilarly (non-inductively) wound around the mica "cross" and placed in the copper-glass tube; the No. 28 platinum wire leads are then brought out the end through the mica spacers. The whole open thermometer is placed in a vacuum line, and while evacuated a current of 0.175 amps is passed through the wires for one minute for annealing purposes. (For temperature control purposes, this is not critical.) Low heat capacity silicone oil (General Electric 9981 ITNV 70) is then added to cover completely the "spring," and the thermometer sealed under vacuum. (In a similar situation, such oil was found to give added stability to the regulating mechanism.⁸)

C. Calibration of Resistance Thermometer L. N. 55366.

At the start of this research it was hoped that the temperature control in the oil bath would be such, that a calibrated resistance thermometer with Mueller Bridge would be desirable for measuring these temperatures. Because of the unforeseen behavior of the oil upon prolonged heating, it later turned out that the oil tarring and thickening became the limiting factor for temperature regulating insofar as it interfered with adequate stirring and rapid heat exchange. (The extent of this temperature variation is given under each separate equilibrium determination.) Consequently, the highly precise temperature measurements afforded by such a thermometer were not really necessary.

However, a 2 ohm resistance thermometer L. N. 55366 was calibrated in conjunction with Mueller Bridge L. N. 85316 (which itself was auto-calibrated and calibrated against a standard resistor) and did prove useful as a check on the mercury thermometers, so its calibration is described here briefly.

The constants of an equation of the form $R_T = R_0 (1 + \alpha T + \beta T^2)$ are to be evaluated by measuring the thermometer resistance at at least three standard temperatures.

R_T = the thermometer resistance at any temperature T.

R_0 = the thermometer resistance at the ice point.

α and β are empirical constants to be evaluated.

The standard points in the temperature range under study are the ice point, the steam point, and the sulfur boiling point.

For the ice point measurement, it is simply necessary to immerse the thermometer in a dewar containing pure chopped ice and water in thermal equilibrium, making sure that the ice is present over the whole length of the sensing element of the resistance thermometer, and not just floating on water with the thermometer below.

C-1. Glass Hypsometer. For the steam point measurement, a hypsometer was built as per Figure 3A. Connections were provided for admitting the steam either at the top or bottom as a double check for superheating or cooling. (None was found.) The heat was adjusted under the distilled water steam generator for smooth boiling by means of a variac; glass or metal boiling chips were used. Moving the thermometer up and down in the inside tube over an 8 cm. range gave no variation in thermometer resistance.

C-2. Sulfur Boiling Point Apparatus. To measure the sulfur boiling point, the apparatus pictured in Figure 3B was built. The recrystallized sulfur gave a negative test for Se with hot concentrated H_2SO_4 . A radiation shield (here of black sheet iron) is essential to obtain proper experimental values. Again, moving the thermometer up and down did not affect the resistance value. For both the sulfur and steam points, barometric pressure should be read

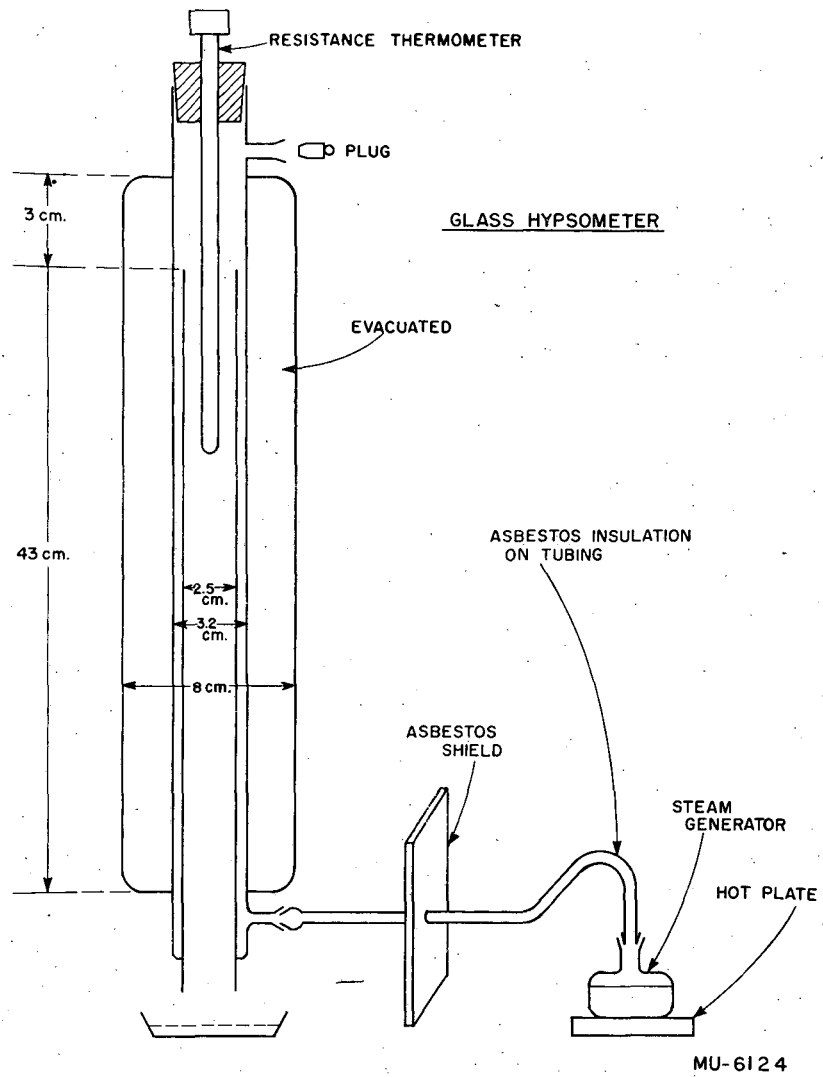
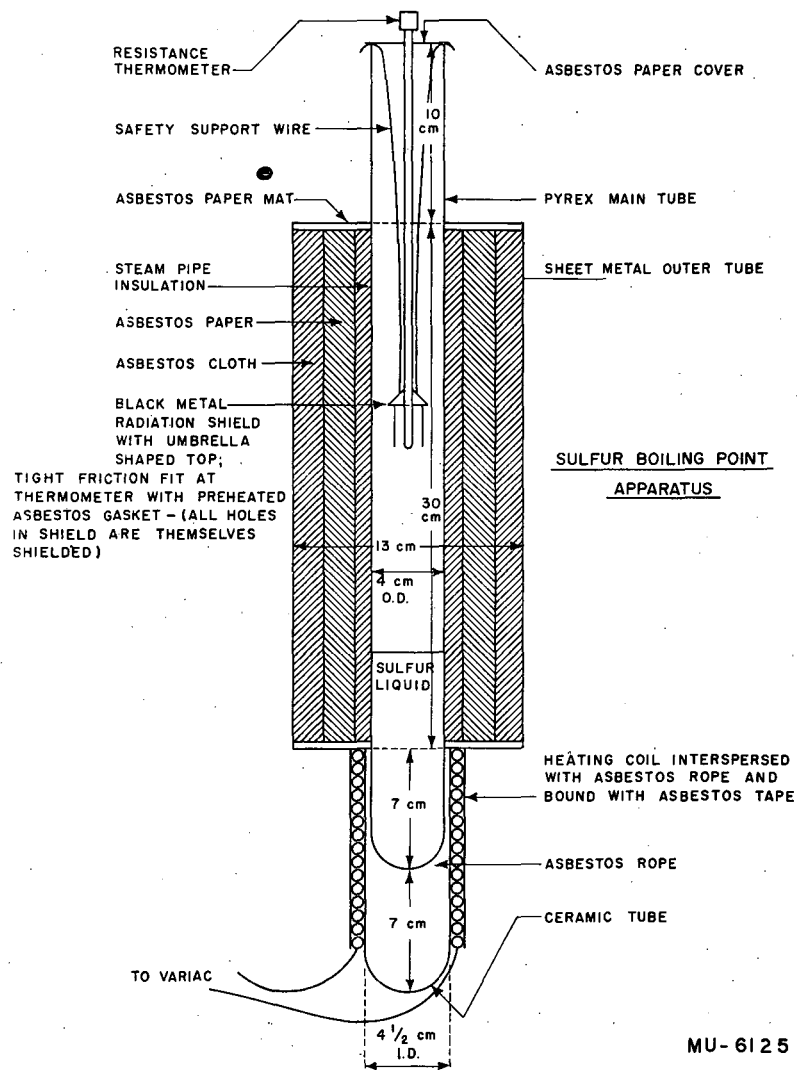


Fig. 3-A



MU-6125

Fig. 3-B

simultaneously with the resistance. At all three points, resistances were reproducible to better than .0001 ohms at constant pressure (the smallest division on the Mueller Bridge).

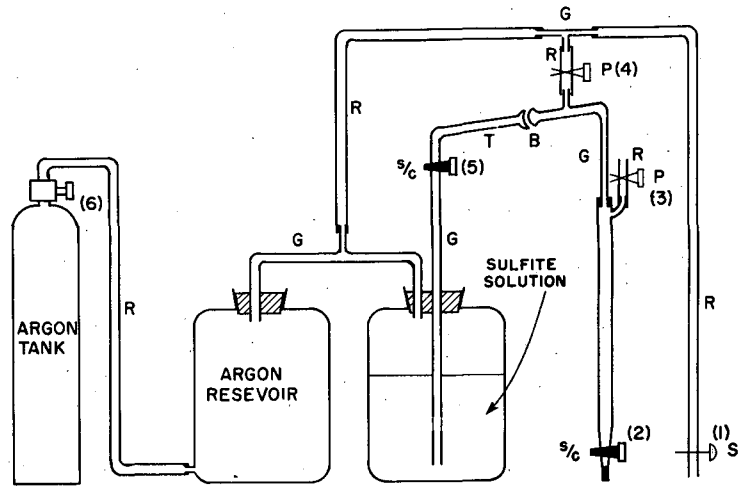
For more detailed information on resistance thermometer and equipment calibration, see the references (9) - (13).

D. Sulfite Delivery Apparatus.

After the early equilibrium measurements, it was determined that considerable air oxidation of the sodium sulfite solutions was occurring, so the apparatus in Figure 4 was built to exclude air during the filling and sealing of the equilibrium tubes, and standardization of the sulfite solutions.

Sequence of Operations:

- A. Filling Buret (if for first time, flush whole apparatus and leave filled with argon.)
 - (a) Close (1) and (4). ((2), (3), (5) and (6) also closed.)
 - (b) Open (6) momentarily to build up a little pressure in the reservoir, if not already done.
 - (c) Open (3), then (5) and fill carefully. (Close (5) and repeat (b) if necessary).
 - (d) When done, close (5).
- B. Clearing Liquid and Drips from Tube T
 - (a) Cautiously open (4).
 - (b) Close (3).
 - (c) Open (5) till it drains, then close.
- C. Delivering from Buret
 - (a) Open (6) and immediately (1) until steady stream argon; use from (1) to flush tube filling.
 - (b) With (6) adjusted to just a faint stream, open (2) and deliver.
 - (c) When done, close (2).
 - (d) Close (1), then (6) as soon as slight excess pressure built up in reservoir.



(SEE TEXT FOR OPERATION)

R = RUBBER G = GLASS TUBE S = SCREW CLAMP
 P = PINCH CLAMP 5/8 = GROUND GLASS STOPCOCK.
 B = BALL JOINT

SULFITE DELIVERY APPARATUS

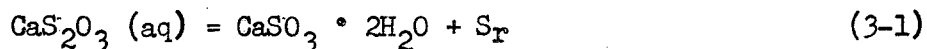
MU-61 26

Fig. 4

Chapter 3

Equilibrium Studies: $\text{Ca}_2\text{S}_2\text{O}_3$

Bichowsky¹ studied the equilibrium between calcium thiosulfate, calcium sulfite and sulfur. For the reaction he wrote:



In view of the simplicity of the determination of the equilibrium constant (just the analysis for $\text{S}_2\text{O}_3^{=}$), this reaction was the first investigated as a method of obtaining the free energy of thiosulfate ion. However, a number of difficulties were encountered. The first involved the composition of the solid hydrate.

A. Calcium Sulfite Hydrate.

The dihydrate of CaSO_3 has been reported in the literature as the stable hydrate at room temperature. Bichowsky¹ described four different ways of preparing it and remarked, "These samples varied strikingly in crystalline habit, but had nearly the same refractive index, and no difference in behavior was noted among them. Above temperatures somewhere near 160° the dihydrate is unstable in contact with water, presumably forming the semihydrate $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$ analogous to $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$." (This statement was based on a microscopic examination of the two phases.) He also made some simple heat capacity measurements on two separately prepared samples of this solid, obtaining the same value, namely, 42.7 cal./mole. The Kopp's law value for the dihydrate is 41.0^{14} while for the hemihydrate it is 28.1.

Kelly,¹⁵ in describing his procedure for making the anhydrous salt, remarked that after five hours heating at 155° the composition was $\text{CaSO}_3 \cdot (0.51 \text{H}_2\text{O})$, but did not describe the dihydrate. In 1949, however, Matthews and McIntosh¹⁶ described five ways of making

crystalline CaSO_3 , which all gave analyses of 8 to 10 percent H_2O (dihydrate is 23 percent H_2O), and they stated that no dihydrate was found. The optical properties for their hemihydrate preparation agreed with those previously claimed for the dihydrate. Samples of CaSO_3 that I precipitated with NaHSO_3 and CaCl_2 solutions, dried at 110° , then ground, did not give consistent results, but generally showed on analysis between one and two waters per CaSO_3 , (when no special care was taken to exclude water vapor of the air.) This method was used in preparing $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$ for the equilibrium studies. In view of Matthews and McIntosh's detailed work and my results indicating less than 2 waters, it is probably safe to assume that the form stable in contact with water solution at room temperature is not the dihydrate, but probably the hemihydrate. I made various attempts to grow crystals of CaSO_3 in aqueous solution by methods such as (a) pumping on a solution of CaSO_3 in a slight excess of acid in a vacuum dessicator, (b) standing a container of CaCl_2 in a larger container of NaHSO_3 solution; then carefully filling both with water, and letting them sit for solution and diffusion to take place. None of these attempts proved successful; when $\text{CaSO}_3 \cdot ?\text{H}_2\text{O}$ was obtained, it was in a finely divided form -- (some clear crystals that might have been this solid were formed in one of the CaS_2O_3 equilibrium tubes, but before they could be tested, they decomposed.)

B. Preparation of CaS_2O_3 Solutions.

After a number of experiments, the following procedure was found most satisfactory for making $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (c): Dissolve 51 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 20 ml H_2O at 40° , and dissolve 35 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in 20 ml H_2O , filtering both solutions if necessary. Slowly and with stirring, pour CaCl_2 solution into $\text{Na}_2\text{S}_2\text{O}_3$ solution, keeping the

temperature down to 40° . After several hours, or over night, when the NaCl precipitate is well packed at the bottom, filter and crystallize out $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ on an ice bath. Decant and wash $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ in the cold and dissolve in water at 40° and recrystallize on an ice bath. These crystals are separated, washed with a small portion of cold water, and dissolved in water to give reagent solution of the desired concentration. (The dried crystals do not keep, but decompose). Note: Samples of reagent grade CaCl_2 of different manufacturers were found to contain one or more impurities as evidenced by an organic chemical odor and a yellow color in concentrated solutions that cannot be removed by ordinary filtering. The impurity can be removed by filtering with charcoal, but then small amounts of charcoal may remain in the solution, even though it looks clear. In some cases, concentrated HCl caused precipitation of yellow needle-like crystals, not readily soluble in water, but volatilized by direct heat.

C. Equilibrium Experiments: CaS_2O_3

These experiments consisted of two series of sealed pyrex tubes; the first containing each 10 -- 15 ml of $0.6 \text{ M } \text{CaS}_2\text{O}_3$ solution, the second containing excess $\text{CaSO}_3 \cdot 1/2 \text{ H}_2\text{O}$, excess S_r and water. These were placed in the air bath at $122^{\circ}, \pm 3^{\circ}$. Some time later, most of the tubes exploded or were demolished by those that did. Some additional tubes were then added, this time each in an iron pipe. Altogether, two survived and were analyzed after two to three weeks, by filtering and titrating an aliquot for $\text{S}_2\text{O}_3^{=}$, with standard I_3^{-} solution. The results showed them to be far from equilibrium at the time of analysis. Both tubes gave a strong odor of H_2S upon opening, and also a positive test for $\text{SO}_4^{=}$.

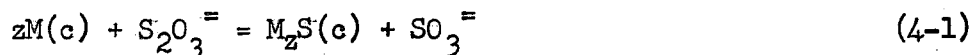
D. Discussion.

Although a thorough study of the above reaction could well yield worthwhile results, we were reluctant to continue with it if a more satisfactory reaction could be found. For one thing, the above reaction has a very large ΔG_p . Also, the form of the sulfur produced is different at different temperatures. CaSO_3 's formula and solubility were uncertain, and the presence of H_2S and SO_4^- , with poor material balance, coupled with the negative equilibrium results, were disappointing. Simultaneous tests being made for other suitable reactions were encouraging, so it was decided to abandon this method in their favor.

Chapter 4

Other Equilibria: The Reaction of Ag(c) with $S_2O_3^{=}$

A survey was made of possible equilibria of the type:



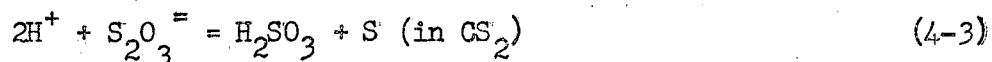
A study of the known free energy data reveals that the only possible mono or divalent metals for which ΔF° would be near zero are Ag, Hg and Cu. Blitz¹⁷ remarks that Cu reacts "apparently irreversibly" with the fused hydrate of $Na_2S_2O_3$ to give Cu_2S and Na_2SO_3 . Preliminary experiments with Ag and Hg at 100° indicated that in three days, the forward reactions did take place to some extent. In the case of Hg, a strong H_2S odor was present, whereas for Ag none was detected. Consequently, we decided to investigate more thoroughly the reaction of $S_2O_3^{=}$ with Ag.

Some tubes, containing in the one case Ag and $S_2O_3^{=}$, and in the other Ag_2S and $SO_3^{=}$, were made up and placed in the air bath at 122° along with the CaS_2O_3 being studied. Most of these were casualties, with the CaS_2O_3 tubes, but additional ones were made and placed in pipes, and enough survived to determine that the reverse reaction did occur and that sulfate formation was minor.

Although the analytical procedure is slightly more involved than for the CaS_2O_3 equilibrium, there was less ambiguity about the solids involved, and side reactions appeared less troublesome. Also, it is a much more "symmetrical" reaction, and the Δc_p should be smaller and activity coefficient corrections less important. These reasons and the fact that it was a new reaction were sufficient to concentrate further equilibrium studies in this direction, i.e., on the reaction:



(Another quite different reaction that might be studied can be written:



A. General Analytical Procedure.

Analytical operations common to many of the equilibrium tubes will be discussed here rather than under the separate equilibrium sets. The determination of various inorganic sulfur species in the presence of one another has been studied by numerous workers, and much of this work has been summarized by Kurtenacker.¹⁸

A-1. Sulfite and Thiosulfate. The procedure for determination of sulfite and thiosulfate in the same solution involves for one portion the titration with iodine of the combined $\text{SO}_3^{2-} + \text{S}_2\text{O}_3^{2-}$, and for a second portion the complexing of the SO_3^{2-} by formaldehyde and then titration of $\text{S}_2\text{O}_3^{2-}$ with iodine. My experience indicated that a modification of the scheme given by Kurtenacker was necessary, for I found that the starch indicator was interacting with the formaldehyde, causing very uncertain endpoints. In general, the greater the ratio of CH_2O to starch in the solution being analyzed, the more quickly must the titration be done in order to get a good blue instead of a pale brownish yellow endpoint. If one knows approximately where the endpoint is, holding off adding starch till just before this improves it.

When the time came for analysis of a tube, it was removed from the oil bath, cleaned and rapidly cooled to room temperature. It was broken by crushing the upper part with pliers while the tube was standing in a beaker, and immediately pipeting the portion to be used for the total $\text{SO}_3^{2-} + \text{S}_2\text{O}_3^{2-}$ analysis into an excess of standard I_3^- with NaAc - HAc buffer. For the later sets, this operation was done in an atmosphere of argon. In a few minutes it was back titrated

with standard $S_2O_3^{=}$.

To prevent sucking up the solid material, the pipeting is done through a removable "filter tip", consisting of a short section of glass tubing packed with glass wool, with a female standard taper joint on the end attaching to the pipet. The attachment is simply a friction fit, with a small piece of filter paper, which is wet with the solution being pipeted acting as a gasket. This prevents air from being drawn in at the point of attachment. The tip is then quickly and easily removed for delivery of the portion pipeted.

The second portion is then delivered into an Erlenmeyer containing two drops of phenolphthalein. In almost every case, the solution gave a pink color so the CH_2O was added immediately. (This basic condition is necessary for the complexing of $SO_3^{=}$ by CH_2O , and NaOH must be added dropwise if the solution is not already basic.) I noticed generally that if the color of the solution was initially a pale pink, addition of the CH_2O intensified the color, while if it was initially a darker red, the color often became paler.

A delay of two or three minutes in pipeting the second portion should not matter, for even if some air oxidation of $SO_3^{=}$ to $SO_4^{=}$ should occur, this does not interfere with the determination of $S_2O_3^{=}$ in the presence of $SO_3^{=}$. The room temperature tubes (Set G) were handled in the same manner except no cooling was necessary.

After standing for five minutes, the first solution is acidified with 10 percent HAc until a 20 ml excess has been added, and then titrated immediately with standard iodine, using starch indicator. The amount of 10 percent HAc necessary for neutralizing the solutions varied with the initial concentration of solutions used in the tubes

and was approximately the same for similar tubes. For example, in equilibrium sets D, E and F, 10 ml, 5 ml or 2 ml were required for the high, medium and low ionic strength sets, respectively.

The amount of CH_2O necessary depended on the amount of the sulfite to be complexed and the amount of starch to be used. For 10 millimoles of $\text{SO}_3^=$, 40 ml CH_2O and 13 ml 0.4 percent starch solution are required. If these are titrated immediately after acidifying, a good blue color will suddenly appear at the endpoint and persist for at least 15 seconds before fading. (Actually the real endpoint is 1/2 to 3/4 of a drop beyond the first faint blue color that persists.) When smaller amounts of $\text{SO}_3^=$ are present, less CH_2O is necessary and proportionately more starch can be used, giving a more permanent endpoint. For the equilibrium runs made from undiluted 0.2 M $\text{SO}_3^=$ and $\text{S}_2\text{O}_3^=$ solutions, 10 -- 12 ml CH_2O and 7 - 8 ml starch were used, depending on the volume of solution pipeted out. For the most dilute solutions, 5 ml CH_2O and 5 ml starch gave good results.

A-2. Standard Solutions. In some cases the I_3^- solutions were standardized against As_2O_3 , and in others the $\text{S}_2\text{O}_3^=$ was standardized with KIO_3 solution. The relative titer of the $\text{S}_2\text{O}_3^=$ - I_3^- solutions was always determined also. The relative and absolute titers of these reagents were checked frequently during the analysis of each set of equilibrium tubes. For the analyses, iodine solutions of 0.1 N and 0.01 N and $\text{S}_2\text{O}_3^=$ solutions of 0.2 N, 0.1 N and 0.02 N were used.

A-3. Blank Correction. For titrations with the 0.1 N or 0.2 N solutions, no blank was necessary. With the more dilute reagents, however, the blank was generally the equivalent of 0.07 to 0.14 ml of 0.01N I_3^- , to be subtracted from the I_3^- volume. This blank was separately determined for the different analytical procedures used.

A-4. Preparation of Reagents.

(a) Na₂S₂O₃ Solutions. For the equilibrium measurements, standard solutions were generally made by dissolving the commercial Na₂S₂O₃ · 5H₂O in freshly boiled distilled water. (When the solutions were to be used for analytical purposes over a period of time, a small amount of Na₂CO₃ preservative was added in accordance with accepted procedure.¹⁹

(b) Na₂SO₃ Solutions. The commercial anhydrous salt was dissolved in distilled water that had been deoxygenated by bubbling argon through it.

(c) Ag. Samples of commercial "precipitated silver" (analytical reagent) were the starting material. Some of these were used with no further treatment other than grinding. Others were first treated with HClO₄, then washed to remove any Ag₂O present. (It was found next to impossible to remove the last traces of Ag⁺, even after many washings and filterings with hot and cold water.) Still others were treated with S₂O₃⁼ solution in the cold, before the tubes were made up.

Some finely divided Ag was also heated in a crucible, which would cause decomposition of any Ag₂O. This was not too satisfactory, however, for the fine particles tend to sinter together, even hundreds of degrees below the melting point of Ag. Since it was desired to have the Ag with as much surface as possible to speed up the reaction with S₂O₃⁼, this method of purification was not used.

No difference was detected in any of the results from the use of different Ag samples, so they will not be individually referred to with the equilibrium data. (These samples all gave good Ag X-ray patterns.)

(d) $\underline{\text{Ag}_2\text{S}}$. (1) H_2S was bubbled through a solution of analytical reagent AgNO_3 , the solid then filtered, washed and dried at 110° . Very often, the solid prepared in this manner, when heated had a peculiar "artichoke" odor; this may have been due to impurities in the H_2S , for it did not occur with all H_2S samples.

(2) A solution of AgClO_4 was made by first precipitating Ag_2O out of a solution of reagent AgNO_3 . This was filtered and washed eight times with hot water and then dissolved in cold 3 M HClO_4 . An H_2S train was set up²⁰ and the purified H_2S passed through the AgNO_3 solution. The solid was washed and filtered eight times, then dried at 130° , ground and rewashed and filtered with hot water. A sulfur-like odor that had persisted through this treatment was now quite faint. After drying, the sample was finely ground. This sample was spectroscopically pure and gave the X-ray pattern for the α (low temperature) form. A test also showed it to be free of Ag^+ .

(3) Some commercial Kahlbaum reagent was used. The sample was spectroscopically pure and gave a good α -form X-ray pattern.

(4) Some bottled Ag_2S marked "Reserved for Randall" was used in some determinations, both untreated and after treatment with $\text{S}_2\text{O}_3^{=}$ in the cold. Spectroscopic and X-ray examination showed some PbS impurity present, which microchemical analysis gave as less than one percent. Possibly some other undetermined impurity was present also.

From a careful examination of the equilibrium results, no systematic differences can be detected in the values for the equilibrium constants as a function of the particular solids used.

B. Equilibrium Sets A--E at 122.5°

B-1. Introduction. These sets were all run in the oil bath. It was apparent from the preliminary work that the glass tubes would have to be improved to withstand the increased pressure on heating. The first step was to change to heavier glass for the tubes. Pyrex test tubes 30 cm long, 22 mm i.d. with 1 1/2 mm wall thickness, were pulled with a heavy walled constriction at half their length. The upper portion served as a funnel for filling the tubes and was then pulled off in a flame, taking particular care that the glass at the constriction was "sucking in" at the instant the seal was made. With these precautions only one tube broke among all the sets at 122.5°. (The vapor pressure of water is slightly over two atmospheres at this temperature.) Each tube was placed in an iron pipe with screwed-on ends and was suspended in the oil bath with a wire.

In all cases, samples of both solids along with one or both of the solutions, were added to the equilibrium tubes, regardless of whether equilibrium was being approached from the high $\text{SO}_3^=$ side or high $\text{S}_2\text{O}_3^=$ side. (The appropriate solid must be present in excess, of course.) The concentration equilibrium quotient is defined for future purposes as

$$K_c = \frac{(\text{SO}_3^=)}{(\text{S}_2\text{O}_3^=)} \quad (4-4)$$

where the sulfite and thiosulfate concentrations can be expressed in any consistent units, since only their ratio is being considered. Since analyses were volumetric, units used here are moles/liter.

We shall also refer to the quantity $\left(\frac{\text{SO}_3^=}{\text{S}_2\text{O}_3^=} \right)_i$ which is the initial ratio of these concentrations at the time of filling the tubes.

Material balance calculations have been made by comparing the total number of moles of $S_2O_3^{2-} + SO_3^{2-}$ initially in a given volume, with the total number present in the same volume at the time K_c is measured. It is expressed as a percent loss = $\frac{\text{(Init. Moles - Final Moles)}}{\text{(Init. Moles)}} \times 100$.

It should be emphasized that during the "Delay Times" listed in Tables 4-1 to 4-6, the tubes have already been cooled to room temperature. For practical purposes, no change in equilibrium can occur in those short times before analyses.

Temperatures were read with Hg in glass thermometers graduated to 0.1 degrees. These were checked against other thermometers, including Bureau of Standards calibrated thermometers, and the resistance thermometer described in Chapter 2-C. The values given for the equilibrium sets have been corrected if necessary.

Some attack on the glass was noticed for many of the runs, but it appeared to have no effect on the results.

B-2. Set A. For Set A, all the tubes were made up with the initial ratio $R = SO_3^{2-}/S_2O_3^{2-}$ either 0 or ∞ . The results from the "low" side (i.e., $R = 0$) have no meaning, since by mistake an excess of Ag was not present. The results from the "high" side showed 6 out of 7 K_c 's to be in the range from 18 to 26. Initial concentrations of SO_3^{2-} of 0.1 M (and one of 0.05 M) were used with Ag_2S sample (1). At the times of analyses, the oil bath had been up to the proper temperature ($122.5 \pm .6^\circ$) for periods of from one to nineteen days. The mercury regulator and electronic relay were being used. For the two-week period preceding this, the oil temperature was 116° to 120° , so the above K_c 's may have reflected this lower temperature. A material balance check showed 32 percent to 54 percent loss, the worst being for the more

dilute solutions. A maximum of two and one-half hours elapsed between the time of removal of these tubes from the oil bath and the start of the analysis.

No real conclusions could be drawn from these data for the above reasons, and also because of the small titration volumes (less than 1 ml). It did appear possible that equilibrium could be reached starting with more concentrated solutions, allowing more certain analysis procedures. Also, a rough calculation for the amount of oxygen in the air sealed in with the equilibrium solutions, indicated that this could account for the material balance loss, and using more concentrated solutions should minimize this.

B-3. Set B.

Materials and Conditions.

$$\left(\frac{SO_3}{S_2O_3} \right); \quad \text{initially either } 0 \text{ or } \infty$$

20 ml S_2O_3 1 M with approximately 20 ml air

20 ml SO_3 1 M with approximately 20 ml air

Ag_2S : Sample (3), Section A-4, (d)

Ag : See Section A-4, (c).

Temperature: $123.2 \pm .5^\circ$; Mercury Regulator.

See Table 4-1 for results.

Comments. On the basis of this set, K_c is limited to a value between 11.0 to 21.8 at this ionic strength and temperature (123°). The titration volumes were large enough so that good accuracy (at least 3 ml on a buret reading to .001 ml) could be attained. The greatly improved material balance over Set A is also apparent, but so is the slowness of the reaction at this concentration. At the end of the

Table 4-1

Equilibrium Measurements Set B

Tube No.	Delay	mm (a) Final	mm (a) Initial	Percent Loss	Days in Bath	$\left(\frac{SO_3^{=}}{S_2O_3^{=}}\right)_i$	K_c
1	1 1/4 hr.	.968	.984	1.6	7	∞	> 64.6
2	1 1/3 hr.	.963	.984	2.2	16	∞	43.2
3	1/3 hr.	.967	.984	1.7	28	∞	28.9
4	1/4 hr.	.961	.984	2.3	70	∞	21.8
5	3 1/2 hr.	.899	.938	1.2	7	0	> .80
6	2 1/2 hr.	.917	.938	2.2	16	0	2.01
7	1 hr.	.935	.938	0.3	28	0	3.43
8	1 hr.	.933	.938	0.5	70	0	11.03

(a) Total millimoles of $SO_3^{=}$ + $S_2O_3^{=}$ per ml. solution

For definitions of other quantities, see Section B-1.

run, when the tubes were opened, the solids were usually packed into a fairly firm mat at the bottom of each tube. Even with the convection currents that must be present in the tubes while being heated, it was felt that quite possibly not enough fresh surface of the solids was being rapidly exposed to the reacting solutions, so that this may have been the limiting factor as far as the rate of reaction was concerned. A calculated excess of each solid was present, but if the reaction had to proceed by "eating into" the centers of the particles from the outside and through a coating of the newly formed solid (note that one solid is formed and one used up for both the direct and reverse reactions) then this could definitely slow the whole process. In an attempt to speed the reaction we decided to take the following steps:

- (1) Particular care would be exercised in grinding the initial solids to a very fine state.
- (2) A greater excess of solids would be used.
- (3) Somewhat less concentrated solutions would be tried.
- (4) Even these steps might not be sufficient if the solid particles were going to pack firmly together at the bottoms of the tubes. Therefore, it seemed logical to try to hold these solids dispersed throughout the solutions during the runs by means of glass wool put in at the start. To check on the possibility of additional harmful side reactions, only some of the tubes would be tried with glass wool.

B-4. Sulfite Oxidation in Air. We had wanted to verify that this was actually the main cause of the poor material balance in Set A. Consequently, at the time Set B was prepared, some separate tubes containing only SO_3 solution (of the concentration used in Set A) were also readied. Two of these were heated in the oil bath, the third

simply left at room temperature. The results of these determinations are given in Table 4-2:

Table 4-2

Oxidation of $\text{SO}_3^=$ by Air

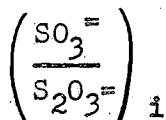
Tube No.	mm ^(a) Final	mm ^(a) Initial	Percent Loss	Days	Temp. °C
1	0.554	0.982	44	17	123
2	0.557	0.982	43	27	123
3	0.562	0.982	43	27	Room Temp.

(a) Total number millimoles $\text{SO}_3^=$ per 10 ml solution

Comparing these 43 to 44 percent losses with the 32 to 48 percent losses of Set A, it seems safe to conclude that air oxidation of the $\text{SO}_3^=$ is indeed the principal cause of the poor material balance. It should also be noted that heating had no apparent effect on the material balance, i.e., that this side reaction is essentially complete in twenty-seven days at room temperature. Future tubes should therefore be made up excluding air at the time of filling, (and, for safety's sake, reducing the total volume of any gas over the solutions in the tubes.)

Note: There is no real reason to believe that this side reaction has interfered with establishing the proper K_c ; nevertheless, on general principles, it is wise to prevent it.

B-5. Set C.

Materials and Conditions

initially either 0 or ∞

25 ml $\text{SO}_3^=$: 0.2 M with approximately 5 ml argon

25 ml $\text{S}_2\text{O}_3^=$: 0.2 M with approximately 5 ml argon

Ag_2S : Sample (3), Section A-4, (d)

Ag: See Section A-4, (c)

Temperature: $123^\circ \pm 0.5$ until 38th day, then $\pm 1.5^\circ$ until the 56th day. On the 56th day the mercury regulator broke and the temperature was \pm two degrees for two days. On the 66th day, when the stirring belt broke, the temperature went up to 136° and was not properly regulated for two days. After this, the temperature was again $123^\circ \pm 0.5$ until the end of the run. For the purposes of this set, these temperature excursions are unimportant. To prepare these and future sets where glass wool was used, it was placed in the lower part of the 30 cm test tube before the constriction was blown. The solids were added, then the liquid, and after sealing, the tube was well shaken so that the solids were thoroughly dispersed throughout the glass wool, -- like snow on the branches of a Christmas tree. The results are given in Table 4-3.

Table 4-3

Equilibrium Measurements, Set C

Tube No.	Delay	Glass Wool	mm (a) Final	mm (a) Initial	Percent Loss	Days in Bath	$\left(\frac{SO_3^-}{S_2O_3^-}\right)_i$	K_c
1	1 1/3 hr.	yes	0.999	1.063	6.0	11	∞	31.53
2	1/3 hr.	yes	0.997	1.063	6.2	35	∞	19.04
3	1/5 hr.	no	1.070	1.063	0.0	76	∞	18.38
4	2 1/5 hr.	yes	0.966	1.012	4.5	11	0	1.97
5	1/2 hr.	no	1.005	1.012	0.7	15	0	1.61
6	1 hr.	yes	0.952	1.012	5.9	35	0	6.42
7	1 hr.	no	1.011	1.012	0.1	76	0	7.57

(a) Total millimoles of $SO_3^- + S_2O_3^-$ per 5 ml solution

For other definitions -- see Section B-1

Comments.

Some striking features are immediately apparent upon studying this table. In the first place, when no glass wool was used, within experimental error, the material balance is practically perfect, even after 76 days heating. (The seeming slight increase of material in tube No. 3 has no real significance.) This means that in the absence of glass wool, all significant side reactions have been eliminated. Further tests for any other species such as $S_4O_6^{=}$, $S^{=}$, etc., were not deemed worthwhile in view of this result.

The comparison of reaction rates, both with and without glass wool, can best be made from a study of tubes No.'s 4 and 5. The K_c for No. 5, after being in the oil four days longer than No. 4 (36 percent longer) still is considerably lower than that for No. 4. (The difference between 1.61 and 1.97 is significant, for in this region of values, the ratio $SO_3^{=} / S_2O_3^{=}$ changes much more slowly than it does for larger values of the constant. There, only a small change in the number of moles of $S_2O_3^{=}$ present in the solution, appearing in the denominator of the fraction, makes a big change in the ratio). By this same argument, the K_c for No. 7 has increased relatively little over that for No. 6, for the tube having been in the oil more than twice as long. Thus, the advantage of glass wool in this respect is clearly established.

However, an additional complication has been added by the use of glass wool; namely, the significantly poorer material balance. The presence of some surface-induced side reaction immediately suggests itself for an enormous amount of additional surface is present when glass wool is used; for the purposes of this study, the most important question is not so much what is the side reaction, but whether it interferes with the values of K_c . This can best be determined by measuring

a unique K_c , both from above and below, with and without glass wool, and then comparing the values.

It should also be observed that several of the tubes had a faint whitish deposit on the top part of the inside glass surface. Possibly this was more prevalent in the tubes containing glass wool, though not definitely so. Some of it may have been caused by the direct heat necessary during the sealing process.

The results of Set C, combined with those of Set B, have further narrowed the probable limits of K_c to the range 11.0 to 18.4 at 123° (at this ionic strength.) Another factor now seems apparent; the reaction rate probably cannot be increased much further without the construction of some sort of heavy duty shaker, which also would likely require reconstruction of the oil bath. However, knowing the above limits on K_c , the same effect ought to be realized by making up future tubes having initial ratios of $SO_3^{=} / S_2O_3^{=}$ straddling this range instead of with the values 0 and coheretofore used.

B-6. Set D.

Materials and Conditions

- $\left(\frac{SO_3^{=}}{S_2O_3^{=}} \right)_i$ initially spaced in range 10 to 22
- | | | | |
|--------------|---|------------------------------|---|
| $SO_3^{=}$ | : | 0.2 <u>M</u> | } About 35 ml total with 10 --
15 ml A |
| $S_2O_3^{=}$ | : | 0.2 <u>M</u> | |
| Ag_2S | : | Sample (3), Section A-4, (d) | |
| Ag | : | See Section A-4, (c) | |

(An earlier version of the $SO_3^{=}$ delivery apparatus pictured in Figure 4 was used for the first time with this set.)

Temperature: When the stirring belt broke on the fourth day, the temperature rose to 136°, and regulation was not established until

the fifth day; otherwise, for the first forty days, the temperature was $123^{\circ} \pm 0.5^{\circ}$. From the 41st to the 55th day it averaged about two degrees higher. The mercury regulator broke again, but was replaced in a few hours. From the 61st to the 67th day, it averaged about 130° , even going as high as 135.5° . This was due to the bath's rapidly becoming nearly completely tarred up. During this time large gradients existed in the bath and at two remote spots, the temperature was as much as 35° lower. However, from the location of the equilibrium tubes with respect to the temperature pattern in the bath, I would judge that the tubes were not appreciably influenced by these low temperatures, but rather reflected fairly closely the high values described above. This temperature situation is significant in the interpretation of the equilibrium results. For details and results of this set, see Table 4-4.

Table 4-4

Equilibrium Measurements, Set D

Tube No.	Delay	Glass Wool	mm (a) Final	mm (a) Initial	Percent Loss	Days in Bath	$\left(\frac{SO_3^{=}}{S_2O_3^{=}}\right)_i$	K_G
1	1 1/4 hr.	no	1.052	1.087	3.2	64	10.8	16.73
2	1/2 hr.	yes	1.029	1.087	5.3	67	10.8	16.05
3	1 hr.	no	1.083	1.089	0.5	68	15.5	15.47
4	1/3 hr.	yes	1.000	1.089	8.2	68	15.6	12.25
5	3/4 hr.	no	1.066	1.090	2.2	64	19.2	17.45
6	1 1/4 hr.	yes	1.005	1.090	7.8	67	19.0	16.50
7	1 1/2 hr.	no	1.069	1.090	1.9	68	20.5	16.64
8	1 hr.	yes	1.064	1.090	2.4	68	21.5*	16.66

Average of all but No. 4: 15.50 ± 0.42 16.50

(a) Total millimoles of $SO_3^{=}$ + $S_2O_3^{=}$ per 5 ml solution

(*) Estimated

For other definitions -- see Section B-1.

Comments.

The first feature that catches the eye in Table 4-4 is the nearly constant values of K_c . Since half of these approach equilibrium from each side, and furthermore, half the runs were made with glass wool, the value $K_c = 16.50 \pm .42$ (average of seven of the eight runs) looks like a good equilibrium constant at this ionic strength. At least it would appear safe to say that the use of glass wool does not cause any significant shift in the K_c values, thus answering one of our problems. (There are some minor qualifications to this, which will be discussed below).

Again, we find the result that the tubes without glass wool showed a considerably better material balance (2 percent average loss) than those with glass wool (7.1 percent average loss, not considering the estimated Tube 8 result). Furthermore, the spread in sulfite concentration during initial standardization was greater than the average loss where no glass wool was used, so again we can confirm the fact that there are no important side reactions for these tubes. One further remark about glass wool, -- whatever side reaction accompanies its use appears to produce alkali. Tubes containing it were noticeably pinker to phenolphthalein than those without.

The big uncertainty in these results is what temperature to use. In answering this question, we probably also have the answer to the minor variations noted in K_c . As K_c changes with temperature, we might expect the tubes containing glass wool to be able to follow these changes much more quickly. The tube that came out of the bath last (No. 4) did contain glass wool and had been exposed to a significantly higher temperature for six out of the preceding seven days. Tube No. 5, which was out first and four days earlier and did not contain glass wool,

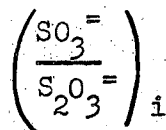
would probably reflect the average lower temperature it had seen most of the time. The fact that No. 4 had the lowest K_c of the eight, with No. 5 having the highest, would then be consistent with the equilibrium constant decreasing with temperature, (which later turns out to be precisely the case). This argument should not be carried much further to attempt to explain all the minute variations, for in the first place the exact temperature is not known as a function of time at every spot in the bath. I do believe, however, that qualitatively this explanation fits the facts, (and furthermore explains the discrepancy between these results and those of Set E.)

All that it seems safe to say about the temperature to accompany the rather well-defined $K_c = 16.50$, is that it is not exactly known, but that it is very likely somewhat higher than 123° , due to higher bath temperature during the final week before analysis. It would be desirable, for this reason, to redetermine the constant at a well-established temperature near 123° .

There is another reason for further work at this temperature. The parenthetical qualification "at this ionic strength" has crept into the discussion several times and implies that we do not know K_c as a function of ionic strength. Since it would be definitely desirable to have such knowledge, it was decided to make a final run at this temperature to remove uncertainties in both the quantities T and μ .

B-7. Set E

Materials and Conditions



Initially ranging from 12 to 21 at high and medium μ ; 1 and 2 at lower μ .

- SO₃⁼ : 0.2 M Total volumes of 40 -- 47 ml
made up from these starting
S₂O₃⁼ : { 0.2 M } materials (and water) to give
 { 0.2 M } groups at three ionic strengths;
 additional small air space over
 tubes filled with argon
- Ag₂S : Various different samples as indicated
- Ag : See Section A-4, (c)

The complete sulfite delivery apparatus shown in
Figure 4 was used.

Temperature: Proportional controller now installed.
Temperature for this set can be considered $122.5 \pm 0.5^{\circ}$ C as a function of
time and position in bath. Sludge formation in the bath prevented new
regulator from exercising more exact control.

Glass wool was now used for all tubes.

Argon atmosphere when analyzing tubes.

Details and results are given in Table 4-5.

Table 4-5

Equilibrium Measurements, Set E - (122.5° C)

Group	Tube No.	Delay	mm ^(a) Final	mm ^(a) Initial	Percent Loss	Days in Bath	μ ^(b) (Molarity)	Ag ₂ S (See ² A-4, d)	$\left(\frac{SO_3^{=}}{S_2O_3^{=}}\right)_i$	K _c
I	1	1 hr.	0.831	0.991	16.1	64	0.595	(4)	19.4	17.97
	2	1 1/2 hr.	0.912	.991	8.0	64	0.595	(3)	13.0	17.95
	3	5/6 hr.	0.855	.991	14.3	63	0.595	(4)	20.3	17.95
	4	1 1/2 hr.	0.891	.991	10.1	63	0.595	(4)	13.2	18.84
II	5	3/4 hr.	0.324	.429	24.5	64	0.257	(4)	21.1	18.83
	6	1 hr.	0.350	.425	17.5	62	0.255	(3)	20.5	17.35
	7	1 1/3 hr.	0.324	.429	24.5	64	0.258	(4)	13.0	17.55
	8	1 3/4 hr.	0.347	.429	19.2	62	0.257	(4)	12.9	17.47
III	9	1 hr.	0.1030	.172	40.0	62	0.103	(4)	1.10	31.86
	10	3/4 hr.	0.0620	.135	54.1	63	0.081	(4)	2.28	17.03
	11	1 1/2 hr.	0.1197	.173	30.6	63	0.104	(2)	1.11	16.82
	12	1/2 hr.	0.0930	.136	31.7	63	0.082	(2)	2.29	16.83

Av
17.96Av
17.46Av
16.89(a) Total millimoles of $SO_3^{=}$ + $S_2O_3^{=}$ per 5 ml solution

(b) Ionic strength based on initial material added (See text, Section B-7)

For other definitions -- see Section B-1.

-17-

7-1

Comments.

For some unknown reason, one value for K_c out of four is notably different from the other three at each of the three ionic strengths. I can find no likely factor common to just these three determinations, so the explanation remains a mystery. However, the internal agreement among the remaining three tubes in each ionic strength group varies from good to exceptionally good, so the anomalous value is rejected in each case, and the averages based on the other three.

Unfortunately due to an error in making up the tubes of Group III, equilibrium was only approached from one side. However, there is no apparent reason for thinking they are not at equilibrium. For example, No. 11 and No. 12 had initial ratios differing by more than a factor of two, yet their final K_c 's agree well. Also the value from No. 10 is in good agreement, yet has nearly twice the material percentage loss of No. 11 or No. 12. Finally the trend of decreasing K_c with decreasing μ appears well established from the results of Groups I and II, and these results of III give a nice qualitative fit with those from I and II. Consequently, it will be assumed that the tubes of each group have come to equilibrium with a value of K_c given by the average for the group, at the average μ . The latter assumption implies a somewhat greater uncertainty in this average point for Group III than for Groups I and II, because of the larger spread in the individual μ values.

The problem now immediately presents itself: What value of μ should be chosen? The values tabulated in Table 4-5 are based on the amount of initial material put into the tubes, and clearly the percentage loss shows that much of the starting material is no longer present at the time of analysis in the form of $SO_3^=$ or $S_2O_3^=$. This

means that whatever side reaction is taking place may be accompanied by an unknown change in ionic strength.

Looking at the most precise data for a moment, that of Group I, we see essentially no change in K_c with a change in percentage material loss from 16.1 to 8.0. There is little reason, then, why there should be any difference in going from 8 percent to 0 percent loss. Likewise in Group III, in going from 54.1 percent to 30.6 percent loss, there is little, if any real change in K_c . Therefore, it seems safe and reasonable to select the μ based on initial material added to the tubes, rather than that based on the analyzed quantities of $S_2O_3^{=}$ and $SO_3^{=}$, considering them to be the only ionic species present.

We should note from these results that K_c (average) from Group I is somewhat higher than the K_c (average) from Set D, for the same ionic strength. Final discussion of this point will be reserved for Section D until after we have considered the results from Set F.

Another point worth noting is the relatively poor material balance for tubes where air has been excluded, even for tubes with glass wool. Direct comparison can be made for Group I with Set D. Here we see a possible correlation with the sample of Ag_2S used, for Tube No. 2 using the same Ag_2S sample as was used for Set D is the only one in Set E-I that has a comparably small material loss. However, the important feature is that Tubes E-1 and E-3 have K_c 's agreeing with that of E-2, which is what we are really interested in.

One final feature of Set E is that the titration volumes were larger than for any previous sets as a result of the use of 0.01 N I_3^- for some of the analyses. This may account in part for the higher precision with these results. Also, starting with this set, the tubes were broken open for analysis and the pipeting done in an atmosphere

of argon.

C. Equilibrium Sets at Other Temperatures.

C-1. Set F (195°).

Materials and Conditions

$$\left(\frac{SO_3}{S_2O_3} \right)_i \quad \text{initially } 0 \text{ or } \infty$$

- SO_3 : 0.2 M
 S_2O_3 : 0.2 M
 Ag_2S : Different samples indicated.
 Ag : See Section A-4, (c).

These solutions were diluted with H_2O to make the tubes of lower μ

Sulfite delivery apparatus, Figure 4, used

All tubes with glass wool

Analyses were done in an atmosphere of argon

Temperature: Proportional controller regulator used, set for 195°. On the 11th day, the temperature rose sharply, the oil having become too tarry for further use. By the 14th day new oil was installed and the bath regulating again. This temperature excursion, up to 238° C for a short time, could not have affected the value obtained for K_c , for it was too brief, too long before the analyses were made (three weeks), and reaction rates are certainly rapid enough at this temperature to cause quick readjustment in K_c , once control had again been restored.

In the additional three weeks time the oil was just about again at the point where it would be unusable for further work. A time-position-temperature study of the bath showed, however, that for Tube No. 1, the temperature should be 195.0°, good to \pm one degree. For Tube No. 2, the temperature might be somewhat lower, though probably not by an important amount.

It was felt to be safe to make up these solutions with initial ratios of o and c instead of nearer a final equilibrium value (as was done for Sets D and E), since the reactions must be much faster at this higher temperature. Furthermore, at the time these tubes were made up, the temperature coefficient of the reaction was not known, so it was next to impossible to predict what the final K_c would be at this temperature. (When Tubes 1 and 2 were removed from the oil bath, a heavy whitish deposit was coated on the inside of the glass, like paint. This was not noticed on Tube No. 3 (whose K_c was erroneous)). For details of the set, see Table 4-6.

Comments.

The explanation for only three results appearing in Table 4-6 undoubtedly lies largely in the brief temperature excursion up to 238° described above, for a total of fourteen tubes was actually placed in the bath. A quick reference to the vapor pressure tables reveals that for water, $p = 13.8$ atmospheres at 195° C, and $p = 31.9$ atmospheres at 238° C. The remarkable thing to me is that any of these glass tubes failed to explode when they were subjected to an internal pressure of 32 atmospheres, and I consider it fortunate that even three results were obtained. The explosion sounds of only one or two tubes were actually heard.

Table 4-6

Equilibrium Measurements Set F (195°)

Group	Tube No.	Delay	mm (a) Final	mm (a) Initial	Percent Loss	Days in Bath	μ (b) (Molarity)	Ag ₂ S ⁺ (See A-4, d)	$\left(\frac{SO_3^{=}}{S_2O_3^{=}}\right)_i$	K _c
I	1	1 3/4 hr.	.880	1.018	13.5	36	.611	(2)	∞	9.74
II	2	1 hr.	.378	.434	12.9	36	.261	(2)	0	9.58
III	3	3 1/3 hr.	.0446	.1001	55.4	37	.0601	(4)	0	23.19

(a) Total millimoles of $SO_3^{=}$ + $S_2O_3^{=}$ per 5 ml solution

(b) Ionic strength based on initial material added (See text, Section B-7)

For other definitions -- see Section B-1.

Luckily, values of K_c were obtained approaching equilibrium from both sides, and the agreement between Tubes 1 and 2 looks quite encouraging. Tube No. 3 is certainly off, as is apparent both from these data and from the data at other temperatures. The reason for this is unknown, but it may be connected with the low ionic strength along with the fact that it was made using the poorest quality Ag_2S sample. With the small total amount of $S_2O_3^{=}$ initially in the tube and a large excess of Ag_2S solid, enough impurity could indeed be present to prevent establishment of the proper K_c . (There was less material present in Tube 3 than in any other tube of any set. Note that the poorest material balance was obtained of any tube in any set.) Although the previous work has indicated that this need not affect the K_c result, it conceivably could in certain cases. Note also that a titration volume of less than one ml appears in the denominator of the ratio for K_c whereas for Tubes 1 and 2 the volumes were greater than 16 ml, so this is added reason to discount the K_c from Tube 3.

The question remains of interpreting ionic strength effects for this set. Judging from the results of Set E, K_c from No. 2 should be lower than that from No. 1, and this is indeed the case. However, as discussed above, the temperature is somewhat less for No. 2 than for No. 1, so if No. 2 were actually at a lower temperature, the smaller K_c might not be enough smaller. Since the temperature is relatively more certain for No. 1, I feel the soundest procedure is to consider for the results of this set, $K_c = 9.74$ at $\mu = 0.611$, $T = 195.0 \pm 1^\circ C$, and then to extrapolate this value to $\mu = 0$ by some theoretical procedure, based on the experimental variation of K_c with μ which was determined from the results at 122.5° . See Section E for the continuation of this discussion.

C-2. Set G (25°)Materials and Conditions

Same as for Set E; the two sets were made up at the same time.

Temperature. $25.0^\circ \pm 0.1^\circ$. As read on a Beckmann thermometer. This set was on a vigorous mechanical shaker in the 25° water bath, having a mercury temperature regulator and an ordinary well-type stirrer. The shaker was shut down for minor repairs during the run, but this should not affect the results.

The details are given in Table 4-7.

Comments.

The variation in μ between No. 3 and No. 4 results from an excess of $\text{SO}_3^=$ solution having been added to No. 4 when it was made up.

The evident feature of Table 4-6 is that all the initial ratios were too small, but as was explained for Set F, this could hardly have been predicted. The important question, however, is whether the highest $K_c = 77$ really represents equilibrium conditions. A decision on this point should probably not be made on the basis of these data alone. It is unfortunate that the initial ratios for Group III of Set F suffered the same error that Group III of E did, having been prepared at the same time. Quite likely, solutions this dilute would come to equilibrium under the conditions of this set, if their initial ratios had been as high as 20.

There is one bit of evidence from the equilibrium measurements themselves that might be considered. It is rather well established from a consideration of all the sets that the more dilute solutions approach equilibrium much more rapidly than the concentrated ones. One interpretation of this is that the number of moles of $\text{S}_2\text{O}_3^=$ that must be

Table 4-7

Equilibrium Measurements Set G. (25°)

Group	Tube No.	mm ^(a) Final	mm ^(a) Initial	Percent Loss	S ₂ O ₃ ⁼ (b) Dif ³	Days in Bath	μ ^(c) (Molarity)	Ag ₂ S ⁼ (See A-4, d)	$\left(\frac{SO_3^{=}}{S_2O_3^{=}}\right)_i$	K _c
I	1	0.917	.991	7.5	.027	105	.595	(4)	19.6	42.4
	2	.890	.991	10.3	.027	105	.595	(3)	13.1	19.5
II	3	.382	.429	11.0	.015	105	.258	(3)	21.0	77.0
	4	.478	.520	8.2	.019	105	.312	(2)	18.6	59.5
III	5	.1041	.1358	23.3	.018	104	.081	(2)	2.28	3.39
	6	.0928	.1363	31.9	.026	104	.082	(4)	2.30	5.03
	7	.1355	.1778	23.8	.026	104	.107	(4)	1.18	1.46
	8	.1414	.1728	18.6	.020	104	.104	(2)	1.11	1.30

(a) Total millimoles in 5 ml

(b) Refers to the number of millimoles of S₂O₃⁼, alone, in 5 ml of the final solution minus the number in 5 ml of the starting solution.

(c) Ionic strength based on initial material added

For other definitions, See Section B-1

converted to SO_3^- roughly determine this speed, where equilibrium is being approached from the low SO_3^- side. Of course, then, the effects of glass wool, etc., must be about the same on all the tubes being considered for this argument to be valid. To put this in a slightly different way, for a series of tubes all removed from equilibrium, we might expect a constant amount of S_2O_3^- to be converted to SO_3^- in a given time, irrespective of the different starting concentrations of S_2O_3^- .

All the tubes in Set G were on the shakers approximately the same period of time, (and all used glass wool). Looking for the moment at the column " S_2O_3^- dif." in Table 4-7, most of these values are the same to an order of magnitude at least. This is true even though the amount of starting material varies by as much as a factor of 7 between tubes of the set. However, a smaller amount of S_2O_3^- was converted in Tube No. 3 than in any other tube of the set, which is consistent with the idea that equilibrium actually has been reached for Tube No. 3. Furthermore, this smaller loss of S_2O_3^- did not result simply from a particularly good over-all material balance, for the material balance for Tube No. 3 is the poorest of any of the four tubes in the high and medium ionic strength groups.

Because of other factors involved, this is not a conclusive argument. Perhaps the best way to judge the value $K_c = 77$ at 25° is to use it on the presumption that it is really an equilibrium value, and see what conclusions this leads to. There may then be some independent check on these conclusions, which would therefore serve as a check on $K_c = 77 (\pm 4)$. The uncertainty ± 4 is estimated from the analytical procedure, for with such a large ratio, titration volumes, even using $.01 \text{ N I}_3^-$ for analysis, are getting quite small. (This would not limit the accurate determination by this procedure of such a K_c for

the higher ionic strengths, however, for more material is then present to titrate.) The consequences of using this K_c for 25° are given in Chapter 6, A-2 and B

The results of Set G do suggest that under experimental conditions similar to these, equilibrium might well be established from both sides and measured accurately at 25° in three to four months time, especially if starting ratios of say 50 and 200 or 50 and 400 were used. This should be quite a sure way to get a value of ΔF_{298} for the reaction, not involving an extrapolation of high temperature data.

D. Summary of Equilibrium Results

In Section B-7 we deferred until later a choice for K_c at 123° between 16.50 from Set D and 17.96 from Set E for the same ionic strength. The fact that the 16.50 value could easily be representative of a somewhat higher temperature was also discussed. Since the trend of decreasing K_c with increasing temperature has now been definitely established, this would nicely explain the lower value 16.50, and provide good reason to reject it in favor of the value 17.96.

Our equilibrium results are summarized in Table 4-8.

D-1. Correction of K_c at 195°. The value $K_c = 9.74$ at 195° is the equilibrium constant for the reaction involving $\text{Ag}_2\text{S} (\beta)$ which is the form stable at this temperature. Since $\text{Ag}_2\text{S} (\alpha)$ is the stable form at 122.5° and 25°, we should correct for this in order to have the K_c 's at different temperatures refer to the same reaction. The transition temperature for the two solids is 179° C (452.16° K) at which temperature $\Delta F_{\text{trans.}} = 0$. At 195° (468.16),

$$\Delta F_{468} = \Delta F_{452} - \int_{452.16}^{468.16} \Delta S_{\text{trans.}} dT \quad (4-5)$$

For all practical purposes over this small temperature range, $\Delta S_{\text{trans.}}$ is constant, and has the value given by:

$$\Delta S_{\text{trans.}} = \frac{\Delta H_{\text{trans.}}}{T_{\text{trans.}}} \quad (4-6)$$

Writing the transition reaction:



$\Delta H_{\text{trans.}} = -1050$, whence from (4-6), $\Delta S_{\text{trans.}} = -2.32$ e.u.

From equation (4-5), $\Delta F_{468} = 0 + (2.32)(16) = 37$ cal./mole. Choose now the activity of $\text{Ag}_2\text{S} (\alpha) = 1$, which is our convention for the other two temperatures. From the relation:

$$\Delta F_{4-7} (468) = RT \ln \frac{1}{a_{\beta}} \quad (4-8)$$

we calculate $a_{\beta} = 0.9610$ at 468.16. We can therefore correct our K_c at 195° C to K'_c , where

$$K'_c = \left(\frac{S_0}{S_2} \right)^3 a_{\beta} = K_c \cdot a_{\beta} \quad (4-9)$$

or $K'_c = (9.74)(0.9610) = 9.360$.

We should use this value for all further thermodynamic calculations.

It has been included in Table 4-8.

Table 4-8

Summary of Equilibrium Results

T °C	$\mu^{(a)}$ (Molarity)	K_c	Number of Determinations	Reliability
122.5 ± 0.5	0.595	17.96	Av. of 3 from each side with other confirmation	Very good
	0.257	17.46	Av. of 3 from each side	Good - very good
	0.0886	16.89	Av. of 3 from each side	Good (More uncertainty than for those above)
195.0 ± 1	0.611	9.74 ^(b)	1 from each side	Fair - good
		9.360 ^(c)		
25.0 ± 0.1	0.258	77.0	1 one side only	Not yet finally evaluated (See Chapt. 6-B)

(a) Ionic strength based on initial material added (See text, Section B-7)

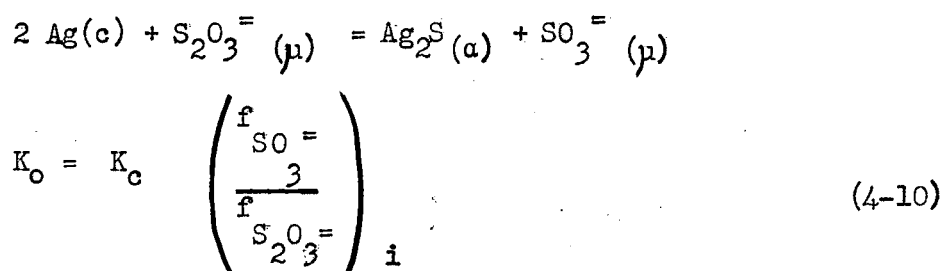
(b) This value is the actual experimental value where the Ag_2S involved in the reaction is in the form stable at 195° C, namely the β form. Since the α form is stable at the other two temperatures, a correction must be applied before directly comparing the K_c values. (See (c) below)

(c) This is the value $K_c^!$ corrected in Section D-1 as described in (b). It is the value that should be used in all future thermodynamic calculations.

D-2. Influence of Side Reactions. It was determined that side reactions, while generally present when glass wool was used (even in the absence of oxygen), had no appreciable effect on the values of K_c selected. It was also determined that use of glass wool and of various different starting materials caused no systematic changes in K_c .

E. Extrapolation of K_c Values to Infinite Dilution.

Before proceeding further, let us reexamine the equilibrium equation:



where $f_{\text{SO}_3^{=}}$ and $f_{\text{S}_2\text{O}_3^{=2}}$ are the activity coefficients for $\text{SO}_3^{=}$ and $\text{S}_2\text{O}_3^{=2}$ respectively, with concentrations in moles/liter. It is often assumed that the size of an ion and its charge are the important facts determining the activity coefficient in solutions of a given ionic strength. Since $\text{SO}_3^{=}$ and $\text{S}_2\text{O}_3^{=2}$ have the same charge and since their sizes in solution probably do not differ greatly, we would suspect that the two activity coefficients in the same solution were approximately equal and that therefore K_c would not be a rapidly varying function of concentration. A glance at the data for 122.5° in Table 4-8 confirms this. Nevertheless, since this relatively small effect appears to be quite real, it must be considered, and a decision made on how best to convert these K_c values to a K_o at infinite dilution.

An immediate consequence of the decreasing K_c with decreasing μ at 122.5° is that by equation 4-10, $f_{SO_3}^f$ is smaller than $f_{S_2O_3}^f$. We will return to this point shortly.

A form of extended Debye-Hückel expression for aqueous activity coefficients that has frequently been used is the following.^{21,22}

$$\log f_i = \frac{-S \sqrt{I}}{1 + A \sqrt{I}} \quad (4-11)$$

$$I = (\text{"ionic concentration"}) = \sum c_i z_i^2 = 2 \mu \text{ (molarity)} \quad (4-12)$$

c_i = concentration in moles/liter for i^{th} ion

z_i = charge on i^{th} ion

$$S = \frac{1.283 \times 10^6}{(DT)^{3/2}} z_i^2 \quad (4-13)$$

D = Dielectric constant of solvent. T in ° K.

$$A = \frac{35.57}{(DT)^{1/2}} a_i \quad (4-14)$$

a_i = effective diameter of hydrated ion in angstrom units.

No experimental value for the dielectric constant of water was immediately available for 122.5° or 195°, but a calculation of these values was kindly made for me by Alder and Harris²³ from an extrapolation of their theoretical expression that well reproduces the experimental data in the range 0 - 100° C. These values together with the values at 25°²¹ are reproduced in Table 4-9.

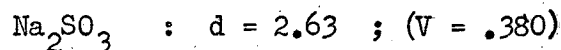
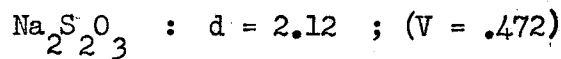
Table 4-9

The Dielectric Constant of Water

25° C	122.5°	195°
78.54	52.3	41.7

The semi-empirical nature of equation (4-11) should be stressed. Since no one really knows what is the "effective diameter of a hydrated ion", the best values for a are generally determined from a curve-fitting procedure of experimental activity data, with such an equation. There are some independent means to estimate a -values which give general agreement, particularly in the relative sizes for different ions.²²

Examining equation (4-11) once again, we see that for two ions in the same solution, identical except for hydrated sizes, the larger one would have a larger a -value, (thus by (4-14) a larger A), and hence a larger activity coefficient. Our experimental data require the activity coefficient for $S_2O_3^{=}$ to be larger, or $S_2O_3^{=}$ to be the larger ion in solution. This seems to me to be entirely reasonable, though by no means absolutely certain. (The entropy of $SO_3^{=}$ is more negative than the entropy of $S_2O_3^{=}$ from our results in Chapter 6-B so that $SO_3^{=}$ will bind a larger amount of water.) The scant density data²⁴ give for the crystalline salt:



One can accurately compare density data only for salts of identical crystal structure, which is not the case here. Nevertheless, it seems safe to say that the molar volume of crystalline $Na_2S_2O_3$ is larger than that for Na_2SO_3 .

The hydrated sizes are another thing again. Experience has shown that the smaller monatomic ions in solution often behave as if their relative aqueous sizes are quite different from their relative crystal sizes, presumably because of greatly different degrees of hydration. On the other hand, for the larger ions, particularly polyatomic ones, the radii in solution generally appear in the same

relative order as in the crystalline state. The presumption here is that all such large ions are hydrated to a smaller extent and that changes in crystal size will have less change on the degree of hydration, so that the relative sizes in the crystals will determine relative sizes in solution. (Bernal and Fowler²⁵ gave arguments that, even for double negatively charged polyatomic ions, hydration effects would be minor.)

What this is all leading up to is a criticism of the a -values for $S_2O_3^{=}$ and $SO_3^{=}$ tabulated by Kielland²², i.e., $a_{SO_3^{=}} = 4.5$ and $a_{S_2O_3^{=}} = 4.0$. Many of the a -values that he tabulates are based on several different types of calculation, as well as on experimental data.

However, there is no indication of where the values for $S_2O_3^{=}$ and $SO_3^{=}$ came from, or even why $SO_3^{=}$ was chosen "larger" than $S_2O_3^{=}$ (and larger than $SO_4^{=}$, also, for which he lists $a = 4.0$). It should be clear then that if we are to use equation 4-11 to extrapolate the results, his values for a should not be used, for they conflict with the experimental observation that $f_{S_2O_3^{=}} > f_{SO_3^{=}}$. The approximate magnitudes of the a 's may be all right. Since it appears that $a_{S_2O_3^{=}}$ should be larger than $a_{SO_3^{=}}$, we will arbitrarily reverse Kielland's order and select $a_{S_2O_3^{=}} = 4.5$ and $a_{SO_3^{=}} = 4.0$. This is not done under the illusion that a strict theoretical interpretation can be placed on these a -values. The whole procedure should rather be looked upon as a convenient way of extrapolating our experimental data in accordance with a semi-theoretical, semi-empirical procedure, with the final test being how it works with the data. Also, the experience accumulated in the use and interpretation of equations like (4-11) may allow us to suggest that the experimental data are evidence that aqueous thio-sulfate ion is "larger" than aqueous sulfite ion. Note that since we are only interested in the ratio of the two activity coefficients, the

absolute values of the a's we choose are not so vital, but the values relative to each other are, if we are to use this procedure at all.

The form of the equation we will use is:

$$\log \left(\frac{f_{\text{SO}_3^=}}{f_{\text{S}_2\text{O}_3^=}} \right) = -S \sqrt{\Gamma} \left(\frac{1}{1 + A_{\text{SO}_3^=} \sqrt{\Gamma}} - \frac{1}{1 + A_{\text{S}_2\text{O}_3^=} \sqrt{\Gamma}} \right) \quad (4-15)$$

From equation (4-10) we have:

$$\log K_o = \log K_c + \log \left(\frac{f_{\text{SO}_3^=}}{f_{\text{S}_2\text{O}_3^=}} \right) \quad (4-16)$$

which we can combine with equation (4-15) and rearrange to give

$$\log K_c - S \sqrt{\Gamma} \left(\frac{1}{1 + A_{\text{SO}_3^=} \sqrt{\Gamma}} - \frac{1}{1 + A_{\text{S}_2\text{O}_3^=} \sqrt{\Gamma}} \right) = \log K_o \quad (4-17)$$

For convenience in plotting, we will add a term to equation (4-17) to give:

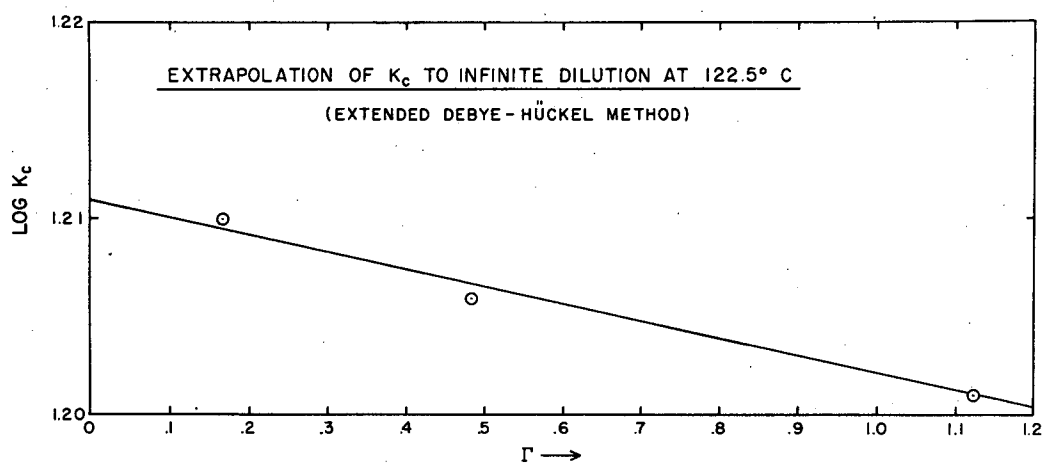
$$\log K_c = M = \log K_o - (B_{\text{SO}_3^=} - B_{\text{S}_2\text{O}_3^=}) \Gamma \quad (4-18)$$

Actually, such B terms are often added to equations like (4-11) in order for them to fit activity data at high ionic strengths. In our case, where we are dealing with a ratio of activity coefficients (i.e., a difference of B values) and only at medium ionic strengths, all variation of f's with μ would probably result from the different a values so we omitted the B term originally in equation (4-11). We will plot equation (4-18) as $(\log K_c - M)$ vs. Γ and take the intercept at $\Gamma = 0$ as $\log K_o$ realizing that the slope, $(B_{\text{SO}_3^=} - B_{\text{S}_2\text{O}_3^=})$ should be nearly zero. (If we had accurate a values and if this theory has any real significance, then the value of the slope would be considered a check on the application of the above argument.)

Before we can make a plot of equation (4-18) we should decide about the a -values at other temperatures. Little is known of the temperature dependence of a -values. However, Harned and Ehlers²⁶ and Harned and Hecker²⁷ concluded that the a -values for NaOH and HCl at least, were constant over a considerable range of temperatures (and concentrations). For lack of any further information, we will make the similar assumption for $S_2O_3^{=}$ and $SO_3^{=}$ and use the same a -values at all temperatures. If the values do change with temperature, some of this change at least should cancel because of the form of equation (4-17).

In Section B-7 the intention was expressed to base our extrapolation to infinite dilution at 195° on the method used at 122.5°. Assume that the β -values (if any) will change similarly with temperature for the two ions. This means that for the single points at both 195° and 25° we may calculate and plot values for the left side of equation (4-18). A line through these points, with the same slope, $-(\frac{B}{S_2O_3^{=}} - \frac{B}{SO_3^{=}})$, as at 122.5°, will then allow extrapolation to K_0 values at infinite dilution in a self-consistent manner for all three temperatures. (For the above arguments regarding size and activity coefficients to be valid, this slope should be approximately 0, As discussed above.)

We can now use the values previously given for T , D , A , Z ($=2$) and K_0 , along with the various assumptions made, to calculate the quantities in equations (4-17) and (4-18) for the different temperatures. These quantities are tabulated in Table 4-10. The quantity $(\log K_0 - M)$ for the points at 122.5° is plotted against Γ in Figure 5-a, and the value $\log K_0$ at $\Gamma = 0$ read from the graph. On another graph, $(\log K_0 - M)$ was plotted against Γ for the points at 25° and 195°. Lines were drawn through them parallel to the line in Figure 5-a, and the $\log K_0$'s read also. These values along with the K_0 values



MU-6127

Fig. 5-A

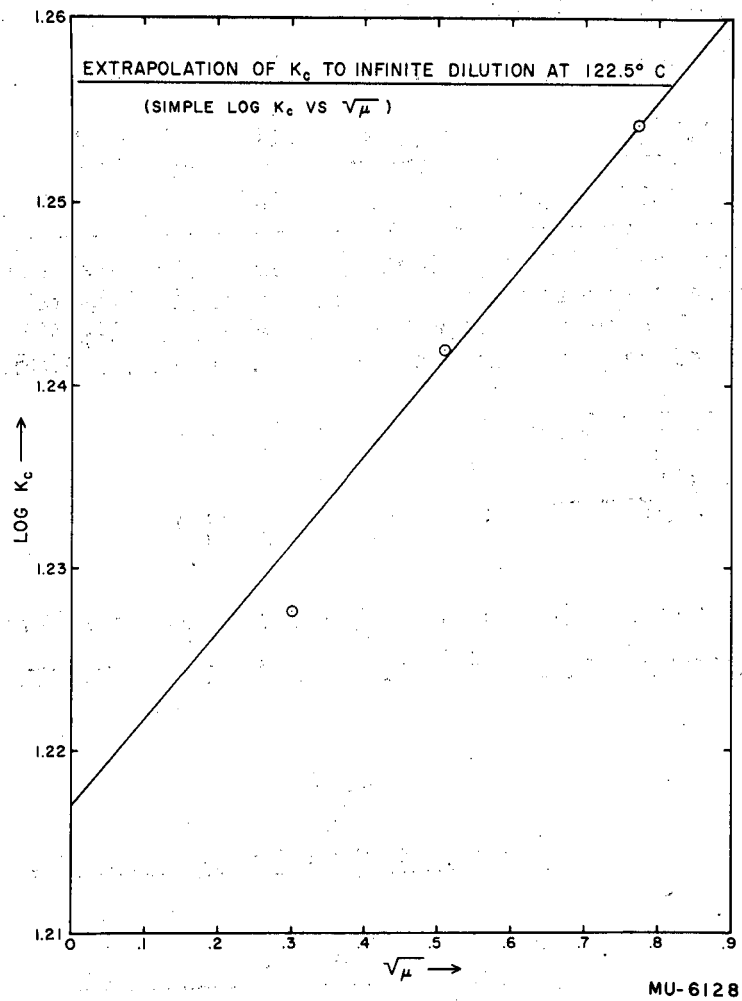


Fig. 5-B

are summarized in Table 4-11.

Table 4-10

Quantities in Equations (4-17) and (4-18)

t° C	S	$\Gamma^{(a)}$	$A_{SO_3=}$	$A_{S_2O_3=}$	log K_c	$M^{(c)}$	log K_{c-M}
25.0	1.432	0.515	0.930	1.046	1.8865	0.0294	1.8571
122.5	1.724	1.123	0.989	1.113	1.2543	0.0537	1.2007
122.5	1.724	0.485	0.989	1.113	1.2420	0.0345	1.2059
122.5	1.724	0.1675	0.989	1.113	1.2277	0.0174	1.2103
195	1.882	1.064	1.018	1.146	0.9713 ^(b)	0.0570	0.9143

(a) Values for Γ ($= 2 \mu$ (molarity)) were calculated from the concentrations at room temperature and the change in density of water with temperature. For these reasonably dilute solutions, the density change of water closely approximates that for the solutions.

(b) This is log K_c^0 - See Section D-1

$$(c) M = S \sqrt{\Gamma} \left(\frac{1}{1 + A_{SO_3=} \sqrt{\Gamma}} - \frac{1}{1 + A_{S_2O_3=} \sqrt{\Gamma}} \right)$$

See Equations (4-11) to (4-14) for additional definitions

Table 4-11

K_o Values as a Function of Temperature

t° C	log K_o	K_o
25.0	1.862	72.78
122.5	1.211	16.26
195.0	0.924	8.40

It should be noted that Figure 5-a is drawn to quite an expanded scale, and that the slope - $(B_{\text{SO}_3} - B_{\text{S}_2\text{O}_3})$ is indeed very small. The straight line from the graph is at least as good as could be expected, if not too good.

A simple plot of $\log K_c$ vs $\sqrt{\mu}$ was also made for comparison in Figure 5-b, and for it not such a good straight line can be drawn. Whether the better appearance of Figure 5-a has any real significance is hard to say. However, in one respect, the method of Equation (4-18) does possess a real advantage, namely by providing a means for extrapolating the data at the other temperatures. It recognizes the fact that the slope of such a $\log K_c - \sqrt{\mu}$ plot changes with temperature, and thus provides a consistent treatment for all three temperatures. Furthermore, the slope of Figure 5-b is somewhat steeper and the scatter of the points greater, so the extrapolation, even at 122.5° is considerably less certain. (The "best" values obtained from Figure 5-b and from drawing parallel lines at the other temperatures, were 72.8, 16.5 and 8.95 at 25.0, 122.5 and 195.0°. These are to be compared with the values in Table 4-11.) As would be indicated from the earlier discussion, the use of this method with Kielland's a-values makes the plot more uncertain yet. (Of course no meaning should be read into the magnitude of the slope in Figure 5-a, for it is determined by the a-values we selected.)

In conclusion, we might remark that the problem of correcting activity coefficients to different temperatures would be quite simple if we only had accurate heat of dilution data (as a function of temperature). Very little such data is known, and none has been measured for Na_2SO_3 , so the method is not useful in this case.

Chapter 5

Oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ with Br_3^- A. Introduction

Although it was planned to study the temperature dependence of the equilibrium constant for the equilibrium reaction (4-2), in order to calculate the ΔH_f° of $\text{S}_2\text{O}_3^{2-}$, we were also aware of the advantages of having an independent check on this quantity and thus, indirectly, on the free energy measurements also.

There is not a wide choice of aqueous reactions available which would be especially desirable for calorimetric study and suitable for obtaining ΔH_f° for $\text{S}_2\text{O}_3^{2-}$. We concentrated on searching for reactions which would oxidize the $\text{S}_2\text{O}_3^{2-}$ to the plus six oxidation state.

The literature was not too helpful in this respect. I tried to find conditions under which such oxidation would be rapid and complete with several oxidizing agents, including IO_3^- and Ce^{+4} , but was not successful. Work with BrO_3^- showed that it might be worth further investigation, but the large heat, over 200 kcal./mole, was not encouraging.

Carrière and Dalpa²⁸ report some conditions under which the products of oxidation, using IO_3^- , are $\text{S}_4\text{O}_6^{2-}$ and HSO_4^- . Conceivably, the use of ClO^- would be feasible, although a rough calculation showed that nearly 300 kcal. of heat would be evolved per mole of $\text{S}_2\text{O}_3^{2-}$ oxidized which again means that high calorimetric accuracy could not be expected. Also, the work of Maksimyuk and Ptitsyn²⁹ indicated that H_2S was often formed as a side product, although they suggested circumstances to circumvent this. They remarked that sulfur formed initially and then later redissolved.

Thompson³ and Bichowsky¹ both measured the heat of decomposition of $S_2O_3^{=}$ in acid solutions (see Chapter 1) but the reaction is not clean cut, likely to be slow, finely divided sulfur is formed, and in high acid concentrations where the reaction is most rapid, numerous important dilution reactions should also be measured. (See further discussion in Chapter 6, C-1.)

Permanganate is reported to oxidize $S_2O_3^{=}$ to $SO_4^{=}$,³⁰ but the uncertain state of the reduction product or products of $MnO_4^{=}$ discourages its use for a calorimetric study.

Berthelot⁴ used Br_3^- as an oxidizing agent and obtained general agreement with the results of Bichowsky¹ and Thompson.³ However, all of these results (in the range ΔH_f° for $S_2O_3^{=}$ = -145 to -149 kcal./mole) were being viewed with a suspicious eye, along with the reactions used to arrive at them. There is another report in the literature of the oxidation of $Na_2S_2O_3$ by Br_2 water to Na_2SO_4 ,³¹ but the original article was not available to check the details. (This was an analytical, not a heat study.) An estimation of the heat of oxidation by Br_3^- gave the result 154 kcal/mole, which is still high, but better than the other values previously mentioned.

It was found possible to titrate an aqueous Br_3^- (in dilute HCl) solution, with $S_2O_3^{=}$ being oxidized to the +6 state, to within 0.5 percent of the theoretical yield. As in the case of ClO^- , S first precipitated and then redissolved, with the rates of these processes dependent on relative and absolute concentrations. Where a small amount of $S_2O_3^{=}$ would react with large excess of Br_2 in the calorimetric reaction, the oxidation up to $SO_4^{=}$ should be rapid. This condition of relative excess could also result in an even more complete oxidation than in our titration above. (These results generally

agreed with Berthelot's⁴ who also reported that in dilute $S_2O_3^{=}$ with at least a twofold excess of Br_3^- , no sulfur at all precipitated.)

For lack of any better choice, then, we decided to study the heat of this reaction calorimetrically; it appeared to have at least as good a chance of success as any of the reactions considered.

B. Preparation of Reagents.

B-1. $Na_2S_2O_3 \cdot 5H_2O(c)$ and its Reagent Solution.

Kolthoff and Sandell¹⁹ describe a procedure for making stoichiometric $Na_2S_2O_3 \cdot 5H_2O$ crystals, which consists of placing the wet crystals in a hygrostat over a saturated solution of $CaCl_2 \cdot 6H_2O$ and excess of its solid. Some reagent $Na_2S_2O_3 \cdot 5H_2O$ was recrystallized and dried by suction, then placed in such a hygrostat. Samples were withdrawn and analyzed with standard I_3^- solution after varying periods of time, with the results shown in Table 5-1.

Table 5-1

Composition of $Na_2S_2O_3 \cdot 5H_2O(c)$			
	Number of Days in Hygrostat		
	<u>4</u>	<u>8</u>	<u>27</u>
Number H_2O 's in Samples Analyzed	5.52	5.29	4.92
	5.47	5.31	4.79

When the 27-day samples were removed, there were visible signs of decomposition on the surface of many crystals. An attempt was made to select the best looking material but Table 5-1 shows that this was still not too good. Conceivably, in some period of time intermediate between 8 and 27 days an analysis of 5.00 H_2O could be obtained, but with decomposition occurring so easily, further tests would be necessary

to establish that this was not an average figure representing some over-hydrated and some partially decomposed solid. Further examination of the literature revealed that Foz and Colomina³² had experienced the same sort of difficulty and had concluded that preparation of the perfectly stoichiometric pentahydrate in this manner was not feasible. Consequently, we decided to use aqueous solutions for the calorimetric study. Note: Samples from various commercial samples of the pentahydrate were analyzed directly from the bottle. The results from one bottle varied from 4.95 to 5.07 waters, and other older bottles showed 4.93 and 4.83 waters respectively. Thus, even in previously unopened (older) samples, there is some evidence of decomposition. If SO_3^{\equiv} is formed as a decomposition product, this could contribute to the changing titer often reported for fresh $\text{Na}_2\text{S}_2\text{O}_3$ solutions, until such time as the SO_3^{\equiv} had been oxidized by air.

Such solutions would have some additional advantages for calorimetric work. In the first place, it would not be necessary to know the heat of solution of the solid salt. Secondly, for a reaction such as this which is known to proceed through intermediate products and therefore not be "instantaneous", an aqueous starting material would most certainly favor a faster reaction than would a solid. The reagent solutions were prepared by dissolving freshly recrystallized wet salt in recently boiled distilled water, and their titer was established with a standard KIO_3 solution.

B-2. Other Reagents. The standard Br_3^{\equiv} solutions were prepared by weighing out samples of recrystallized KBrO_3 (described in Part II Chapter 2-B of this thesis), and adding a weighed excess of dried reagent NaBr and a known amount of standard HClO_4 . Sufficient time was allowed (3 1/2 to 17 hours, during which time the solution was

covered) to insure complete reduction of the KBrO_3 .

C. Calorimetric Procedure.

The experimental equipment (which was also used for Part II of this thesis) has been previously described.³³ In the first few runs (for which the details are not given in this paper) the sample bulb was broken by thrusting through it a rod which moved through the center of the stirring shaft. The calorimetric heats for three runs (on the same sample basis as used for the runs described in this section) varied from 133 to 147 calories. It was felt that perhaps the concentration of Br_3^- was insufficient to cause rapid enough oxidation, so another run was performed in a similar manner, but using more Br_3^- , with the resulting heat of 138 calories. Finally, some runs were tried, breaking the sample bulb on the bottom, with the results described in the next section. (159 to 161 calories) The probable explanation for this phenomenon lies in the initial precipitation of sulfur described earlier. When the sample is broken with the rod, the solution pressure would immediately force some of the thio-sulfate high up into the previously dry stirring shaft on the end of which the bulb was attached. Some of the acid Br_3^- solution would quickly follow, causing precipitation of sulfur on the inside walls of the shaft, but since relatively poor circulation is effected in this small part of the apparatus, all the sulfur might not dissolve during the run. Some sulfur was noticed on the inside walls at the completion of these early runs. However, by breaking the bulb on the bottom, this stirring shaft is not immediately accessible to the $\text{S}_2\text{O}_3^{2-}$ solution, so essentially all of it is released into a great excess of oxidizing agent which should promote rapid and complete oxidation.

All weights are reduced to weight in vacuo. The heats were measured at $25.0^\circ \pm 0.5$ and are reported in terms of the defined calorie.

D. The Heat of Oxidation of $S_2O_3^{2-}$ by Br_3^- .

In this series of runs, 5 ml (weighed) samples of standard $Na_2S_2O_3$ solution were broken into an excess of aqueous Br_3^- and $HClO_4$. The details are given in Table 5-2. (Br_3^- production described in previous section.)

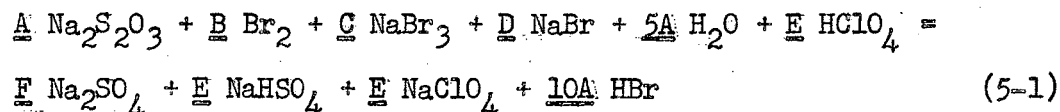
Table 5-2

The Heat of Oxidation of $S_2O_3^{2-}$ with Br_3^- (Part 1.)

Runs	Total Grams Water Added	Grams $KBrO_3$	Grams $NaBr$	Moles $HClO_4$	Moles (a) $Na_2S_2O_3$	Q_c cal.
1	1068.9	2.5851	15.076	0.2326	.0010030	161.29
2	"	"	"	"	"	159.14
3	"	"	"	"	"	159.46
4	"	"	"	"	"	<u>160.46</u>
					Av.	160.09 \pm .8

(a) The Quantity A in Equation (5-1).

The quantity Q_c refers to the actual heat evolved in the calorimeter. By the "net" calorimetric reaction, we shall refer to reaction (5-1), the simplest reaction that can be written which includes all the neutral substances whose concentrations change during the reaction.



(Values for the coefficients are given in Tables (5-1), (5-2), (5-3) and (5-4).)

$$(\underline{B} + \underline{C} = \underline{4A}; \underline{F} + \underline{E} = \underline{2A}; \underline{C} + \underline{D} = \underline{2A}; \text{ see text;})$$

The quantities A through F refer to the number of moles of the different species as indicated by the equation. It is understood that these salts are considered completely ionized in the aqueous solution. They are written in this form rather than ionized, to emphasize that these are the substances present in the solution which will be considered for dilution purposes. (Of course, this particular choice is not necessarily unique, for since there is also K^+ ion in the solution e.g., some of the above salts might have been written as potassium salts. However here we are not considering the potassium salts as taking part in the reaction. Naturally, they do contribute to the ionic strength, however.) Also, $\underline{F} \text{ Na}_2\text{SO}_4$ and $\underline{E} \text{ NaHSO}_4$ means that the solution contains \underline{F} moles of $\text{SO}_4^{=}$ and \underline{E} moles of HSO_3^- after the H^+ , $\text{SO}_4^{=}$ and HSO_4^- have come to equilibrium (there is no additional $\text{SO}_4^{=}$ or HSO_4^- in the solution not participating in the net reaction).

Since this is a balanced net reaction, certain relationships can be immediately deduced for the coefficients. The sum of B and C, the total moles of oxidizing agent reacting with the A moles of $\text{Na}_2\text{S}_2\text{O}_3$, must = 4A. Similarly, $\underline{F} + \underline{E}$ (the "total $\text{SO}_4^{=}$ ") = 2A, and $\underline{C} + \underline{D} = \underline{2A}$. In order to calculate B, C and D, we must know the total number of moles of Br_3^- , $\text{Br}_2(\text{aq})$ and Br^- in both the initial and final solutions and then determine these quantities by differences. These were calculated using the equilibrium constant $K_{298} = 17$ (See Section II, Chapter 5). In Table (5-3) are given the results of this calculation both in moles and molality (along with the differences which are the coefficients B, C and D. A calcu-

lation showed that vaporization of Br_2 could be neglected.)

During the course of the reaction, the total ionic strength changed very little, so we will adopt the average value $\mu = 0.290$ for both the initial and final solutions.

Table 5-3

Bromine Species in Calorimetric Solution

Substance	Before Reaction		After Reaction		Net Moles Reacting (Difference)
	Moles	Molality	Moles	Molality	
H_2O	59.332	--	59.605	--	--
Br_2 (aq)	.026141	.024456	.022297	.020765	.003844 = <u>B</u>
NaBr_3	.020292	.018984	.020124	.018741	.000168 = <u>C</u>
NaBr	.033330	.031182	.031500	.029335	.001830 = <u>D</u>
KBr	.015478	.014480	.015478	.014414	0
HBr	--	--	.010030	.009341	.010030 = <u>10A</u>

Calculation of the coefficients E and F requires a knowledge of the equilibrium constant

$$K_d = \frac{(\text{H}^+)(\text{SO}_4^{=})}{(\text{HSO}_4^-)} \quad (5-2)$$

where the bracketed quantities are the total concentrations (strictly speaking in molality) of the separate substances in the solution.

Furthermore, K_d must be known at the ionic strength of the reaction mixture. Bray and Liebafsky³⁴ determined K_d as a function of ionic strength, and tabulated these values in their paper along with those of Skrabel and Weberitsch.³⁵ These data are reproduced in Table (5-4).

Table 5-4

 K_d as a Function of Ionic Strength

Skrabel and Weberitsch ³⁵		Bray and Liebhafsky ³⁴	
$\mu^{1/2}$	K_d	$\mu^{1/2}$	K_d
0.210	0.0243	0.299	0.0336
.324	.0290	.312	.0377
.328	.0069 (?)	.330	.0480
.338	.0370	.344	.0570
.340	.0675	.345	.0595
.347	.0443	.443	.0654
.416	.0675	.525	.0754
.442	.0566		
.456	.0760		
.464	.110		

I plotted these data as $1/4 \log K_d$ vs. μ , the form adopted by Bray and Liebhafsky,³⁴ and drew the best line through them, reading off the value at $\mu^{1/2} = 0.539$ (i.e., $\mu = 0.29$, my ionic strength). The result was $K_d = 0.12$. (Essentially no extrapolation is involved.) Bray and Liebhafsky³⁴ treated their data in a slightly different manner. They drew a curve through the data in the low concentration range (there was data for more dilute solutions from conductance measurements of Sherrill and Noyes³⁶ which they also used) and then drew the curve in the high concentration range to correspond to the shape of the Na_2SO_4 activity coefficient curve. This amounted to ignoring all the data in the high concentration range, and the value of K_d read from their smooth curve at $\mu^{1/2} = 0.539$ is accordingly lower than mine. However, we know today that the interpretation of activity data on a theoretical basis, correlating it with ionic strength alone, is an extremely complicated if not unsound process in more concentrated solutions, and furthermore, no completely satisfactory treatment has been worked out. I feel that the best procedure is to base my choice of K_d on the actual experimental data in the

concentration range in question.

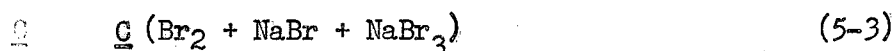
With our choice of K_d , we are now in a position to calculate the coefficients \underline{E} and \underline{F} ; these quantities are tabulated in Table(5-5).

Table 5-5

Sulfate and Bisulfate Formation (See Eq. (5-1))

Substance	Moles	Molality
Total H^+	.1487	.1384
Total $SO_4^{=}$.000931 = \underline{F}	.000867
Total HSO_4^-	.001075 = \underline{E}	.001001

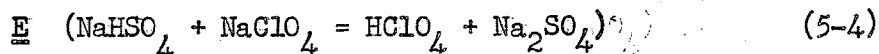
This completes the calculation of all the coefficients in equation (5-1). The next step is to eliminate the extra species in equation (5-1) by combining additional reactions with it. For the reaction:



We choose our $\Delta H = \Delta H^\circ = -2.0$ kcal./mole. (See Part II, 4 and 5)

Thus $Q_{5-3} = \underline{G} (2000) = 0.34$ cal.

The other reaction we must consider is



The values $\Delta H_f = -331.23$ and -31.45 kcal./mole for Na_2SO_4 and $HClO_4$ respectively are simply interpolated from the Bureau of Standards tables⁶ entering the tables with the concentration for each that would be necessary to make up the entire ionic strength of the solution. For $NaHSO_4$, a value is listed for ΔH_f° in 200 H_2O but this value is probably incorrectly based on heats of reaction that were not corrected for the heat of ionization of HSO_4^- ; in any case, its apparent heat of dilution seems too high (1.6 kcal./mole). Instead of this, we will calculate a value from the infinitely dilute solution values for Na^+ and HSO_4^- , using

a small heat of dilution estimated from NaNO_3 or NaBrO_3 . (This choice of analogy is discussed in Chapter 6-E.) In this manner we calculate $\Delta H_f = -269.1$ kcal./mole for NaHSO_4 . For NaClO_4 , we must estimate part of a dilution correction, with the final result $\Delta H_f^\circ = -88.90$.

Combining the above values, we have the result $\Delta H_{5-4} = -4.68$ kcal./mole, or $Q_{5-4} = (4,680) \underline{E} = +5.03$ cal.

These results are now summarized in Table 5-6; the values being valid for all 4 runs.

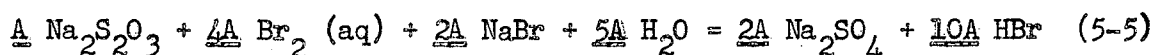
Table 5-6

The Heat of Oxidation of $\text{S}_2\text{O}_3^{2-}$ with Br_3^- (Part 2)

Q_{5-1} av. cal.	Q_{5-3} cal.	Q_{5-4} cal.	Q_{5-5} cal.	ΔH_{5-5} kcal./mole	$\Delta H_{5-5}^\circ = \Delta H_{5-6}^\circ$ kcal./mole
160.09	0.34	5.03	165.46	-164.97	-167.07

If we add reactions (5-1), (5-3) and (5-4), we have reaction (5-5), with

$$Q_{5-5} = Q_{5-1} + Q_{5-3} + Q_{5-4} \text{ shown in the Table.}$$



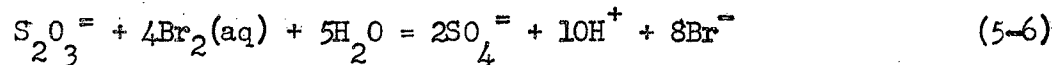
ΔH_{5-5} is obtained from the relation:

$$\Delta H_{5-5} = \frac{-Q_{5-5}}{A} \frac{\text{kcal.}}{\text{mole}}, \text{ and is the heat for reaction}$$

(5-5) where $A = 1$ mole, uncorrected to infinite dilution.

Dilution corrections for water and Br_2 are neglected, and those for Na_2SO_4 , HBr and NaBr obtained from interpolation in Bureau of Standards data. I made one calorimetric run for the heat of dilution of my $\text{Na}_2\text{S}_2\text{O}_3$ solution and found general agreement with the results of Plake.³⁷ The balance of this small correction was estimated by comparison with Na_2SO_4 solutions. The combined value of all of these corrections was -2.10 kcal./mole (of which, -2.00 kcal. arises from the dilution of 10

moles of HBr) and ΔH°_{5-6} in Table 5-6 was calculated by applying it to ΔH°_{5-5} . Now that we have the value of ΔH° , we can rewrite equation (5-5) in its equivalent ionic form:



$$\Delta H^\circ_{5-6} = -167.07 \text{ kcal./mole.}$$

Now, combining our ΔH°_{5-6} with Bureau of Standards data,⁶ we calculate our final calorimetric result, $\Delta H^\circ_f = -152.0 \text{ kcal./mole}$ for $\text{S}_2\text{O}_3^{2-}$ at 298.16° K. Further discussion and evaluation of this quantity will be reserved for Chapter 6-B. For a discussion of the heat of formation data for Br_3^- and $\text{Br}_2(\text{aq})$ see Part II, Chapter 6.

Chapter 6

Calculations, Conclusions, DiscussionA. Calculation of Heat of Reaction from Equilibrium Data.

From the values of $\log K_o$ at the three temperatures summarized in Table 4-10, we are now ready to calculate ΔH°_{4-2} , the heat for our experimental equilibrium reaction:



However, in order to do this, we must adopt a value for ΔC_p for the reaction.

A-1. Heat Capacity Change. We are not in a position to specify this quantity exactly, for there are no data at all for the partial molal heat capacity of Na_2SO_3 . Furthermore, no empirical techniques are available for accurately estimating values for partial molal heat capacities. In fact in this area there exists a wide gap in our fundamental knowledge of the chemical thermodynamics of aqueous solutions. Values are known for the heat capacities of the solids Ag_2S and Ag .³⁸ If we chose, we could base the reaction ΔC_p solely on the solid values, with the argument that the roughly similar ions $\text{SO}_3^{=}$ and $\text{S}_2\text{O}_3^{=}$ would have approximately equal values of \bar{C}_p° . This calculated value of ΔC_p (4-2) varied from 11.9 at 25° to 16.3 at 195°.

Harned and Owen²¹ list data for two salts of this valence type, with considerable uncertainty indicated. These are: Na_2SO_4 , $\bar{C}_{p2}^\circ = (-50)$; K_2SO_4 , $\bar{C}_{p2}^\circ = (-60.6)$. We cannot really conclude much from these data except that the values appear not to differ greatly.

If the species in equation (4-2) were all uncharged, we might have a good argument for saying ΔC_p (4-2) = 0 just on the basis of the mass effect. If we then knew or could calculate the separate

effect of charging up the ions in the aqueous medium, we might be close to a good answer. The trouble is, we do not know how to make such a calculation. We feel that the most justifiable assumption under the circumstances is to select the value $\Delta C_p = 0$ for the whole reaction (4-2) in view of the general symmetrical nature of the reaction, with the understanding that this may be off by 10 or even 20 C_p units.

A-2. Calculation of ΔH_{4-2}° for $S_2O_3^{2-}$. On the above basis, we can calculate ΔH_{4-2}° by plotting $-4.575 \log K_0$ vs $1/T$, drawing the best straight line through the points and taking the slope = ΔH_{4-2}° . If ΔC_p really = 0, this curve should be an exact straight line. Such a plot has been made in Figure 6, from which we read the value $\Delta H_{4-2}^\circ = -3.45$ kcal./mole. It might be argued that the value for K_0 at 25° is just not certain enough to read too much significance into the unusually good straight line shown in Figure 6. On the other side of the ledger, we have the fact that since the ΔH_{4-2}° is relatively small, the error in kcal./mole from errors in slope is also small, whether the error arises from ΔC_p errors or equilibrium errors.

As an example, I also made a plot (not shown here) of Σ vs. $1/T$, where Σ represents all terms other than the $1/T$ term in the free energy equation that show variation with temperature. The ΔC_{p4-2} used for this plot was that discussed above, based only on the solids (values between 11.9 and 16.3, 25° to 195°). This plot gave not quite such a good straight line, but the best slope value was -4.81 , differing from the previous value by less than 1.5 kcal./mole. Also, there is no compelling reason for us to say a priori that the equilibrium point at 25° is no good, and in fact we gave an argument based on the equilibrium data alone why it might represent a true equilibrium value. (Note that if the 25° point had not yet "come up" to its equilibrium

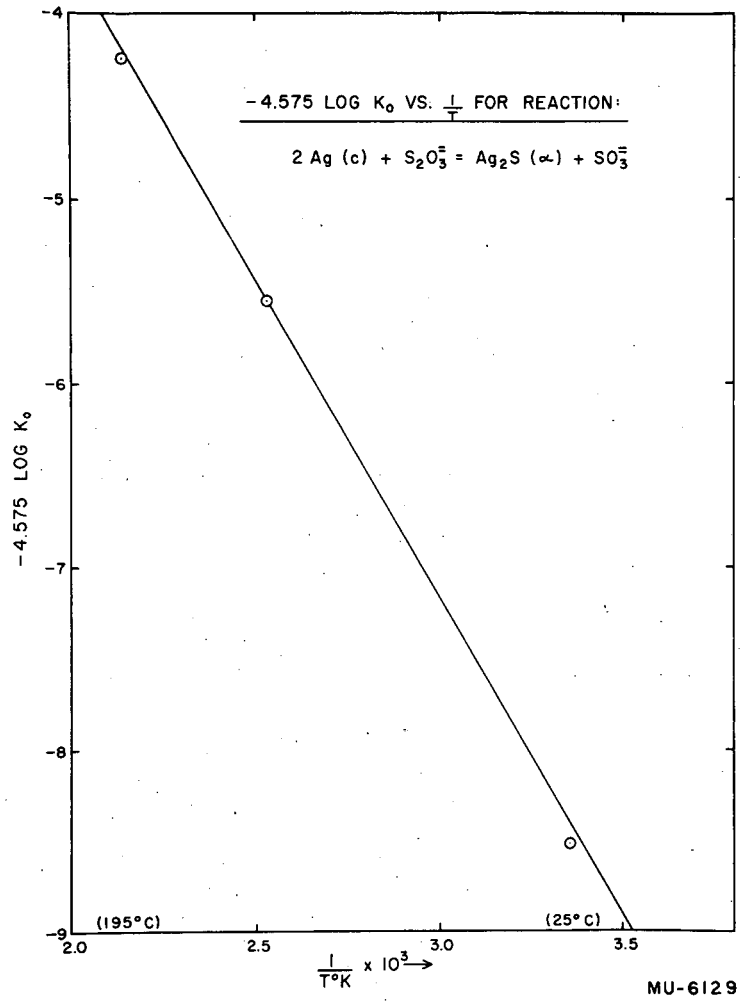


Fig. 6

value the curvature from a plot like Figure 6 would require an even more positive ΔC_p for reaction (4-2).) Finally, note that the values here represent an unusually wide temperature variation (175°) compared with that usually found in aqueous solution studies which means that the slope is relatively insensitive to an error in the 25° (or 195°) point.

Combining the value $\Delta H_{4-2}^\circ = -3.45$ kcal./mole with Latimer's data⁷ for SO_3^\ominus (see Section B-1 for discussion) and Bureau of Standards data⁶ for the other species, we calculate for $\text{S}_2\text{O}_3^\ominus$ $\Delta H_f^\circ = -156.05$ kcal./mole.

B. Selection of "Best" Values for Thermodynamic Properties of $\text{S}_2\text{O}_3^\ominus$ at 298.16° K.

Comparing the above value for ΔH_f° with our calorimetric result: $\Delta H_f^\circ = -152.0$ we see the agreement is neither outstandingly good nor outstandingly poor. On the one hand, for the calorimetric data we have the uncertainties in equilibrium constants for HSO_4^\ominus dissociation, and $\text{Br}^\ominus - \text{Br}_2$ complexing at the experimental ionic strength, as well as possible uncertainties in heats of formation of $\text{Br}_2(\text{aq})$ and Br_3^\ominus (see discussion Part II, Chapter 6). Moreover, heat of dilution corrections are by no means unimportant especially where multiplied by large coefficients (up to 10). Also, the large value for the heat of the calorimetric reaction ($\Delta H^\circ = -167$ kcal./mole) means the results are less precise in kcal./mole.

On the other hand, for the equilibrium measurements, we have the uncertainty in the 25° point (also some in the 195° point) plus our lack of an exact ΔC_p value for our reaction. Thus, the general agreement from these entirely independent investigations is really

considered to be encouraging, taking into account the circumstances described above. Therefore we will adopt as our heat of formation of $S_2O_3^=$ the average value $\Delta H_f^\circ = -154.0$ kcal./mole with an uncertainty of perhaps ± 2 to 2.5 kcal./mole. (It is interesting to note that this is approximately equivalent mathematically to making a Σ plot of the equilibrium data using a ΔC_p somewhat more positive than that for the solids alone.) From this comparison, we will say that K_o at 25° and our assumption of ΔC_p approximately 0 are probably reasonably good.

With this average value for ΔH_f° we recalculate the value $\Delta H_{4-2}^\circ = -5.5$ and then correct our best equilibrium point at 122.5° to 25° according to the equation:

$$\log K_o(298.16) = \log K_o(395.16) - \frac{\Delta H_{4-2}^\circ}{4.575} \left(\frac{1}{395.16} - \frac{1}{298.16} \right) \quad (6-1)$$

or $\log K_o(298.16) = 2.205$.

From this we calculate the value $\Delta F_{4-2}^\circ = -3.01$ kcal./mole, whence $\Delta F_f^\circ = -122.7 \pm 1$ kcal./mole at 298.16 for $S_2O_3^=$. Our final calculation then is to combine ΔH_f° and ΔF_f° to calculate $\Delta S_f^\circ = -105.0$ e.u. and $S_{298}^\circ = 15.0$ e.u. We should set an uncertainty of 5 or 6 e.u. on this value.

These calculated best values for the thermodynamic properties of $S_2O_3^=$ are tabulated in Table 6-1. For the sake of comparison, the latest Bureau of Standards values are included also.

"Best" Values for Thermodynamic Properties of $\text{SO}_3^=$ at 298.16°K

	ΔH_f° (kcal/mole)	ΔF_f° (kcal./mole)	S° (cal./mole°C)
This Thesis	$-154.0 \pm 2^+$	-122.7 ± 1	15.0 ± 6
N. B. S. ⁶	-154.	-127.2	29

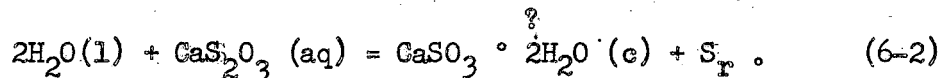
(Estimated maximum uncertainties are shown)

B-1. $\text{SO}_3^=$ Thermodynamic Properties. In the introduction of this thesis and in the preceding section, the remark was made that thermodynamic properties for $\text{SO}_3^=$ would be adopted from Latimer⁷ rather than from the Bureau of Standards.⁶ Powell³⁹ has calculated the free energy of formation of $\text{H}_2\text{SO}_3(\text{aq})$ starting with vapor pressure data for SO_2 over aqueous solutions as a function of temperature and correcting for H_2SO_3 dissociation. He obtained consistent answers from results of many observers taken over a period of many years. On the basis of this revised quantity, Latimer⁷ adjusted the free energies of formation of HSO_3^- and $\text{SO}_3^=$ to give a reasonable fit with the free energies of ionization and entropies of formation and ionization. The Bureau of Standards data⁶ apparently are not corrected for dissociation of H_2SO_3 , so we shall adopt the values calculated by Latimer.⁷

C. Previous Studies.

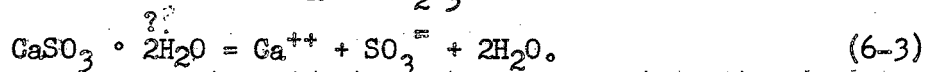
Although $S_2O_3^{=}$ has been relatively little studied thermodynamically, some previous work has been done, so it will be desirable to examine in more detail two of these works. It is felt that there are too many uncertainties in the very old heat measurements of Thompson³ and Berthelot⁴ to make more detailed examination worthwhile here. (Their results were given in Chapter 1.)

C-1. Bichowsky's Study. By far the most detailed investigation of $S_2O_3^{=}$ thermodynamics was that conducted by Bichowsky¹ in his study of the reaction



The difficulty with the formula of $CaSO_3 \cdot 2H_2O$ was previously described in Chapter 3, A. An erroneous Kopp's law value is calculated for the heat capacity of $CaSO_3$ hydrate if it is considered the dihydrate when actually it is the hemihydrate. It is difficult to understand the cause for Bichowsky's measured value agreeing with such a Kopp's law value unless the solid was impure or wet.

Another place where the formula must be considered is in the calculation of the solubility of the salt in moles from the weight in grams that dissolve in water. One of the reactions that Bichowsky used to calculate the free energy of $S_2O_3^{=}$ is written:

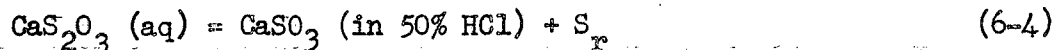


Unlike the earlier workers, Bichowsky titrated the number of moles of $SO_3^{=}$ in a saturated solution though his results showed a spread of a factor of 8. Because of cancelling errors the free energy of $S_2O_3^{=}$ thusly determined from the sum of reactions (6-2) and (6-3) would, then, not be affected if all the samples of the calcium sulfite hydrate used

had the same composition. The Bureau of Standards⁶ values for thermodynamic properties of "CaSO₃ • 2H₂O" were calculated from his data however by equation (6-3), so as they stand they would not represent a true value for any substance (considering that the dihydrate does not exist). There appears to be an error of sign involved in this calculation, also.

Bichowsky's equilibrium measurements for reaction (6-2) were made between 80 and 141° C with the equilibrium concentrations of CaS₂O₃ varying from 0.27 to 1.12 M. To correct these data to 25° a knowledge of ΔC_p for the reaction is vital, for from the nature of equation (6-2) this should be very important. The possible error in the C_p value for CaSO₃ • (?) H₂O has already been mentioned above and in Chapter 3-A. For CaS₂O₃ solutions, he did measure some specific heats at 25°, and calculated values for the partial molal heat capacities at the equilibrium concentrations. His results showed a variation of C_{p2} from -3.4 to -2.6 C_p units over the concentration range of 0.16 to 1.12 M. This is a remarkably small change (less than 1 C_p unit) over such a concentration range compared with that of other known salts. For example, Na₂SO₄ shows a variation of about 55 C_p units over this same concentration range.⁴⁰ (Bichowsky's measured activity coefficients for CaS₂O₃ show no such abnormality, giving approximate agreement with those of other sulfates.) I tried to recalculate the heat capacities from his specific heat values, but could get neither reasonable answers nor his answers. Another difficulty is that for his reaction, (6-2), the change in ΔC_p with temperature might be important, and this is an undetermined quantity. This general uncertainty in ΔC_p for the reaction would easily explain the poor results for a Σ plot, described in Chapter 1.

In this paper Bichowsky also calorimetrically measured the heat for the reaction

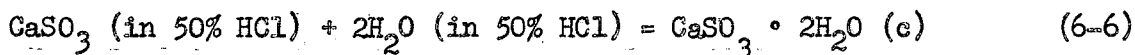


No dilution corrections were included for the right side of the equation, nor was account taken of H_2SO_3 and SO_2 formation. For these concentrations such dilution effects alone would amount to many kilocalories of energy. Bichowsky and Rossini² in calculating ΔH_f° of $\text{S}_2\text{O}_3^{=}$ from this reaction assumed the net reaction to be:

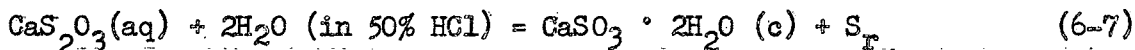


so these errors would show up directly in the ΔH_f° .

In order to get the value he needed for the heat of reaction (6-2), Bichowsky also determined the heat of reaction (6-6):



The result of adding (6-4) and (6-6) is reaction (6-7):



In assuming that this is the same reaction as (6-2), the important heat effect for correcting water in 50% HCl to the pure liquid state has been neglected.

There are other questionable quantities in his paper that might be discussed. However, the above points should make quite understandable the apparent thermodynamic inconsistency in these data for $\text{S}_2\text{O}_3^{=}$ ion brought out in Chapter 1.

G-2. Ballezo and Kaufmann's Study.⁵ These workers reported equilibrium constants for reaction (6-2) at 40° and 36° C. Although they approached equilibrium only from the CaS_2O_3 side, after varying periods of many months, the $\text{S}_2\text{O}_3^{=}$ concentration remained unchanged. Even if the solution had reached equilibrium, however, it is difficult to see how any thermodynamic significance can be placed on their results.

In the first place the equilibrium concentrations of CaS_2O_3 (aq) (i.e., the equilibrium constants for the reaction, as used by Bichowsky) were 6.9 and 9.2 $\underline{\text{M}}$ respectively. They plotted $\log K$ vs. $1/T$ and drew a straight line through their data and Bichowsky's.¹ In order for the slope of this curve to represent a ΔH° for the reaction, activity corrections in 7-9 $\underline{\text{M}}$ solutions must be negligible and ΔC_p for the reaction (6-2) (discussed in previous Section) must be 0. Since neither assumption is good for this reaction, we shall not try to interpret their data further. Their reported heat on the basis of reaction (6-5) was $\Delta H_{6-5} = 12.8$ kcal. and from this we calculated the value of $\Delta H_f = -164.7$ kcal./mole mentioned in Chapter 1. (Our final average value was $\Delta H_f^\circ = -154.0$ kcal./mole.)

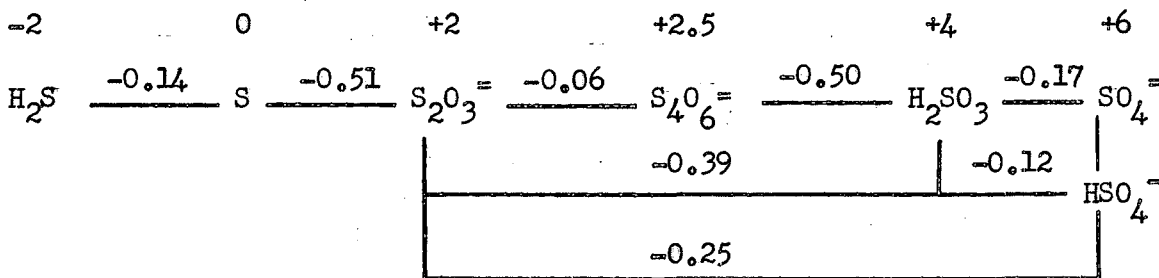
D. Sulfur Potential Diagram.

It may be profitable to examine the sulfur potential diagram in view of the new value of $\Delta F_f^\circ = -122.7$ kcal./mole. To calculate the free energy of formation of $\text{S}_4\text{O}_6^{2-}$, the entropy was estimated as 52 e.u. from the method of Connick and Powell⁴¹ considering this substance to be a dimer with a monomeric unit like NO_3^- ($\bar{S}^\circ = 35$). All other data were taken from Latimer.⁷ The results are shown in Table 6-2.

From the potentials shown, $\text{S}_2\text{O}_3^{2-}$ should be relatively easily oxidized to HSO_4^- . The fact that even with powerful oxidizing agents such as Ce^{+4} the reaction is not rapid or complete serves to emphasize the complicated mechanisms that must be involved. At least, with several oxidizing agents, such as Br_3^- and ClO^- , the first step is likely the familiar decomposition into S and SO_3^{2-} (as evidenced by the frequent momentary appearance of sulfur in the solutions.)

Table 6-2

Sulfur Potential Diagram



Values are in volts/equivalent.

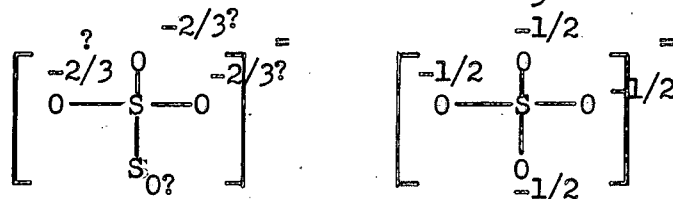
E. Discussion of Entropy of S₂O₃²⁻

It will be worthwhile now to interpret the value of the entropy of S₂O₃²⁻ in terms of what we have previously referred to as a "reasonable value" without ever having defined more precisely.

Undoubtedly the crystal size of S₂O₃²⁻ is somewhat larger than that of SO₄²⁻; since these two ions have the same total charge, one might expect S₂O₃²⁻ to have a slightly more positive entropy than SO₄²⁻, in accordance with the rather well-established trend with other aqueous ions. It was on this basis, that Latimer⁷ estimated the value 8 e.u. (c.f. 4 for SO₄²⁻).

This picture conceivably could be more complicated, however.

Consider for a moment the structure of S₂O₃²⁻ and SO₄²⁻.

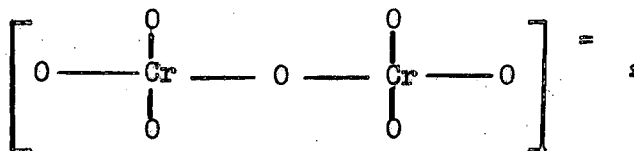


One could imagine that the more electronegative oxygen atoms could "rob" the outer sulfur atom of some or most of its charge. Assume the 4 outer oxygen atoms of SO₄²⁻ to be the charge carrying groups, each bearing 1/2 unit of negative charge. If all the charge shifted

away from the outer sulfur on $S_2O_3^{=}$, each O atom would end up bearing 2/3 instead of 1/2 unit of negative charge. The net effect of such a transfer might be that the $S_2O_3^{=}$ group in this configuration "ties up" a larger total amount of water than in a configuration with the outer S atom carrying its full 1/2 unit of charge. Since it is our understanding that the amount of water "bound" by an aqueous ion is a direct measure of how much "negative entropy" the ion has, the resulting entropy for $S_2O_3^{=}$ could be more negative than that for $SO_4^{=}$.

The treatment of Powell and Connick⁴¹ for aqueous entropies of polyatomic oxygenated anions allows a slightly different approach to this problem; by its application and by analogy, we can set limits on the value expected for the entropy of $S_2O_3^{=}$. They consider as the important factors to be used in evaluating an entropy, the number of charges and the number of charge carrying centers - (i.e., for them, oxygens). Relative sizes, masses, and other factors are not considered relevant. Thus, in the event of shift of all charge from the sulfur to the oxygens in $S_2O_3^{=}$, there would remain 3 charge carrying groups with a total of 2 charges, so $S_2O_3^{=}$ would look more like $SO_3^{=}$ or $CO_3^{=}$ (-7 and -13 e.u.). (By analogy, as our model for estimating the heat of dilution of $NaHSO_4$ in Chapter 5-D, we used $NaNO_3$. In the HSO_4^{-} ion, the oxygen participating in the OH group apparently carries little or no charge, so the OH can be eliminated from consideration, leaving SO_3^{-} approximately like NO_3^{-} .)

For the other extreme, there is a different model that can best be illustrated by an example, such as $Cr_2O_7^{=}$. Writing its structure:



they say its entropy can be thought of as consisting of twice the entropy of a monomeric unit MO_3^- , minus a fixed figure representing the entropy of dimerization. This figure (experimentally about 18 e.u.) should be a constant value for all ions where the separation is great enough for the separate monomeric units to act independently on the water. This is mathematically equivalent in their formulation to adding the constant 25.5 e.u. to the value of the entropy for the simple unextended ion to get the value for the extended ion. For this extreme case, we consider the outer S of S_2O_3^- to carry all its share of charge, and furthermore to be sufficiently large to have its influence on hydration independent of that of the rest of the ion. Thus we would calculate the entropy to be 25.5 e.u. more positive than the value for SO_4^- , or 29.6 e.u. Now, since it is quite certain that all of the charge would not shift away from the S, and it is also certain that sulfur is larger than oxygen, one might almost predict that the positive effect would predominate, it being the larger one. (i.e., the lower limit is approximately 11 to 17 e.u. below the SO_4^- value, and the upper limit 25 e.u. above.)

A requirement that I believe should hold for the entropy of S_2O_3^- can be deduced from examination of the entropies of OH^- and SH^- . These are both well-known quantities, for which the Bureau of Standards⁶ lists -2.52 and 14.6 e.u. respectively. (The \bar{S}° for HS^- was recently measured to be 15.0 ± 0.4 e.u. by Kury, Zielen and Latimer.⁴²

Note that the value for HS^- is 17 e.u. more positive than that for OH^- . It would seem then, that the entropy of S_2O_3^- should be no more than 17 e.u. greater than that for SO_4^- . The replacement of one out of 4 oxygens of SO_4^- by a sulfur to make S_2O_3^- , could hardly

cause a greater effect on the total ionic hydration than would the replacement of the only oxygen in OH^- with a sulfur atom. In fact, one would probably expect the difference between SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ entropies to be somewhat less than this 17 e.u. The experimental entropy value of 15.0 for $\text{S}_2\text{O}_3^{2-}$ obtained in this research is 11 e.u. more positive than SO_4^{2-} 's, which is entirely consistent with the above discussion. (Of course in SH^- , the possibility of charge transfer to other oxygen atoms does not exist, so we probably could not say with certainty from this argument that the entropy of $\text{S}_2\text{O}_3^{2-}$ is greater than that of SO_4^{2-} . This result appears quite reasonable, however. The fact that S^{4-} does not have a very negative entropy (-4 e.u.⁴²) for a small doubly charged ion lends further support to this idea of a relatively positive entropy contribution from sulfur atoms.)

Chapter 7. REFERENCES

1. F. R. Bichowsky, J. Am. Chem. Soc., 45, 2225-2235 (1923).
2. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Publishing Corp., New York, N. Y., 1936.
3. J. Thompsen, "Thermochemische Untersuchungen", J. A. Barth, Leipzig, 1882-1886.
4. A. Berthelot, Ann. chim. et phys. (6), 17, 436-480 (1889).
5. H. Ballezo and O. Kaufmann, Osterr. Akad. Wiss., Math-naturw. Kl. Sitzber., Abt. IIb, 158 (1949); or Monatsh. Chem., 80, 220-31 (1949).
6. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Nat. Bur. Standards Circ. 500, 1952.
7. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", Prentice-Hall, New York, N. Y., 2nd ed., 1952.
8. W. Weltner, Jr., Thesis, University of California, June, 1950.
9. E. Mueller and T. S. Sligh, Jr., J. Opt. Soc. Amer., 6, No. 9, 958-964 (1922).
10. T. S. Sligh, Jr., J. Research Nat. Bur. Standards, 49-63 (1921).
11. E. F. Mueller, J. Research Nat. Bur. Standards, 13, 547 (1921).
12. E. F. Mueller and H. A. Burgess, J. Am. Chem. Soc., 41, 745-63 (1919).
13. American Institute of Physics, "Temperature, its Measurements and Control in Science and Industry", Reinhold Publishing Corp., New York, N. Y., 1940.
14. G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances", McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 77.
15. K. K. Kelley, J. Am. Chem. Soc., 66, 293-5 (1944).
16. F. W. Matthews and A. O. McIntosh, Can. J. Research, 26B, 747-51 (1948).
17. H. Blitz and W. Blitz, "Laboratory Methods in Inorganic Chemistry", John Wiley and Sons, New York, N. Y., 1909, p.131.
18. A. Kurtenacker, "Analytische Chemie der Sauerstoff Sauren des Schwels", V. Wilhelm Brottger, Stuttgart, 1938.

19. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", The Macmillan Co., New York, N. Y., 3rd ed., 1952.
20. H. S. Booth, "Inorganic Syntheses", Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 112.
21. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Corp., New York, N. Y., 2nd ed., 1950.
22. J. Kielland, J. Am. Chem. Soc., 59, 1675 (1937).
23. F. E. Harris and B. J. Alder, J. Chem. Phys., 21, 1031 (1953).
24. "Gmelins Handbuck der Anorganische Chemie", Vol. 21, Verlag Chemie G.M.B.H., Berlin, 8th ed., 1928.
25. J. O. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933).
26. H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc., 55, 2179 (1933).
27. H. S. Harned and J. C. Hecker, J. Am. Chem. Soc., 55, 4838 (1933).
28. E. Carrière and M. Dalpa, Compt. Rend., 205, 1157-8 (1937).
29. E. A. Maksim'yuk and B. V. Ptitsyn, J. Gen. Chem., (USSR), 16, 1791-6 (1946).
30. T. Murooka, Bull. Inst. Phys. Chem. Research (Tokyo), 21, 1150-5 (1942).
31. L. Rosenthaler, Pharm. Acta Helv., 7, 45-8 (1932).
32. O. R. Foz Gazulla and M. Colomina, Anales fis. y quim. (Madrid), 42, 429-74 (1946).
33. See Part II, Chapter 2-A; see also references (6) and (7) of Part II.
34. W. C. Bray and H. A. Liebafsky, J. Am. Chem. Soc., 57, 51 (1935).
35. A. Skrabel and S. R. Weberitsch, Monatsh. Chem., 36, 211-35 (1915).
36. M. S. Sherrill and A. A. Noyes, J. Am. Chem. Soc., 48, 1861-73 (1926).
37. E. Plake, Z. physik. Chem., A-162, 257-80 (1932).
38. K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy", U. S. Dept. of the Interior, Bureau of Mines, Bulletin No. 476, U. S. Government Printing Office, Washington, D. C., 1949.
39. R. E. Powell, University of California, unpublished calculations.

40. M. Randall and F. D. Rossini, J. Am. Chem. Soc., 51, 323-345 (1929).
41. R. E. Connick and R. E. Powell, J. Chem. Phys., (in press).
42. J. W. Kury, A. J. Zielen and W. M. Latimer, J. Electrochem. Soc., 100, 468 (1953).

Part II. THE HEAT AND FREE ENERGY OF FORMATION OF BROMATE ION

TABLE OF CONTENTS - II

Bromate Thermodynamics

Chapter 1.	<u>Introduction</u>	Page	100
Chapter 2.	<u>Experimental</u>		101
	A. Calorimeter		101
	B. Reagents		101
Chapter 3.	<u>Heat of Solution of KBrO_3</u>		102
Chapter 4.	<u>Heat of Reduction of KBrO_3 with I^-</u>		103
Chapter 5.	<u>Heat of Reduction of KBrO_3 with Br^-</u>		104
Chapter 6.	<u>Interpretation of Data</u>		105
Chapter 7.	<u>Conclusion</u>		106
Chapter 8.	<u>References</u>		107
	Acknowledgement		108

TABLE OF CONTENTS

Tables

Table I	The Heat of Solution of KBrO_3	Page 102
II	The Heat of Reduction of KBrO_3 with I^-	103
III	The Heat of Reduction of KBrO_3 with Br^-	104

II. The Heat and Free Energy of Formation of Bromate Ion

1. Introduction

Lewis and Randall¹ calculate from the measurements of Sammet² on the bromine-bromate electrode that the free energy of formation of BrO_3^- is 2.3 kcal./mole. The National Bureau of Standards³ gives 10.9 kcal./mole for the free energy of formation. This latter quantity was calculated from Thomsen's⁴ heat for the reduction of BrO_3^- by Sn^{++} and Ahlberg and Latimer's⁵ entropy data for BrO_3^- . The large discrepancy was thought to be primarily due to an inaccurate value for the heat of formation of BrO_3^- . Hence, the present investigation was undertaken to establish a more accurate value for this quantity. Two main reactions were studied, (1) the heat of reduction of KBrO_3 by iodide, and (2) the heat of reduction by bromide. The heat of solution of KBrO_3 in water was also measured.

Unless specifically stated, all heat calculations were made using heats of formation tabulated by the Bureau of Standards.³

2. Experimental

Calorimeter. The calorimeter has been described previously.^{6,7} The possibility of variation in the calorimeter stirring rate has been reduced by the use of a synchronous motor with chain and sprocket drive. The standard resistances in the calorimeter circuit were calibrated against resistances recently certified at the Bureau of Standards.

The samples of KBrO_3 (weighed in thin-walled glass bulbs) were either fastened to a glass rod running through the calorimeter stirring shaft and broken on the bottom of the calorimeter, or were fastened directly to the stirring shaft itself and broken by thrusting a rod through them. The reactions were calorimetrically complete in 5 to 25 minutes. The heats were measured at $25.0 \pm 0.5^\circ$ and are reported in terms of the defined calorie.

Reagents. All weighings were corrected to weight in vacuo when necessary. Two separate lots of reagent grade KBrO_3 were recrystallized and dried for several hours at 160° . One lot was analyzed by gravimetric titration with thiosulfate and was found to be 100.17% pure. The other lot was not analyzed, but samples from it were used at random, with no systematic differences in the calorimetric results. The thiosulfate solution was standardized with recrystallized KIO_3 . The KI , NaI , KBr and NaBr used in the reduction runs were reagent chemicals dried for several hours at 110° . The perchloric acid was a double vacuum distilled reagent and was standardized before use.

3. The Heat of Solution of KBrO_3

Three determinations were made of the heat of solution of KBrO_3 in water. The details are given in Table I.

Table IThe Heat of Solution of KBrO_3

<u>Run</u>	<u>KBrO_3, g.</u>	<u>H_2O, g.</u>	<u>ΔH_1, kcal./mole</u>
1	2.4074	1053	9.74
2	1.5186	1053	9.79
3	2.8477	1043	9.80
		Av.	9.78

Using the heat of dilution calculated from the Bureau of Standards³ data we correct the average value to $\Delta H^\circ = 9.76 \pm 0.05$ kcal./mole for



This compares with the value 9.8 kcal./mole calculated from the Bureau of Standards data.³

4. The Heat of Reduction of KBrO_3 with I^-

In this series of measurements, solid KBrO_3 was dissolved in an aqueous solution of HClO_4 and either NaI or KI . The details are given in Table II.⁸

Table II

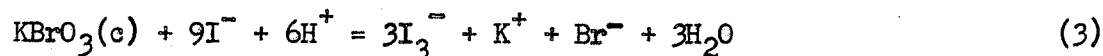
The Heat of Reduction of KBrO_3 with I^-

Run	KBrO_3 , g.	H_2O , total g.	KI , g.	HClO_4 , moles	Q_c , cal.	Q_2 , cal.	$-\Delta H_3$, kcal./ mole
1	0.3787	1060	10.07	0.139	273.48	0.90	121.01
2	.5460	1057	17.74	.093	410.6	.69	125.8
3	.4996	1066	16.96	.093	367.40	.65	123.04
4	.4162	1060	11.39*	.116	304.94	.75	122.67
5	.3070	1057	17.00	.093	225.82	.35	123.04
6	.5299	1070	17.74	.093	388.27	.67	122.59
7	.3872	1060	7.92*	.116	285.11	1.15	123.47
*NaI used.						Av.	123.09

Q_c refers to the heat evolved in the calorimeter. Q_2 refers to the calculated heat for the conversion of the aqueous iodine (formed in the calorimetric reaction) to triiodide⁹



The sum of Q_c and Q_2 is then the heat of the hypothetical calorimetric reaction where all the oxidized iodide has formed triiodide



The quantity ΔH_3 refers to the heat (in kcal./mole) for reaction (3), uncorrected to infinite dilution. We shall use our weighted average, $\Delta H_3 = -122.98$ kcal./mole. By assuming that the heats of dilution of HI and KBr (in our calorimetric solutions¹¹) are the same as those for

0.18 M HI and 0.18 M KBr, we calculated $\Delta H_3^\circ = -122.26 \pm 0.8$ kcal./mole for the infinitely dilute ions.

5. The Heat of Reduction of KBrO_3 with Br^-

Solid KBrO_3 was dissolved in an aqueous solution of HClO_4 and NaBr. The details are given in Table III.¹²

Table III
The Heat of Reduction of KBrO_3 with Br^-

Run	KBrO_3 , g.	H_2O , total g.	NaBr, g.	HClO_4 , moles	Q_3^1 , cal.	Q_4 , cal.	Q_5 , cal.	$-\Delta H_6^\circ$, kcal./ mole
1	1.1417	1061	15.32	0.174	280.38	15.59	0.16	43.32
2	0.6897	1058	14.89	.174	170.64	8.65	.09	43.44
							Av.	43.38

Q_3^1 refers to the heat evolved in the calorimeter, Q_4 refers to the calculated heat for the conversion of the aqueous bromine (formed in the calorimeter) to tribromide¹³

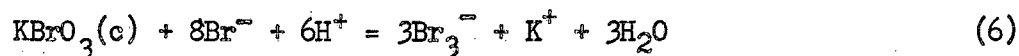


Q_5 refers to the calculated heat correction for the slight vaporization of bromine from the solution into the dead air space in the calorimeter



The partial pressure of $\text{Br}_2(\text{g})$ was calculated assuming complete equilibrium. A calculation showed that the hydrolysis of bromine in our solutions was entirely negligible -- as was also the case for our iodine solutions.

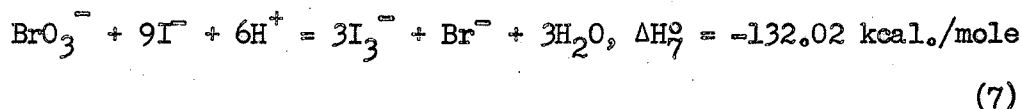
The sum of Q_3^1 , Q_4 and Q_5 is then the heat of the hypothetical calorimetric reaction where all the oxidized bromide has formed tri-bromide



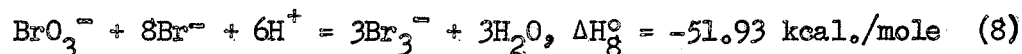
The quantity ΔH_6 refers to the heat (in kcal./mole) for reaction (6), uncorrected to infinite dilution. We shall use the average $\Delta H_6 = -43.38$ kcal./mole. For these runs, the average ionic strength was about $\mu = 0.29$. Using methods similar to those described in Section 4, we correct this for dilution effects to $\Delta H_6^\circ = -42.17 \pm 0.3$ kcal./mole.

6. Interpretation of Data

Subtracting reaction (1) from reaction (3) we obtain



Using Bureau of Standards heat data³ we calculated $\Delta H_f^\circ = -18.70$ kcal./mole for BrO_3^- . Similarly from reactions (1) and (6) we obtain



from which we calculate $\Delta H_f^\circ = -17.82$ kcal./mole. Combining the average value of ΔH_f° (-18.3 kcal./mole) with the entropy of formation,³ we calculate $\Delta F_f^\circ = 2.1$ kcal./mole. The close agreement with Sammet's² value may be fortuitous, as may be seen from a careful examination of the iodine and bromine heat data.

The Bureau of Standards value for ΔH_f° of $\text{I}_2(\text{aq})$ (5.0 kcal./mole) is based on the temperature coefficient of fifty-year old solubility data. We calculate from more extensive and more recent data¹⁵ the value 5.6 kcal./mole (corrected for hydrolysis). For the heat of iodide complexing of iodine (reaction (2)), the following values have been reported in the literature: $\Delta H_2^\circ = -4.30,$ ¹⁶ $-3.87,$ ¹⁰ -5.10 ¹⁷ kcal./mole. All of these are based on the temperature coefficients of the equilibrium constant measured in different ways. From the Bureau of

Standards heat data³ one calculates the value -4.03 kcal./mole. It is apparent that the considerable uncertainty in ΔH_f° of I_3^- causes three times this uncertainty in ΔH_f° for BrO_3^- (see reaction (7)).

In the case of bromine some calorimetric measurements have been made for the heat of solution of $Br_2(l)$ and for ΔH_4 . Again, however, the data are old, rather limited, and not obtained at 25° . Calculations from solubility data¹⁵ lead to ambiguous results, so we must say that at least as much uncertainty exists in the Bureau of Standards value for ΔH_f° of Br_3^- as does in the I_3^- value, with the corresponding uncertainty existing in ΔH_f° for BrO_3^- calculated from equation (8). (Presumably, I^- , Br^- and H_2O heats of formation are accurately enough known so that they will not introduce significant error.)

From this discussion it should therefore be evident that our final calculations of ΔH_f° for BrO_3^- from both types of reductions may be uncertain by as much as several kcal./mole. This uncertainty arises at least as much from the uncertainty in the heats of formation of triiodide and tribromide as from our own experimental uncertainties.

7. Conclusion

We will take as our final values for the heat and free energy of formation of BrO_3^- our calculated averages: $\Delta H_f^\circ = -18.3 \pm 2$ kcal./mole and $\Delta F_f^\circ = 2.1 \pm 2$ kcal./mole. Additional evidence for these values is provided by Myers¹⁸ who has recently determined ΔF_f° to be 2.5 ± 0.3 kcal./mole from kinetic measurements.

8. References

1. G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 521.
2. V. Sammet, Z. physik. Chem., 53, 678 (1905).
3. National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952.
4. J. Thomsen, "Thermochemische Untersuchungen," Leipzig, J. A. Barth, 1882.
5. J. E. Ahlberg and W. M. Latimer, Journal of the American Chemical Society 56, 856 (1934).
6. B. J. Fontana, "National Nuclear Energy Series IV-19B," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.
7. H. W. Zimmerman and W. M. Latimer, J. Am. Chem. Soc. 61, 1550 (1939).
8. One run, not described because of the possibility of the precipitation of KClO_4 , gave a value of $\Delta H_3 = -123.0$ kcal./mole.
9. In calculating Q_2 , we have used the iodine-triiodide constant of Davies and Gwynne.¹⁰ It can be seen that Q_2 is of the order of 0.2% of Q_3 , and errors due to neglect of activity coefficients and heats of dilution in the calculation of Q_2 are negligible.
10. M. Davies and E. Gwynne, J. Am. Chem. Soc. 74, 2748 (1952).
11. In all runs, the ionic strength was approximately the same and, since it changed little during the course of the reaction, we adopt the average $\mu = 0.18$.
12. One run, not described because of the use of KBr and the possible precipitation of KClO_4 , gave a value of $\Delta H_7 = -43.4$ kcal./mole.
13. In calculating Q_4 , we have used the bromine-tribromide constant Griffith, McKeown and Winn¹⁴ corrected to 25°, $K_4 = 17 = (\text{Br}_3^-)/(\text{Br}_2)(\text{Br}^-)$. Activity coefficient and heat of dilution corrections have been neglected.
14. R. O. Griffith, A. McKeown and A. G. Winn, Trans. Faraday Soc. 28, 101 (1932).
15. A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940.
16. Calculated by Davies and Gwynne¹⁰ from the data of G. Jones and B. B. Kaplan, J. Am. Chem. Soc. 50, 1845 (1928).
17. A. D. Awtry and R. E. Connick, *ibid.*, 73, 1842 (1952).
18. O. Myers, private communication.

Acknowledgment

I am primarily indebted to two persons for this research, Professor Wendell M. Latimer and Professor Z Z. Hugus. Before his departure for the University of Minnesota, Dr. Hugus' sympathetic attention and direction were invaluable, and he has maintained his interest through correspondence since that time. Professor Latimer has been overly generous with his assistance, encouragement and chemical insight, and I consider it a real privilege to have had this association with him during this important part of my professional education.

Dr. W. L. Jolly has been helpful in a variety of ways; Section II of this thesis was done in collaboration with him. Also, I feel very grateful to Professor Leo Brewer who has been willing to discuss problems at any time, and whose advice has been greatly appreciated.

To Mrs. W. M. Latimer I am deeply indebted for her kind assistance in time of need with the preparation of the manuscript. Mrs. J. A. Waite has performed many services that were important to the progress of this work, for which many thanks.