[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Thermodynamics of Thiosulfate Ion[1]

BY HOWARD C. MEL, Z Z. HUGUS, JR.,[2] AND WENDELL M. LATIMER

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The equilibrium $2Ag + S_2O_3^= = Ag_2S + SO_3^=$ has been studied at 25, 122.5 and 195° and the heat of the reaction has been calculated from the temperature coefficient of the equilibrium constant. The heat of oxidation of $S_2O_3^=$ to $SO_4^=$ by Br_3^- has been measured calorimetrically. From these data the following values are obtained for the heat of formation, free energy of formation and partial molal entropy of $S_2O_3^=$ at 298.16°K., $\Delta H_f^\circ = -154.0$ kcal./mole, $\Delta F^\circ = -122.7$ kcal./mole, and $\bar{S}^\circ = 15.0$ e.u.

There has been considerable uncertainty in the thermodynamic data for thiosulfate ion in aqueous solution. Bichowsky[3] studied the equilibrium

$$2H_2O + Ca^{++} + S_2O_3^= = CaSO_3 \cdot 2H_2O + S(r)$$

over the temperature range 80 to 140°, thence calculating ΔF_f° for $S_2O_3^=$ to be -125.11 kcal./mole. In a recalculation of ΔH_f° of $S_2O_3^=$ from Bichowsky's data we obtained values ranging from -145 to -157 kcal./mole. Bichowsky and Rossini[4] recalculated the calorimetric data of Thomsen and Berthelot and reported ΔH_f° as -145.9, -147.2 and -149.1 kcal./mole. Recently Ballczo and Kaufmann[5] made determinations near room temperature of the equilibrium studied by Bichowsky. They plotted log K *vs.* $1/T$ using their data and the data of Bichowsky for higher temperatures and calculated for $S_2O_3^=$ $\Delta H_f^\circ = -164.7$ kcal./mole. This value together with the Bichowsky free energy yields $\bar{S}_{298}^\circ = -13$ e.u. for $S_2O_3^=$ while $\Delta H^\circ = -145$ kcal./mole gives 52 e.u. The former appears to be too negative and the latter too positive in comparison to $\bar{S}_{298}^\circ = 4.1$ e.u. for $SO_4^=$ (aq).

Matthews and McIntosh[6] in a recent study of crystalline calcium sulfite in equilibrium with its saturated solution at room temperature report only the hemi-hydrate $CaSO_3 \cdot {}^1/_2\, H_2O$, and not the dihydrate as assumed by Bichowsky. This work casts considerable doubt on the free energy of the reaction as calculated from the previous investigations.

In view of this situation, it seemed desirable to find another equilibrium involving $S_2O_3^=$ which might lead to more satisfactory results. After various preliminary studies it was decided to investigate the reaction

$$2Ag(c) + S_2O_3^= = Ag_2S(\alpha) + SO_3^= \qquad (1)$$

Preparation of Reagents. (a) $Na_2S_2O_3$ **Solutions.**—For the equilibrium measurements, standard solutions were generally made by dissolving reagent grade $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled distilled water.

(b) Na_2SO_3 **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 $HClO_4$, and then washed to remove any Ag_2O present.

No difference was detected in any of the results from the use of different Ag samples, so they will not be individually referred to in connection with the equilibrium data.

(d) Ag_2S.—(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 odor described by one of us (H. C. M.) as similar to that of "rotten artichokes"; 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 from a solution of reagent grade $AgNO_3$. The silver oxide was washed repeatedly with hot water and then dissolved in cold 3 M $HClO_4$. An H_2S train was set up and the purified H_2S passed through the $AgClO_4$ solution. The solid was washed repeatedly and dried at 130°. It was then ground and rewashed with hot water. A sulfur-like odor that had persisted through this treatment was now quite faint. After drying, the sample was finely ground. Samples of Ag_2S prepared in this fashion were spectroscopically pure and gave the X-ray pattern for the α (low temperature) form. A test with chloride showed no detectable Ag^+.

(3) Some commercial Kahlbaum reagent was used. The sample was spectroscopically pure and gave a good X-ray pattern for the α-form of Ag_2S.

(4) Some bottled Ag_2S of unknown origin was used in some determinations, both untreated and after treatment with $S_2O_3^=$ in the cold. Spectroscopic and X-ray examination showed some PbS impurity present, which microchemical analysis gave as less than 1%. Possibly some other undetermined impurity was present also.

From a careful examination of the equilibrium results, no systematic differences could be detected in the values for the equilibrium constants as a function of the particular solids used. However in solutions of low ionic strength sample (4) gave erratic results on runs at 195°.

Analytical Procedures. 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 $SO_3^= + S_2O_3^=$, and for a second portion, the complexing of the $SO_3^=$ by formaldehyde and then titration of $S_2O_3^=$ with iodine. Experience indicated that a modification of the scheme given by Kurtenacker[7] was necessary, since the starch indicator interacted with the formaldehyde, causing very uncertain end-points. In general, the greater the ratio of formaldehyde 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 end-point. If one knows approximately where the end-point will be, it is desirable to hold off the addition of starch till just before the end-point is reached.

The first step in the analysis of a tube, was to remove it from the oil-bath, and to clean it and rapidly cool it to room temperature. The tube was then opened by crushing the top, and a sample immediately pipeted out into an excess of standard I_3^- in NaAc–HAc buffer. For the later sets, this operation was done in an atmosphere of argon. A back titration with standard $S_2O_3^=$ was then carried out. In this way, total $SO_3^= + S_2O_3^=$ was determined.

The second portion was next delivered into an erlenmeyer containing two drops of phenolphthalein. In almost every

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[1] This work was presented by H. C. Mel in a Ph.D. thesis, University of California, 1953. See also Atomic Energy Commission Document UCRL-2330.

[2] School of Chemistry, University of Minnesota, Minneapolis, Minn.

[3] F. R. Bichowsky, THIS JOURNAL, **45**, 2225 (1923).

[4] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

[5] H. Ballczo and O. Kaufmann, *Monatsh. Chem.*, **80**, 220 (1949).

[6] F. W. Matthews and A. O. McIntosh, *Can. J. Research*, **26B**, 747 (1948).

[7] A. Kurtenacker, "Analytische Chemie der Sauerstoff Säuren des Schwefels," V. Wilhelm Bottger, Stuttgart, 1938.

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.) A delay of two or three minutes in pipeting the second portion should not matter, since air oxidation of $SO_3^=$ to $SO_4^=$ should not interfere with the determination of $S_2O_3^=$ in the presence of $SO_3^=$. After standing for five minutes, the first solution was acidified with 10% HAc until a 20-ml. excess had been added, and was then titrated immediately with standard iodine, using starch indicator. For further details see reference 1.

Standard Solutions.—In some cases the I_3^- solutions were standardized against As_2O_3, and in others the $S_2O_3^=$ was standardized with KIO_3 solution. The relative titer of the $S_2O_3^=$–I_3^- solution 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 and 0.01 *N* and $S_2O_3^=$ solutions of 0.2, 0.1 and 0.02 *N* were used.

Apparatus.—Equilibrium measurements were made at 25, 122.5 and 195°. An excess of solid Ag and Ag_2S and solutions of $Na_2S_2O_3$ and Na_2SO_3 were placed in Pyrex tubes 30 cm. long and 2.2 cm. in diameter with 1.5 mm. walls. The tubes were sealed off and each placed in an iron pipe equipped with threaded caps. Only one tube broke at 122.5° but only three of fourteen survived at 195°. The tubes were placed in an oil-bath containing Aeroshell 120, SAE 60. Upon prolonged heating this oil tended to smoke, thicken and tar even with the addition of oxidation inhibitors. Complete details of the heater, stirrer, temperature regulator and resistance thermometer are given in reference 1. The temperature of the bath could be controlled to 0.005° under optimum conditions but when the oil began to thicken much larger deviations would sometimes occur before an oil change was made.

Measurements at 122.5°.—From a large number of preliminary runs, it was estimated that equilibrium would be reached in 50 to 70 days depending upon how far the initial ratio of $(SO_3^=)$ to $(S_2O_3^=)$ differed from its equilibrium ratio. The rate of reaction was increased by the addition of glass wool to disperse most of the solid Ag and Ag_2S and thus prevent the solids from caking in the bottom of the tube. Unknown side reactions occurred to a greater extent in the presence of the glass wool but these reactions did not appear to affect the measured equilibrium constant. Since it was necessary to eliminate oxygen from the tubes and from the titration flasks, argon was used to displace the air. The preliminary runs located the value of $K_C = (SO_3^=)/(S_2O_3^=)$ between 11 and 18 and indicated that this constant depended upon the ionic strength of the solution.

In the final set of measurements four tubes were made up at each of three values of the ionic strength. The initial ratios of $SO_3^=$ to $S_2O_3^=$ were to be taken so that in each set, two were greater and two less than the preliminary value for the constant, but due to an error this was not done for the low ionic strength group. The results are given in Table I.

For some unknown reason, one value for K_c out of the four in each group is notably different. Result number 9 is rejected outright since it differs vastly from any of the other measurements and in addition is inconsistent with the trend of decreasing K_c with decreasing ionic strength (whether or not tubes 4 and 5 are included in the averages). Further calculations were made both including and excluding tubes 4 and 5 from the averages, with no difference in the final result. (See discussion at the end of the section on extrapolation to infinite dilution.) No systematic change of K_c is seen with the wide variation of material lost which permits neglecting the side reactions for our purposes.

TABLE I

EQUILIBRIUM MEASUREMENTS AT 122.5°

62–64 Days in Bath

Group	Tube no.	Mm.[a] final	Mm.[a] initial	Loss, %	Ionic[b] strength	$\left(\frac{SO_3^-}{S_2O_3^-}\right)_i$	K_c
	1	0.831	0.991	16.1	0.595	19.4	17.97
	2	.912	.991	8.0	.595	13.0	17.95
I	3	.855	.991	14.3	.595	20.3	17.95
	4	.891	.991	10.1	.595	13.2	18.84
	5	0.324	0.429	24.5	0.257	21.1	18.83
	6	.350	.425	17.5	.255	20.5	17.35
II	7	.324	.429	24.5	.258	13.0	17.55
	8	.347	.429	19.2	.257	12.9	17.47
	9	0.1030	0.172	40.0	0.103	1.10	31.86
	10	.0620	.135	54.1	.081	2.28	17.03
III	11	.1197	.173	30.6	.104	1.11	16.82
	12	.0930	.136	31.7	.082	2.29	16.83

[a] Millimoles of $SO_3^= + S_2O_3^=$ per 5 ml. solution. [b] Based on initial material added.

Equilibrium at 195°.—Fourteen tubes were made up with initial ratios of sulfite concentration to thiosulfate concentration of 0 and ∞. Only three tubes survived. The results are given in Table II.

TABLE II

EQUILIBRIUM DATA AT 195°

36–37 Days in Bath

Tube no.	Mm.[a] final	Mm.[a] initial	Loss, %	Ionic[c] strength	$\left(\frac{SO_3^-}{S_2O_3^-}\right)_i$	K_c	K_c'[b]
1	0.880	1.018	13.5	0.611	∞	9.74	9.36
2	.378	0.434	12.9	.261	0	9.58	
3	.0446	0.1001	55.4	.0601	0	23.19	

[a] Millimoles of $SO_3^= + S_2O_3^=$ per 5 ml. of solution. [b] Corrected to Ag_2S (α) (see below). [c] Based on initial material added.

The constant at the lowest ionic strength is obviously inconsistent with the two other values. In this case the poorest Ag_2S sample was used and the impurities in the sample and the low concentrations of $SO_3^=$ and $S_2O_3^=$ may account for the very high result. Fortunately in the other two cases the equilibrium was approached from opposite sides. The lower value of K_c at the lower ionic strength is consistent with our results at 122.5°.

Silver sulfide has a transition at 179° and it therefore is necessary to correct for the different activity of the high temperature form, Ag_2S (β), in order to compare with the constants for lower temperatures which involve Ag_2S (α), our standard of unit activity. The heat of transition $\Delta H_{\beta \rightarrow \alpha}$ is -1050[8] cal./mole and $\Delta S_{\beta \rightarrow \alpha}$ is therefore -2.32 e.u. We then calculate the free energy of the transition at 195° to be

$$Ag_2S(\beta) = Ag_2S(\alpha),\ \Delta F_{195°} = 37 \text{ cal./mole} \qquad (2)$$

$$\text{where } \Delta F_{195°} = RT \ln \frac{a(\alpha)}{a(\beta)}$$

The free energy change for reaction (1) with Ag_2S (α) would therefore be more positive by 37 cal./mole and the constant smaller by the ratio of the

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[8] National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952.

activities of the two solids. The corrected K_c for tube 1 is given in the final column of Table II as K_c'. Due to aging of the oil the temperature was not quite so constant for tube no. 2 as for no. 1. Consequently it was deemed slightly better to use just K_c' for tube no. 1 and extrapolate to infinite dilution in a consistent manner for all three temperatures as indicated below.

Equilibrium at 25°.—A number of tubes were made up and placed in a water thermostat with shaking for 105 days. At that time even the direction of the effect of temperature on K_c was unknown. Unfortunately it turned out that in no case was the ratio $(SO_3^=)/(S_2O_3^=)$ initially large enough and the equilibrium was therefore approached from only one side. The results are given in Table III.

Table III

Equilibrium Results at 25°

Tube no.	Mm.[a] final	Mm.[a] initial	Initial ionic strength	$\left(\frac{SO_3^=}{S_2O_3^=}\right)_i$	K_c
1	0.917	0.991	0.595	19.6	42.4
2	.890	.991	.595	13.1	19.5
3	.382	.429	.258	21.0	77.0
4	.478	.520	.312	18.6	59.5

[a] Millimoles of $SO_3^=$ + $S_2O_3^=$ in 5 ml.

The highest value $K_c = 77.0$ will be taken as a tentative figure since it is felt that the tube no. 3 has the best chance of having reached equilibrium.

Extrapolation of K_c Values to Infinite Dilution.—A calculation of K_0 requires values of the activity coefficients of the two ions $f_{SO_3^=}$ and $f_{S_2O_3^=}$

$$K_0 = K_c \frac{f_{SO_3^=}}{f_{S_2O_3^=}} \quad (3)$$

From the extended Debye–Hückel[9,10] expression

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

where

Γ = ("ional concn.") = $\Sigma c_i z_i^2 = 2\mu$ (molarity)
c_i = concn. in moles/l. for ith ion
z_i = charge on ith ion
$S = \dfrac{1.283 \times 10^6}{(DT)^{3/2}} z_i^2$
D = dielectric constant of solvent. T in °K.
$A = \dfrac{35.57}{(DT)^{1/2}} a_i$
a_i = effective diameter of hydrated ion, Å.

Values for the dielectric constant of water at the three temperatures were taken from the National Bureau of Standards tables.[11] We do not know the effective hydrated diameters of $SO_3^=$ and $S_2O_3^=$. The trend of K_c with ionic strength at 122.5° implies that $S_2O_3^=$ is larger than $SO_3^=$ and we have arbitrarily chosen $a_{S_2O_3^=}$ = 4.5 Å. and $a_{SO_3^=}$ = 4.0 Å. This is a reversal of the values listed by Kielland.[10]

We will combine equations 3 and 4 and add to (4) the "B" terms often used in treating such data.[9] Whence

$$\log K_c - M = \log K_0 - (B_{SO_3^=} - B_{S_2O_3^=})\Gamma \quad (5)$$

where

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

A plot can be made of $\log K_c - M$ *vs.* Γ where $\log K_0$ is the intercept at $\Gamma = 0$ and $(B_{SO_3^=} - B_{S_2O_3^=})$, essentially an arbitrary constant, is the slope. This was done for the data at 122.5°, then lines of this same slope drawn through the "best" values of $K_c - M$ for 25 and 195°, from tube 1 Table II, tube 3 Table III. The data employed are summarized in Table IIIA and the final K_0 values are given in Table IV.

Table IIIA

Quantities in Equation 5

t, °C.	S	Γ[a]	$A_{SO_3^=}$	$A_{S_2O_3^=}$	log K_c	M	log $K_c - M$
25.0	1.432	0.515	0.930	1.046	1.8865	0.0294	1.8571
122.5	1.849	1.123	1.013	1.139	1.2543	.0572	1.1971
122.5	1.849	0.485	1.013	1.139	1.2420	.0369	1.2051
122.5	1.849	0.1675	1.013	1.139	1.2277	.0188	1.2089
195	2.400	1.064	1.104	1.242	0.9713	.0727	0.8986

[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.

Table IV

K_0 Values as a Function of Temperature

t, °C.	log K_0	K_0
25.0	1.864	73.1
122.5	1.211	16.3
195.0	0.912	8.16

These and the subsequent calculations were made (1) including data for tubes 4 and 5 in the averages for 122.5°; (2) excluding tubes 4 and 5. Apart from the increased scatter of points, there was a negligible effect on the calculated thermodynamic quantities (*i.e.*, ΔH_{rx} remained constant to within 0.01 kcal./mole). The data actually shown in the tables are for (2). However, the nearly perfect linearity of the line plotted from (2) should be regarded as fortuitous.

The Heat of Oxidation of $S_2O_3^=$ by Br_3^-.—In order to obtain an independent check on the heat of formation of $S_2O_3^=$, it was decided to measure its heat of oxidation to $SO_4^=$. The oxidizing agent appearing to have the best chance of success was Br_3^-.

Reagents.—Thiosulfate solutions were made by dissolving freshly recrystallized $Na_2S_2O_3 \cdot 5_2O$ in recently boiled distilled water and their titer was established by titration with a standard KIO_3 solution.

The standard Br_3^- solutions were prepared by weighing out samples of recrystallized $KBrO_3$ and adding an excess of reagent NaBr and a known amount of standard $HClO_4$. Sufficient time was allowed to ensure complete reduction of the $KBrO_3$.

Calorimetric Procedure.—The experimental equipment has been described previously.[12,13]

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[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 2nd Ed., 1950.

[10] J. Kielland, This Journal, 59, 1675 (1937).

[11] United States Department of Commerce, National Bureau of Standards Circular 514, "Tables of Dielectric Constants of Pure Liquids."

[12] B. J. Fontana, "Nuclear Energy Series IV-19B," McGraw-Hill Book Co., New York, N. Y., 1950, p. 321; H. W. Zimmerman and W. M. Latimer, This Journal, 61, 1550 (1939).

[13] See H. C. Mel, W. L. Jolly and W. M. Latimer, *ibid.*, 75, 3828 (1953).

Sample bulbs containing 5 ml. of $S_2O_3^{=}$ solution were broken on a spiked glass plate on the bottom of the calorimeter flask. The process was carried out in such a manner that excess of Br_3^- solution oxidized the $S_2O_3^{=}$ to $SO_4^{=}$ with no visible formation of free sulfur at the end of the runs. At least for certain conditions of concentrations, however, sulfur is formed in an intermediate stage of the reaction. The results of four runs are summarized in Table V.

TABLE V

THE HEAT OF OXIDATION OF $S_2O_3^{=}$ WITH Br_3^- (Part 1)

Run	Total g. water added	$KBrO_3$, g.	NaBr, g.	$HClO_4$, moles	$Na_2S_2O_3$, moles	Q_c, cal.
1	1068.9	2.5851	15.076	0.2326	0.0010030	161.29
2	1068.9	2.5851	15.076	.2326	.0010030	159.14
3	1068.9	2.5851	15.076	.2326	.0010030	159.46
4	1068.9	2.5851	15.076	.2326	.0010030	160.46
					Av.	160.09 + 0.8

The quantity Q_c refers to the actual heat evolved in the calorimeter. For the "net" reaction we write

$$A\ Na_2S_2O_3 + B\ Br_2 + C\ NaBr_3 + D\ NaBr + 5A\ H_2O + E\ HClO_4 = F\ Na_2SO_4 + E\ NaHSO_4 + E\ NaClO_4 + 10A\ HBr \quad (6)$$

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. The occurrence of Na_2SO_4 and $NaHSO_4$ on the right of (6) implies that the solution contains F moles of $SO_4^{=}$ and E moles of HSO_4^- after the H^+, $SO_4^{=}$ and HSO_4^- have come to equilibrium (there is no additional $SO_4^{=}$ or HSO_4^- in the solution, not formed by the net reaction).

TABLE VI

BROMINE SPECIES IN CALORIMETRIC SOLUTION

Substance	Before reaction Moles	Before reaction Molality	After reaction Moles	After reaction Molality	Net moles reacting (diff.)
H_2O	59.332	......	59.605	......	......
Br_2(aq)	0.026141	0.024456	0.022297	0.020765	0.003844 = B
$NaBr_3$	.020292	.018984	.020124	.018741	.000168 = C
NaBr	.033330	.031182	.031500	.029335	.001830 = D
KBr	.015478	.014480	.015478	.014414	0
HBr	....	......	.010030	.009341	.010030 = $10A$

Since this is a balanced net reaction, certain relationships can be deduced immediately for the coefficients. The sum of B and C, the total moles of oxidizing agent *reacting* with the A moles of $Na_2S_2O_3$, must $= 4A$. Similarly, $F + E$ (the "total $SO_4^{=}$") $= 2A$, and $C + D = 2A$. In order to calculate B, C and D, we must know the *total* number of moles of Br_3^-, Br_2(aq) and Br^- in both the initial and final solutions. These were calculated using $K_{298} = 17$[13] for the equilibrium: $Br_2(aq) + Br^- = Br_3^-$. B, C and D were then computed from the difference between the final and initial concentrations of Br_2(aq), Br_3^- and Br^-. In Table VI 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 calculation showed that vaporization of Br_2 could be neglected.

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

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

$$K_d = \frac{(H^+)(SO_4^{=})}{(HSO_4^-)} \quad (7)$$

where the bracketed quantities are the *total* concentrations (molality) of these species in the solution. Furthermore, K_d must be known at the ionic strength of the reaction mixture. Bray and Liebhafsky[14] determined K_d as a function of ionic strength, and tabulated their values together with values of K_d given by Skrabal and Weberitsch.[15] We plotted these data as $^1/_4 \log K_d$ *vs.* $\mu^{1/2}$ and drew the best line through them, reading off the value at $\mu^{1/2} = 0.539$ (*i.e.*, $\mu = 0.29$). The result was $K_d = 0.12$. Bray and Liebhafsky ignored the experimental values for the higher ionic strengths in favor of a theoretical correlation and thus calculated a different value of K_d at $\mu = 0.29$. (See discussion in reference 1.)

With this choice of K_d, we are now in a position to calculate the coefficients E and F; these quantities are tabulated in Table VII.

TABLE VII

SULFATE AND BISULFATE FORMATION

Substance	Moles	Molality
Total H^+	0.1487	0.1384
Total $SO_4^{=}$	.000931 = F	.000867
Total HSO_4^-	.001075 = E	.001001

This completes the calculation of all the coefficients in reaction (6). The next step is to eliminate the extra species in equation 6 by the combination of additional reactions. For the reaction

$$C(Br_2 + NaBr = NaBr_3) \quad (8)$$

we choose our $\Delta H = \Delta H° = -2.0$ kcal./mole, from Bureau of Standards data. Thus $Q_8 = (2000)C = 0.34$ cal.

The other reaction we must consider is

$$E(NaHSO_4 + NaClO_4 = HClO_4 + Na_2SO_4) \quad (9)$$

The values $\Delta H_f = -331.23$ and -31.45 kcal./mole for Na_2SO_4 and $HClO_4$, respectively, are derived from interpolation of the Bureau of Standards tables.[8] For $NaHSO_4$, a value is listed for $\Delta H_f°$ in 200 H_2O but this value is probably incorrectly based on heats of reaction that were not corrected for the

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[14] W. C. Bray and H. Liebhafsky, THIS JOURNAL, **57**, 51 (1935).

[15] A. Skrabal and S. Weberitsch, *Monatsh. Chem.*, **36**, 211 (1915).

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 values for Na^+ and HSO_4^- at infinite dilution, and a small heat of dilution estimated from the heats of dilution of $NaNO_3$ and $NaBrO_3$. In this manner we calculate $\Delta H_f = -269.1$ kcal./mole for $NaHSO_4$. For $NaClO_4$, we estimate part of a dilution correction, with the final result $\Delta H_f{}^\circ = -88.90$ kcal./mole.

Combining the above values, we have the result $\Delta H_9 = -4.68$ kcal./mole, or $Q_9 = (4{,}680)\ E = +5.03$ cal.

These results are now summarized in Table VIII; the values being valid for all four runs.

TABLE VIII

THE HEAT OF OXIDATION OF $S_2O_3^=$ WITH Br_3^- (PART 2)

Q_6 av., cal.	Q_8, cal.	Q_9, cal.	Q_{10}, cal.	ΔH_{10}, kcal./mole	$\Delta H_{10}^\circ = \Delta H_{11}^\circ$, kcal./mole
160.09	0.34	5.03	165.46	−164.97	−167.07

If we add reactions (6), (8) and (9), we have reaction (10), with $Q_{10} = Q_6 + Q_8 + Q_9$ as shown in Table VIII

$$A\ Na_2S_2O_3 + 4A\ Br_2(aq) + 2A\ NaBr + 5A\ H_2O = 2A\,Na_2SO_4 + 10A\ HBr \quad (10)$$

ΔH_{10} is obtained from the relation

$$\Delta H_{10} = \frac{-Q_{10}}{A}\ \text{kcal./mole}$$

and is the heat for reaction (10) where $A = 1$ mole, uncorrected to infinite dilution.

Dilution corrections for Br_2 have been neglected, and those for Na_2SO_4, HBr and NaBr obtained from interpolation in Bureau of Standards data.[8] One calorimetric run was made for the heat of dilution of the $Na_2S_2O_3$ solution and general agreement was found with the results of Plake.[16] 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_{11}° in Table IX was calculated by applying these dilution corrections to ΔH_{10}. Now that we have the value of ΔH°, we can rewrite equation 10 in its equivalent ionic form

$$S_2O_3^= + 4Br_2(aq) + 5H_2O = 2SO_4^= + 10H^+ + 8Br^- \qquad \Delta H_{11}^\circ = -167.07\ \text{kcal./mole.} \quad (11)$$

Now, combining our ΔH_{11}° with Bureau of Standards data, we calculate our final calorimetric results, $\Delta H_f^\circ = -152.0$ kcal./mole for $S_2O_3^=$ at 298.16°K.

It should be pointed out that the method of estimating heat of dilution corrections based on the principle of ionic strength is not rigorous but amounts to neglecting certain heats of mixing as compared with the actual heats of dilution. However for similar substances at $\mu = 0.29$, such corrections are generally small. A great many additional precise calorimetric reactions would have to be carried out to eliminate this uncertainty and it is felt that this is not justified in this case. If a more clean-cut oxidation reaction could be found having a smaller heat and with the other heats of formation involved exactly known, then it would be worthwhile to carry out the additional experiments to evaluate heats of mixing.

Final Calculation of $\Delta H_f{}^\circ$, $\Delta F_f{}^\circ$ and $\bar{S}^\circ$ for $S_2O_3^=$.—We shall now calculate ΔH° of reaction (1) from the equilibrium data and compare the result with the calorimetric value. We do not know the $\bar{C}_p$ for $SO_3^=$ or $S_2O_3^=$ with any certainty (even at room temperature) but from the symmetry of the equation one would expect ΔC_p for the reaction to be quite small. Using the data from Table IV, a plot was made of log K_0 against $1/T$, °K. The three points fall very well on a straight line, and give some weight to our belief that the K^0 at 25° is approximately correct.

The value of ΔH° from the plot is −3.58 kcal./mole. In order to calculate ΔH° of formation of $S_2O_3^=$ we use the Bureau of Standards[8] data for $Ag_2S(\alpha)$ $\Delta H_f^\circ = -7.60$ kcal./mole and the value given by Latimer[17] for $SO_3^=$, $\Delta H_f{}^\circ = -151.9$ kcal./mole. The latter is based upon calculations of Powell[18] from the vapor pressure of SO_2 over aqueous solutions and the dissociation constants of H_2SO_3. From these values, the heat of formation of $S_2O_3^=$ is $\Delta H_f^\circ = -155.9$ kcal./mole.

Conclusions.—Our two heat of formation values for $S_2O_3^=$, −155.9 kcal./mole from the equilibrium measurements and −152.0 kcal./mole from the direct calorimetric experiments, do not show highly precise agreement. Calorimetric uncertainties are in the thermodynamic data for HSO_4^- dissociation, bromine species and complexing, heats of dilution and the large heat of reaction. For the equilibrium measurements there is the uncertainty in the 25° point and in the ΔC_p for the reaction. We will consider the average, $\Delta H_f{}^\circ$ (298.16°K.) = −154.0 ± 2 kcal./mole, as the probable value for this quantity.

Using this value the calculated heat of reaction (1) of silver with thiosulfate is −5.5 kcal./mole. Since our best value for K_0 is at 122.5° we shall use this constant and the calculated heat to calculate log K_0 at 298.16. The result log K_0 (298.16) = 2.205 and ΔF° (298.16) = −3.01 kcal./mole. The free energy of formation of $S_2O_3^=$ then may be calculated, $\Delta F_f{}^\circ$ (298.16) = −122.7 ± 1 kcal./mole, with the uncertainty essentially all in the extrapolation from 122.5°. The partial molal entropy of $S_2O_3^=$ then is $\bar{S}^\circ(298.16) = 15.0 \pm 6$ e.u. This value, which is 11 e.u. more positive than $\bar{S}^\circ$ for $SO_4^=$, seems reasonable as the larger "sulfide" in $SO_3S^=$ would not tie up as much water as the corresponding "oxide" in $SO_4^=$.[19] Further, such a value is consistent with the fact that the entropy of HS^- is 17 e.u. more positive than the entropy of OH^-.

BERKELEY, CALIFORNIA

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[16] E. Plake, *Z. physik. Chem.*, **A162**, 257 (1932).

[17] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 2nd ed., 1952.

[18] R. E. Powell, University of California, unpublished.

[19] N. Konopik concludes (*Monatsh.*, **84**, 1243 (1953)) that in $SSO_3^=$ the central sulfur is +4 and the outer S in the zero oxidation state. On this basis also, $SSO_3^=$ should tie up less water and hence have a more positive entropy than $SO_4^=$.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA RADIATION LABORATORY AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Complexing of Iron(III) by Fluoride Ions in Aqueous Solution: Free Energies, Heats and Entropies

BY R. E. CONNICK, L. G. HEPLER, Z Z. HUGUS, JR., J. W. KURY, W. M. LATIMER AND MAAK-SANG TSAO

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The potential of the ferrous–ferric half-cell has been studied as a function of hydrofluoric acid concentration at 15, 25 and 35°. Equilibrium quotients and free energy, heat and entropy changes at an ionic strength of 0.50 are calculated for the reactions: $Fe^{+3} + HF = FeF^{+2} + H^+$, $FeF^{+2} + HF = FeF_2^+ + H^+$ and $FeF_2^+ + HF = FeF_3 + H^+$.

In order to investigate the fluoride complexing of sundry cations[1-3] as a function of temperature using the "ferri"[4,5] method, it was necessary to extend the work of Dodgen and Rollefson[5] with iron to 15 and 35°.

The experimental technique used in the present investigation of the fluoride complex ions of iron(III) is essentially the same as theirs.[5] Several experiments were also carried out at 25°, the results of which deviated slightly from those of the above investigators.

Experimental

The cell, solutions and potentiometer circuit used in these experiments have been described previously.[1,6] Experiments were carried out at 15, 25 and 35°.

Before each run the assembled cell and the stock solutions were brought to the temperature of the experiment. One-hundred-milliliter aliquots of stock solution containing the desired concentrations of $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $HClO_4$ and $NaClO_4$ were pipetted into each half-cell. The stirrers were activated and after observing the small initial potential (usually less than 0.2 mv.) standard sodium fluoride solution was added to one half-cell. The potential of the cell was read after each addition. The stirrers were left on both while adding sodium fluoride and reading the potential. The potential became constant to within 0.02 mv. approximately one minute after each addition.

The variation of potential with total fluoride concentration at 15, 25 and 35° as well as the initial concentrations of $HClO_4$, $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ are given in Table 1 for a typical run at each temperature. In all runs the initial compositions of the two half-cells were the same. Sodium perchlorate was used to bring the initial ionic strength to 0.50. The half-cell to which fluoride was added is designated as "B" and the other as "C." The measured potential after each addition of sodium fluoride minus the initial potential is designated as "E." The total fluoride concentration in half-cell B is (ΣF^-). The equal initial volumes in the half-cells is V_i; V is the volume in half-cell B after adding sodium fluoride. The total initial concentrations are designated with the symbol "Σ" and the subscript "i."

Several experiments were run at each temperature with varying hydrogen ion concentrations and with smaller ferrous and ferric concentration changes. The initial conditions and the range of fluoride concentration are given in Table II. In each experiment anywhere from seven to eighteen e.m.f. determinations were made at different fluoride concentrations. The complete data may be found in references 6 and 12.

Analysis of Results

The experimental results may be interpreted by considering the following equilibria

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad Q_1 \qquad (1)$$

$$FeF^{+2} + HF = FeF_2^+ + H^+ \qquad Q_2 \qquad (2)$$

$$FeF_2^+ + HF = FeF_3 + H^+ \qquad Q_3 \qquad (3)$$

$$HF = H^+ + F^- \qquad Q_{HF} \qquad (4)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^+ \qquad Q_H \qquad (5)$$

The Q's are equilibrium quotients, for example

$$Q_1 = \frac{(FeF^{+2})(H^+)}{(Fe^{+3})(HF)}$$

where ( ) signifies concentration in moles/l.

TABLE I

DATA FOR TYPICAL RUNS AT DIFFERENT TEMPERATURES

(μ = 0.50)

	$(\Sigma F^-) \times 10^4$, moles/l.	E, mv.	V, ml.
14.97 ± 0.03°	9.08	39.88	110.2
$(\Sigma H_i^+) = 0.01838\ M$	18.10	71.56	110.4
$(\Sigma Fe_i^{+2}) = 2.315 \times 10^{-4}\ M$	27.13	92.82	110.6
$(\Sigma Fe_i^{+3}) = 5.866 \times 10^{-4}\ M$	36.12	109.75	110.8
V_i = 110.0 ml.	45.08	124.30	111.0
	54.00	136.99	111.2
	62.86	148.78	111.4
	71.73	159.50	111.6
	80.52	169.60	111.8
	89.38	179.40	112.0
	98.09	188.88	112.2
	106.79	197.90	112.4
25.00 ± 0.01°	3.78	13.83	105.0
$(\Sigma H_i^+) = 0.04946\ M$	7.55	26.32	105.1
$(\Sigma Fe_i^{+2}) = 6.338 \times 10^{-4}\ M$	11.31	36.65	105.1
$(\Sigma Fe_i^{+3}) = 4.277 \times 10^{-4}\ M$	15.07	45.17	105.2
V_i = 104.9 ml.	18.83	52.57	105.3
	28.77	68.22	105.5
	38.68	80.24	105.7
	48.55	90.28	105.9
	68.18	107.32	106.3
	87.66	121.46	106.7
	107.0	133.84	107.1
	126.2	144.98	107.5
35.00 ± 0.02°	4.57	14.69	105.0
$(\Sigma H_i^+) = 0.05645\ M$	13.21	38.76	105.1
$(\Sigma Fe_i^{+2}) = 6.338 \times 10^{-4}\ M$	20.06	51.91	105.2
$(\Sigma Fe_i^{+3}) = 4.277 \times 10^{-4}\ M$	27.03	62.54	105.3
V_i = 104.9 ml.	34.18	71.30	105.5
	43.16	81.12	105.6
	56.93	93.39	105.8
	79.95	110.34	106.2
	104.3	125.56	106.6
	119.8	134.17	106.9
	133.4	141.51	107.1

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