chloride mixtures,[18b] it was assumed that the $SO_2 \cdot Cl^-$ formation constant was very small, no adequate explanation being offered for the increase in rate constant in excess thionyl chloride as compared to excess liquid sulfur dioxide. More recently, we have assumed the absence of important medium effects on the rate and equilibrium constants as the solution components are varied from one extreme to the other. Thus we have been able, by nonlinear least-squares procedures, to employ the variation in the apparent third-order rate constant (k_3 in ref 18b) to obtain values for (1) the bimolecular rate constant for radiosulfur exchange between $SO_2 \cdot Cl^-$ and $SOCl_2$ and (2) the formation constant for $SO_2 \cdot Cl^-$ (K).[31] The K value at 0.0° is 0.17 ± 0.03. The meager data at other temperatures give ~0.18 (25.2°) and ~0.27 (~−21°). The apparent approximate formation enthalpy and entropy are $\Delta H° \approx -1.6$ kcal/mol and $\Delta S° \approx -9$ eu. Since the original study in the mixed reactants, a further rough preliminary investigation has been made of the same exchange study in the solvent acetonitrile.[32] The same rate law has been found as in the original work, and, furthermore, roughly comparable values for both rate and formation constants are suggested, the value for the latter being ~0.12 (25.2°). Thus some support is provided for the assumption that medium effects are not large, and, further, a basis is furnished for comparison of results from the exchange studies with those in the present research. This comparison leaves us with the observation that the formation constants calculated from the former studies present an apparent quantitative disagreement with the much larger figures of 418–321 (15–35°) now found.

Two possible explanations for this apparent anomaly present themselves. As one possibility, it might be that the complex spectroscopically observed is not catalytically effective, perhaps with an excessive S–Cl bond length and/or an unfavorable geometry. Then the formation constant for the catalytically effective form might be much smaller than for the ineffective. As a second possibility, it might be that further chloride ion complexes besides the 1:1 complex here treated, with either sulfur dioxide or thionyl chloride, may be involved in the kinetics experiments. (Substantially higher concentrations of the sulfur compounds prevailed as compared to sulfur dioxide in the present study.) In such a case the formation constant estimates derived from the exchange studies become quite meaningless. Further work is planned.

Acknowledgment.—We are greatly indebted to Professor N. N. Lichtin for a preliminary report of his complex studies prior to publication.

[31] (a) N. D. Potter, Ph.D. Thesis, Oregon State University, 1962; (b) T. H. Norris, unpublished data.

[32] T. G. Cooper and T. H. Norris, to be submitted for publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Thermodynamic Properties of the Aqueous Sulfide and Bisulfide Ions and the Second Ionization Constant of Hydrogen Sulfide over Extended Temperatures[1,2]

BY H. P. STEPHENS[3,4] AND J. W. COBBLE*

Received March 31, 1970

The heat of formation and entropy for the aqueous sulfide ion and the heat capacity functions for S^{2-}(aq) and HS^-(aq) have been determined calorimetrically by measuring the heat of solution of KHS(c) in basic solutions at 25 and 95°. The value determined for $\bar{S}°(25°)$ for S^{2-}(aq) is −4.1 ± 2 cal mol^{-1} deg^{-1} and the heat capacity function $\bar{C}_p°\big|_{25}^{100}$ for S^{2-}(aq) and HS^-(aq) was found to be −105 ± 9 and −48.8 ± 2 cal mol^{-1} deg^{-1}, respectively. The entropy and heat capacity of aqueous sulfide are incorrectly predicted from empirical considerations based on other simple ions. This fact suggests aqueous sulfide is a complex species or that its hydration sphere is not as tightly bound as would be predicted from its charge density.

I. Introduction

A procedure for determining accurate thermal data over extended temperatures for an aqueous ionic species which can only be formed in equilibrium with other species has been described in a preceding paper of this series.[5] The method involved a simple extension of the integral heat method,[6] and it has been further modified in the present research to obtain thermal data on the chemically important sulfide and bisulfide ions. Measurements have been made of the heat of solution of crystalline potassium bisulfide in aqueous solutions of potassium hydroxide. The resulting heat is the sum of the heat of solution of KHS(c) and the heat of reaction of HS^-(aq) with OH^-(aq) to form an equilib-

---

[1] This communication constitutes paper XIII of a series of communications from these laboratories on the thermodynamic properties of high-temperature aqueous solutions.

[2] Supported by the National Science Foundation under Grant No. GP-8664.

[3] From the Ph.D. Thesis of H. P. Stephens, Purdue University, June 1970.

[4] National Science Foundation Predoctoral Fellow, 1966–1969.

[5] J. M. Readnour and J. W. Cobble, *Inorg. Chem.*, **8**, 2174 (1969).

[6] C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **83**, 3223 (1961).

rium amount of S^{2-}(aq). Previous investigators[7-9] have used the heat of neutralization of H_2S(aq) to obtain values of $\Delta H_f°$ and $\bar{S}°$ for the aqueous sulfide ion. However, the present method is more accurate because the heat of solution of KHS(c) is smaller than the heat of neutralization of H_2S to HS^-. Consequently, more of the observed heat is due to the reaction of HS^-(aq) with OH^-(aq).

Thirty-seven heats of solution of crystalline potassium bisulfide in potassium hydroxide solutions were measured at ionic strengths between 0.02 and 0.22 *m* and at two temperatures, 24.91 and 95.14°. From these measurements and previously reported experimental values of K_2^0 for H_2S(aq) from 0 to 90°, the thermodynamic properties for the sulfide ion and the second ionization of H_2S(aq) have been calculated up to 100°, and estimates of K_2^0 up to 250° are given.

II. Experimental Section

Apparatus.—A new submarine-type heat of solution calorimeter was constructed to operate under a nitrogen atmosphere. The calorimeter consisted of a commercially available 250-ml silvered dewar flask which was Teflon coated on the inside to prevent attack by basic solutions and a top which was machined from Kel-F. Three probes and a stirring shaft made of Teflon-coated Monel tubing (0.25-in. outside diameter and 0.008-in. wall thickness) extended through the calorimeter top. A small glass sample bulb could be attached to the lower end of the stirring shaft and could be broken against the bottom of the dewar by depressing the stirring shaft. The three probes contained calibration components for the calorimeter. One probe was used for the calibration heater, the second contained a thermistor, and the third was used for various accessories such as the rough heater or platinum resistance thermometer. The calibration and temperature-sensing instrumentation for the thermal measurements have been previously described.[10] A rubber O ring located in the calorimeter top provided a tight seal when the top was attached to the dewar. A side-arm tube, through which nitrogen could be passed, was welded to the top of the casing containing the stirring shaft. In use, the calorimeter was located about 15 cm below the surface of a water bath thermostated to ±0.001°. Under these conditions, the thermal modulus was 2.7×10^{-3} min^{-1} at 25° and 3.9×10^{-3} min^{-1} at 95°.

Materials.—Distilled water, purified again by a Barnstead demineralizer, was used for the preparation of reagents and in the calorimeter. The water was freshly boiled before each calorimetric run to remove dissolved CO_2.

Potassium bisulfide was prepared by reaction of hydrogen sulfide with potassium ethoxide in ethanol. The entire preparation was performed in an apparatus with a nitrogen atmosphere (99.9% pure, ≤9 ppm of H_2O). About 250 ml of absolute ethanol (99.5% pure), which had been thoroughly dried by reaction with a few grams of $LiAlH_4$, was distilled into a 500-ml flask containing four 5-g pieces of freshly cut potassium metal. After the potassium had completely dissolved, the resulting solution of potassium ethoxide was saturated with H_2S (CP, 99.6%, Matheson Co., Joliet, Ill.). Additional ethanol was distilled, as needed, into the 500-ml flask to dissolve any KHS which precipitated. The KHS solution was filtered into another 500-ml flask and ethanol was evaporated from the solution at 70°, until about 75 ml of a slurry of KHS(c) and ethanolic KHS solution remained. After the slurry was cooled to 0°, the crystalline KHS was collected by suction filtering. The product (yield 20.5 g) was transferred to a 125-ml vacuum flask which was evacuated to less than 5 μ pressure. The flask containing the product, as fine white crystals, was stored over P_2O_5 in a vacuum desiccator.

Potassium bisulfide was analyzed for sulfur (as sulfide) content by potentiometric titration with $AgNO_3$ using a sulfide ion electrode (Model 94-16, Orion Research, Inc., Cambridge, Mass.) and a saturated calomel reference electrode. *Anal.* Calcd: sulfide, 44.43. Found: sulfide, 44.42 ± 0.11. The potassium content was determined[11] as the sulfate by repeatedly fuming a sample with concentrated sulfuric acid. *Anal.* Calcd: K, 54.18. Found: K, 54.17 ± 0.02.

Carbonate-free potassium hydroxide solutions were prepared by an ion-exchange method which has been described in detail elsewhere.[12] The carbonate in 2 l. of 0.2 *M* KOH solution was precipitated with an excess of $Ba(OH)_2$. A cation-exchange column was used to exchange potassium for any barium remaining in solution. Atmospheric carbon dioxide was excluded from the ion-exchange apparatus and polyethylene storage container by soda lime traps. Tygon tubing was used in place of glass tubing for all connections to prevent contamination with silicates.

The carbonate-free KOH solution was standardized by titration against primary standard potassium acid phthalate to a phenolphthalein end point. Periodic standardizations over 3 months showed that the concentration of KOH did not change by more than 0.1%. Periodic checks with 0.2 *M* $Ba(OH)_2$ solution revealed that the carbonate concentration remained ≤10 ppm.

Procedure.—Thin-walled glass sample bulbs[6] were kept in a drybox for several hours, then placed in weighing bottles with ground-glass tops, and removed from the drybox for weighing. The ground-glass joints of the bottles were covered with a thin layer of Dow Corning silicone grease to form an airtight seal. Each weighing bottle, containing a sample bulb, was weighed to the nearest 0.01 mg and returned to the drybox. After several hours, potassium bisulfide was placed in the sample bulbs and the weighing bottles and contents were reweighed as before. The sample bulb was then attached to a glass stopcock using a rubber connector in the drybox. This assembly was removed from the drybox, connected to a vacuum line, and evacuated to a pressure ≤15 μ. The bulbs were finally sealed with a microtorch.

In order to prevent both reaction of carbon dioxide with the basic solutions and air oxidation of the bisulfide and sulfide solutions, the calorimeter was loaded and operated under a nitrogen atmosphere. A polyethylene sleeve, fitted between the top of the calorimeter and the dewar, excluded the atmosphere during loading. The tips of the two burets, used for addition of water and KOH solution to the calorimeter, and a nitrogen inlet tube were inserted through the polyethylene sleeve. After the sleeve and dewar were flushed with nitrogen for at least 10 min, the nitrogen flow was started into the side arm of the stirring-shaft casing. Precise amounts of water and KOH solution needed for a run were then added to the dewar while the positive nitrogen pressure was maintained in the sleeve. Nitrogen was bubbled through the solution for another 15 min to displace dissolved oxygen. The top of the calorimeter was then attached to the dewar and the calorimeter was mounted in the thermostat. The techniques used to calibrate the calorimeter and calculate the heat of solution were the same as used previously.[6,10]

III. Data

The calorimetrically measured heat of solution of

---

(7) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, N. Y., 1936.

(8) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(9) J. W. Kury, A. J. Zielen, and W. M. Latimer, *J. Electrochem. Soc.*, **100**, 468 (1953).

(10) E. C. Jekel, C. M. Criss, and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5404 (1964).

(11) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961.

(12) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962, pp 24–27.

KHS(c) in KOH solutions, Δh, is the sum of the heats of two nearly simultaneous reactions

$$KHS(c) + aq \longrightarrow K^+(aq) + HS^-(aq) \qquad \Delta h_s \qquad (1)$$

$$HS^-(aq) + OH^-(aq) \rightleftarrows S^{2-}(aq) + H_2O \qquad \Delta h_r \qquad (2)$$

A sample-pairing technique was used to evaluate the molal heat of solution of KHS(c), ΔH_s, and the heat of reaction 2, Δh_r, as follows. From an examination of expression 3 for the equilibrium constant, K_e^0, for reaction 2, it can be seen that the concentration of S^{2-}(aq) formed can be held constant for a pair of runs.

$$K_e^0 = \frac{K_2^0}{K_w^0} = C_\gamma \frac{x}{(a - x)(b - x)} \frac{1000}{g} \qquad (3)$$

$$C_\gamma = \frac{\gamma_{S^{2-}}}{\gamma_{HS^-}\gamma_{OH^-}} \qquad (4)$$

In eq 3 a and b represent the initial moles of KHS used for each run of the pair and x is the equilibrium number of moles of S^{2-}(aq) formed by reaction 2. The factor g is the number of grams of water used in a run (219.0 g at 25° and 211.0 g at 95°). For the first run in a pair, a mol of KHS(c) and a solution containing b mol of KOH were used. For the second run, b mol of KHS and a solution containing a mol of KOH were used. The equilibrium expression, eq 3, is the same for each run of the pair, because only the $(a - x)$ and $(b - x)$ terms in eq 3 have been interchanged. Since K_e^0 is a constant and the ionic strength is held constant, the equilibrium amounts of sulfide, x, must therefore be identical for the pair of runs. Consequently Δh_r is the same for both runs of the pair.

The two simultaneous equations involved are eq 5

$$\Delta h_1 = a\Delta H_s + \Delta h_r \qquad (5)$$

$$\Delta h_2 = b\Delta H_s + \Delta h_r \qquad (6)$$

$$\Delta H_s = \frac{\Delta h_2 - \Delta h_1}{b - a} \qquad (7)$$

and 6. The value of ΔH_s from eq 7 is substituted into either eq 5 or eq 6 to solve for Δh_r (see eq 8). The ini-

$$\Delta h_r = \Delta h_1 - a\Delta H_s \qquad (8)$$

tial thermal data for the paired runs are given in Table I.

Since no numerical value of K_e was required for the above calculations, an accurate value of the heat of solution of KHS(c) to give KHS(aq), ΔH_s, which is independent of the value of K_e, was obtained. However, calculation of the molal heat of reaction 2, ΔH_r, by a method to be described, requires known values for K_e.

Most of the Δh_r values obtained from the paired runs with ionic strengths less than 0.06 m could not be used to calculate ΔH_r. Due to the small amount ($\leq 10^{-4}$ mol) of sulfide formed for these runs, the experimental error in the determination of Δh_r led to a large error in ΔH_r. Consequently, the Δh_r data from paired runs were supplemented with data from unpaired runs up to an ionic strength of 0.22 m. Initial concentrations of KHS from 0.02 to 0.04 m were used for the unpaired runs. The rest of the ionic strength was made up with KOH. This forced the equilibrium of reaction 2 more to the right, forming more sulfide and giving a greater heat of reaction, Δh_r. The thermal data for the unpaired runs are given in Table II.

TABLE I

THERAMAL DATA FOR THE HEAT OF SOLUTION OF KHS(c) IN KOH SOLUTIONS (PAIRED RUNS)

Run no.[a]	Mol of KHS × 10^3	Mol of KOH × 10^3	Δh, cal	ΔH_s, cal mol^{-1}	Δh_r, cal
		24.91°			
1	3.992	8.115	−3.683	−962	0.18[b]
2	8.115	3.992	−7.650		
3	4.178	1.384	−4.108	−1051	0.31[b]
4	1.384	4.178	−1.171		
5	3.945	6.720	−3.869	−1029	0.22[b]
6	6.720	3.945	−6.724		
7	14.87	10.45	−12.923	−863	−0.06
8	10.45	14.87	−9.106		
9[c]	4.374	5.863	−4.018	−967	0.24[b]
10[c]	5.863	4.374	−5.458		
11	6.251	3.880	−5.913	−1001	0.37[b]
12	3.880	6.251	−3.539		
		95.14°			
13	3.927	1.606	−12.774	−3236	0.01[b]
14	1.606	3.927	−5.262		
15	13.094	11.031	−38.637	−3148	2.67
16	11.031	13.094	−32.140		
17	5.809	8.362	−17.908	−3113	0.25
18	8.362	5.809	−25.856		
19	2.626	6.559	−8.284	−3047	−0.20[b]
20	6.599	2.626	−20.390		
21	7.802	10.984	−22.765	−3021	0.88
22	10.984	7.802	−32.378		
23	2.987	5.602	−9.096	−3121	0.30
24	5.602	2.987	−17.259		
25	1.380	2.458	−4.367	−3215	0.15[b]
26	2.450	1.380	−7.833		

[a] The braces indicate paired runs. [b] Not used in the calculations (see text). [c] 8.322 × 10^{-3} mol of KCl was added to these runs to increase the ionic strength.

TABLE II

THERMAL DATA FOR THE HEAT OF SOLUTION OF KHS(c) IN KOH SOLUTIONS (UNPAIRED RUNS)

Run no.	Mol of KHS × 10^3	Mol of KOH × 10^2	Δh, cal
		24.91°	
27	2.092	4.391	−2.253
28	5.317	3.294	−5.311
29	6.545	1.973	−6.158
30	6.367	2.648	−5.772
31	5.176	0.5131	−5.343
32	11.742	0.9548	−11.238
		95.14°	
33	2.256	4.220	−5.964
34	9.638	3.249	−27.019
35	5.691	2.806	−16.172
36	6.539	0.6121	−19.997
37	6.555	1.876	−19.174

Including the experimental difficulties involved when working with KHS(c), the error in the thermal measurements, Δh, was estimated to be about ±0.10 cal. This error limited the precision of Δh_r to ±0.18 cal. A correction of −0.027 cal at 25° and −0.077 cal at 95°

was applied to Δh for the heat associated with breaking an empty sample bulb.

In order to interpret the thermal data, K_e for reaction 2 must be known. Calculation of the number of moles of $S^{2-}(aq)$ formed was necessary for the evaluation of both ΔH_r and the ionic strength of the solutions for extrapolation of the heats to infinite dilution. Values of K_e^0 were calculated from the ionization constant of water, K_w^0, and the second ionization constant for $H_2S(aq)$, K_2^0.

For K_w^0, values of 1.01×10^{-14} at 24.91° and 4.36×10^{-13} at 95.14° were calculated from tabulated values[13] from 0 to 100°. A value of -48.1 ± 4.0 cal mol^{-1} deg^{-1} for the average heat capacity of ionization of water, $\Delta C_p{}^\circ|_{25}^{100}$ (calculated from heat capacity data for HCl(aq) and NaOH(aq),[14] NaCl(aq),[6] and water[15]), and the entropy of ionization[16] at 25°, -19.3 cal mol^{-1} deg^{-1}, were used to smooth the data.

A consistent set of K_2^0 values for H_2S was selected from experimental pK_2^0 values reported over the temperature range 0–90°. This set is given in Table III.

TABLE III

EXPERIMENTAL EQUILIBRIUM CONSTANTS FOR THE SECOND IONIZATION OF $H_2S(aq)$

Temp, °C	pK_2^0 [a]	K_2^0	Exptl method[b]	Ref
0	14.62 ± 0.1	2.40×10^{-14}	Emf, gl	*c*
0	14.7	2.00×10^{-14}	Fp, con	*d*
20	14.15 ± 0.05	7.08×10^{-15}	Emf, gl	*e*
20	14.0 ± 0.1	1.00×10^{-14}	Spect	*f*
22	14.0 ± 0.1	1.00×10^{-14}	Spect	*g*
25	13.78	1.66×10^{-14}	Emf, gl	*c*
30	13.85	1.41×10^{-14}	Spect	*h*
50	12.9 ± 0.2	1.26×10^{-13}	Spect	*g*
90	12.0 ± 0.2	1.00×10^{-12}	Spect	*g*

[a] The error limits are those reported by the authors. [b] Abbreviations: con, conductance; emf, cell measurements; fp, freezing point; gl, glass electrode; spect, spectrophotometric. [c] G. Maronny, *Electrochim. Acta*, **1**, 58 (1959). [d] K. Jellinek and J. Czerwinski, *Z. Phys. Chem.*, **102**, 438 (1922). [e] M. Widmer and G. Schwarzenbach, *Helv. Chim. Acta*, **47**, 266 (1964). [f] A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959). [g] A. J. Ellis and N. B. Milestone, *Geochim. Cosmochim. Acta*, **31**, 615 (1967). [h] S. S. Muhammad and E. V. Sundaram, *J. Sci. Ind. Res., Sect. B*, **20**, 16 (1961).

Values based on solubility,[17] kinetic,[18] and some of the glass electrode methods[19–21] were not used because of the following difficulties. The pK_2 value[17] of 14.92 at 25°, which was obtained from solubility measurements on HgS in sulfide solutions, can be regarded as only approximate for several reasons. Accurate measurement of the solubility of HgS is difficult since the solubility of HgS is extremely low ($K_{sp} \approx 10^{-50}\ M^2$) and the solubility of metal sulfides is known to depend on the age and manner of preparation of the compound.[22] The solubility data and method of calculation of pK_2 suggest errors of ± 1.0 pK unit.

The kinetic method[18] of determining pK_2 is based on the rate of cleavage of diacetone alcohol by hydroxide ions furnished by the hydrolysis of Na_2S. Since various electrolytes have been found to have strong individual effects on the rate of the cleavage reaction,[23] an obvious source of error is that the effect of NaHS on the rate constant is unknown.

Finally, K_2 values obtained from glass electrode methods[19–21] which depend on standardization of the glass electrode with borate buffers (pH ~10), or $Ca(OH)_2$ (pH ~12), were not used because large errors can result from determination of hydroxide activities at high pH using standards of lower pH. The pK_2 values of these determinations were found to be about 1 pK unit lower than the adopted values.

IV. Treatment of Data

An iterative method was used to calculate values of $\Delta F_d{}^\circ(25^\circ)$, $\Delta H_d{}^\circ(25^\circ)$, $\Delta S_d{}^\circ(25^\circ)$, and $\Delta C_{pd}{}^\circ|_{25}^{95}$ for the dissociation of $HS^-(aq)$ and the average value of the heat capacity, $\Delta C_p{}^\circ|_{25}^{95}$, for the solution of KHS (c). The calculations were carried out on a Control Data 6500 computer, and are most conveniently described as a series of steps.

Step 1.—For the first cycle of computations, approximate values of $\Delta F_d{}^\circ(25^\circ)$ and $\Delta S_d{}^\circ(25^\circ)$ for the dissociation of $HS^-(aq)$ and K_e^0 for reaction 2 were estimated from the data summarized in Table III.

Step 2.—The standard heat of solution, $\Delta H_s{}^\circ$, of KHS(c) and the standard heat of reaction 2, $\Delta H_r{}^\circ$, were calculated in this step. The ionic strength of each run was computed from the equilibrium concentrations of HS^-, OH^-, and S^{2-}. Assuming C_γ in eq 3 to be approximately unity as indicated by the data in ref 24 and 25, the sulfide concentration was obtained by substituting the approximate values of K_e^0 and initial bisulfide, $[HS^-]_i$, and hydroxide, $[OH^-]_i$, concentrations into the equilibrium expression

$$K_e^0 = \frac{[S^{2-}]}{([HS^-]_i - [S^{2-}])([OH^-]_i - [S^{2-}])} \tag{9}$$

and solving the resulting quadratic equation for $[S^{2-}]$. The ionic strength, I, was then given by $I = {}^1/_2 \Sigma_i{}^j[m_j(Z_j)^2]$, where m is the molality of the ion and Z is the ionic charge.

The values of ΔH_s from the paired runs were extrapolated to infinite dilution in the usual manner employed in these laboratories[6] by adding a Debye–

---

(13) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chemical Society, London, 1964.

(14) Th. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

(15) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 42nd ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

(16) "Selected Values of Chemical Thermodynamic Properties," Technical Note 270-3, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C. 1965.

(17) J. Knox, *Z. Elektrochem.*, **12**, 477 (1906).

(18) F. W. Kuster and E. Heberlein, *Z. Anorg. Allg. Chem.*, **43**, 53 (1905).

(19) T. A. Tumanova, K. P. Mischenko, and I. E. Flis, *Zh. Neorg. Khim.*, **2**, 1990 (1957).

(20) H. Kubli, *Helv. Chim. Acta*, **29**, 1962 (1946).

(21) S. S. Zavodnov, and P. A. Kryukov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1704 (1960).

(22) I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2711 (1931).

(23) K. Koelichen, *Z. Phys. Chem.*, **33**, 129 (1900).

(24) A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959).

(25) A. J. Ellis and N. B. Milestone, *Geochim. Cosmochim. Acta*, **31**, 615 (1967).

Hückel term to each ΔH_s value. The quantity obtained, ρ_s, is given by the equation

$$\rho_s = \Delta H_s - (\nu/2)|Z_+Z_-|A_H I^{1/2}\alpha = \Delta H_s^\circ - 2.303RT^2\frac{dB}{dT}\nu_+\nu_-I \quad (10)$$

where ν is the number of ions formed from each molecule of salt, Z is the ionic charge, I is the ionic strength, A_H is the Debye–Hückel limiting thermal slope, dB/dT is a constant,[26] and α is expressed in terms of the equation

$$\alpha = (1 + I^{1/2})^{-1} - I^{-3/2}[1 + I^{1/2} - (1 + I^{1/2})^{-1} - 2\ln(1 + I^{1/2})] \quad (11)$$

A linear least-squares analysis of ρ_s *vs.* I yielded an equation of the form

$$\rho_s = \Delta H_s^\circ(T) + L(T)I \quad (12)$$

which has an intercept of $\Delta H_s^\circ(T)$ and a slope $L(T)$.

The molal heat of reaction 2 was calculated from the Δh_r values by expressing the sulfide concentration as

$$[S^{2-}] = \frac{\Delta h_r/\Delta H_r}{g/1000} \quad (13)$$

and substituting this expression into eq 9.

Values for Δh_r from the paired runs and the appropriate initial OH^- and HS^- concentrations could be used directly to calculate ΔH_r. However, Δh_r for the unpaired runs had to be calculated first from the calorimetric data, Δh, a value of Δh_s obtained from eq 12, and the theoretical heat of dilution of KHS(aq) from eq 10; see eq 14, where n is the number of moles of KHS

$$\Delta h_r = \Delta h - \Delta h_s - \Delta h_b = \Delta h - [\Delta H_s^\circ(T) - L(T)I + A_H I^{1/2}\alpha]n - \Delta h_b \quad (14)$$

(c) dissolved and Δh_b is the heat of bulb-breaking correction.

The ΔH_r values were extrapolated to infinite dilution by adding a Debye–Hückel term to each ΔH_r value. In this case, ρ_r is given by

$$\rho_r = \Delta H_r - \sum(\nu/2)|Z_+Z_-|A_H I^{1/2}\alpha = \Delta H_r^\circ - 2.303RT^2(dB/dT)\sum(\nu_+\nu_-)I \quad (15)$$

where $\Sigma(\nu/2)|Z_+Z_-|$ is the sum of $\nu/2|Z_+Z_-|$ for the product ions of the reaction minus the sum of $\nu/2|Z_+Z_-|$ for the reactant ions. After calculation of I, ΔH_r° was obtained by a least-squares extrapolation of ρ_r *vs.* I to zero concentration.

Step 3.—The average heat capacity change, $\Delta C_p^\circ|_{25}^{95}$, for reaction 2 and the dissolution of KHS(c) were calculated from the standard heats at the two temperatures of the calorimetric runs according to the equation

$$\Delta C_p^\circ|_{25}^{95} = \frac{\Delta H^\circ(95.14^\circ) - \Delta H^\circ(24.91^\circ)}{95.14 - 24.91} \quad (16)$$

For the dissociation of HS^-(aq) $\Delta C_{pd}^\circ|_{25}^{95}$ was computed from the sum of $\Delta C_p^\circ|_{25}^{95}$ for reaction 2 and $\Delta C_p^\circ|_{25}^{95}$ for the ionization of water.

Step 4.—The standard heat, $\Delta H_d^\circ(25^\circ)$, and improved values of $\Delta S_d^\circ(25^\circ)$ and $\Delta F_d^\circ(25^\circ)$ for the dissociation of HS^-(aq) were calculated in this step. $\Delta H_d^\circ(25^\circ)$ is equal to the sum of $\Delta H_r^\circ(25^\circ)$ and $\Delta H^\circ(25^\circ)$ for the ionization of water. $\Delta S_d^\circ(25^\circ)$ was calculated from $\Delta H_d^\circ(25^\circ)$ and the value of $\Delta F_d^\circ(25^\circ)$ from the previous cycle of calculations.

The evaluation of $\Delta C_{pd}^\circ|_{25}^{95}$ in step 3 and $\Delta S_d^\circ(25^\circ)$ in this step allowed the calculation of an improved third-law value of $\Delta F_d^\circ(25^\circ)$ which is based on the entire set of nine experimental K_2^0 values from 0 to 90°. The equation for the average value of $\Delta F_d^\circ(25^\circ)$ obtained from the nine K_2^0 values is

$$\Delta F_d^\circ(25^\circ) = \frac{1}{9}\sum_1^9\{-RT\ln K_2^0 + \Delta S_d^\circ(25^\circ)\Delta T - a(T)\Delta C_{pd}^\circ|_{25}^{t} \quad (17)$$

where ΔT is equal to $(T - 298.15^\circ K)$ and $a(T)$ is $\Delta T - T\ln(T/298.15)$. The use of $\Delta C_{pd}^\circ|_{25}^{95}$ for $\Delta C_{pd}^\circ|_{25}^{t}$ in eq 17 introduces little error into the calculations.

Steps 2–4 were repeated until constant values of the standard-state functions were obtained.

V. Results and Discussion

Table IV gives the final values of ρ_s and ΔH_s° obtained for the dissolution of KHS(c), and Table V gives the final values of ΔH_r, ρ_r, and ΔH_r° for reaction 2. The results for the least-squares analysis of ρ_s *vs.* I and ρ_r *vs.* I are shown in Figures 1 and 2, respectively.

TABLE IV

HEAT OF SOLUTION OF KHS(c)

Run pair no.	Ionic strength × 10^2	ΔH_s, cal mol^{-1}	$-A_H I^{1/2}\alpha$, cal mol^{-1}	ρ_s, cal mol^{-1}
		24.91°		
1, 2	5.625	−962	−92	−1054
3, 4	2.558	−1051	−65	−1116
5, 6	4.948	−1029	−87	−1116
7, 8	11.99	−863	−126	−989
9, 10	8.546	−967	−110	−1077
11, 12	4.699	−1001	−86	−1087
$\Delta H_s^\circ = -1156 \pm 16$ cal mol^{-1} ($d\rho_s/dI = 1.4 \times 10^3$)				
		95.14°		
13, 14	2.647	−3236	−170	−3406
15, 16	11.94	−3148	−323	−3471
17, 18	6.898	−3113	−258	−3371
19, 20	4.439	−3047	−214	−3261
21, 22	9.215	−3021	−291	−3312
23, 24	4.136	−3121	−207	−3328
25, 26	1.833	−3215	−144	−3359
$\Delta H_s^\circ = -3317 \pm 44$ cal mol^{-1} ($d\rho_s/dI = -7.1 \times 10^2$)				

Average Partial Molal Heat Capacity of Aqueous Potassium Bisulfide and the Bisulfide Ion.—A value of −30.8 ± 0.7 cal mol^{-1} deg^{-1} was calculated for $\Delta C_p^\circ|_{25}^{95}$ for the dissolution of KHS(c) from the standard heats of solution at 24.91 and 95.14°. Although the heat capacity of KHS(c) has not been measured, $C_{p_2}|_{25}^{95}$ was estimated to be 17.0 ± 2 cal mol^{-1} deg^{-1}

---

[26] G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N. Y., 1961, p 640.

TABLE V

HEAT OF REACTION FOR

$KHS(aq) + KOH(aq) \rightleftarrows K_2S(aq) + H_2O$

Run no.	Ionic strength × 10	Mol of S^{2-}(aq) formed × 10^4	ΔH_r, cal mol^{-1}	$-A_H I^{1/2}\alpha$, cal mol^{-1}	ρ_r, cal mol^{-1}
		24.91°			
7, 8[a]	1.199	9.389	−66	−126	−192
27	2.213	4.921	−1541	−158	−1698
28	1.792	9.818	−1277	−148	−1424
29	1.235	7.753	−684	−128	−812
30	1.544	9.745	−664	−140	−804
31	0.4786	1.755	−719	−86	−805
32	1.004	6.931	−961	−118	−1079
$\Delta H_r^\circ = -226 \pm 386$ cal mol^{-1} ($d\rho_r/dI = -5.6 \times 10^3$)					
		95.14°			
15, 16[a]	1.194	10.64	2506	−323	2183
17, 18[a]	0.6898	3.840	654	−258	396
21, 22[a]	0.9215	6.551	1348	−291	1057
23, 24[a]	0.4136	1.382	2207	−207	2000
33	2.136	6.081	1683	−405	1278
34	2.094	20.51	1268	−402	866
35	1.652	10.99	1236	−367	869
36	0.6152	3.201	1392	−246	1146
37	1.243	8.972	1196	−328	868
$\Delta H_r^\circ = 1391 \pm 402$ cal mol^{-1} ($d\rho_r/dI = -1.7 \times 10^3$)					

[a] Paired runs.

from the known values[27] on KOH(c). The average partial molal heat capacity of KHS(aq), $\bar{C}_{p_2}{}^\circ|_{25}^{95}$, was found to be -13.8 ± 2 cal mol^{-1} deg^{-1}. Taking the value[28] of 35 cal mol^{-1} deg^{-1} for $\bar{C}_p{}^\circ|_{25}^{100}$ of K$^+$(aq) (based on the scale that $\bar{C}_p{}^\circ|_{25}^{100}$ of H$^+$(aq) is 31 cal mol^{-1} deg^{-1}) and noting that the difference between $\bar{C}_p{}^\circ|_{95}^{25}$ and $\bar{C}_p{}^\circ|_{25}^{100}$ is insignificant, a value of -48.8 ± 2 cal mol^{-1} deg^{-1} was obtained for $\bar{C}_p{}^\circ|_{25}^{100}$ of HS$^-$(aq).

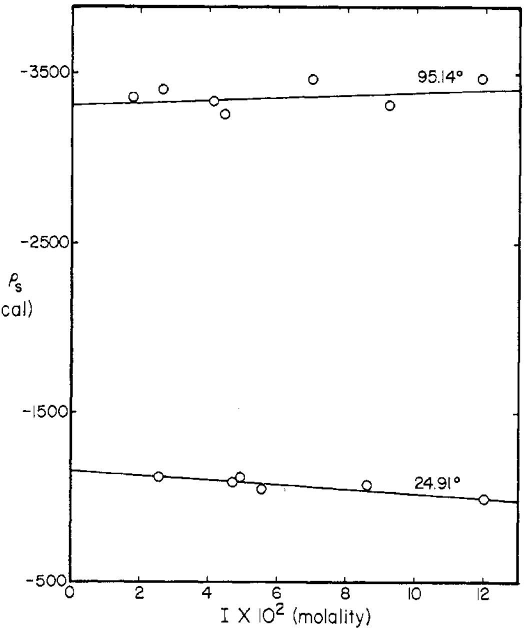

Figure 1.—ρ_s values of KHS as a function of ionic strength and temperature.

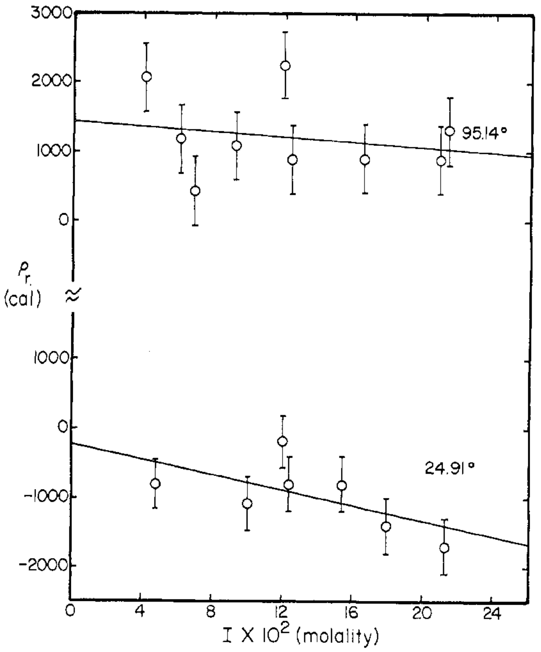

Figure 2.—ρ_r values for KHS(aq) + KOH(aq) = K$_2$S(aq) + H$_2$O as a function of ionic strength and temperature.

Thermodynamic Functions for the Aqueous Sulfide Ion.—From ΔH_r° at 24.91 and 95.14°, $\Delta C_{p_r}{}^\circ|_{25}^{95}$ [$\approx \Delta C_{p_r}{}^\circ|_{25}^{100}$] was computed to be 23 ± 8 cal mol$^-$ deg^{-1}. Using the previously calculated value of -48.1 ± 4 cal mol^{-1} deg^{-1} for $\Delta C_p{}^\circ|_{25}^{100}$ for the dissociation of water, $\Delta C_{p_d}{}^\circ|_{25}^{100}$ for the dissociation of HS$^-$(aq) is -25 ± 9 cal mol^{-1} deg^{-1}. From $\Delta C_{p_d}{}^\circ|_{25}^{100}$, $C_p{}^\circ|_{25}^{100}$ of HS$^-$(aq), and the value[28] of 31 cal mol^{-1} deg^{-1} for $\bar{C}_p{}^\circ|_{25}^{100}$ of H$^+$(aq), $\bar{C}_p{}^\circ|_{25}^{100}$ of S^{2-}(aq) was calculated to be -105 ± 9 cal mol^{-1} deg^{-1}.

The value computed for $\Delta S_d^\circ(25°)$, -19.1 ± 2 cal mol^{-1} deg^{-1}, combined with the latest value[16] of 15.0 cal mol^{-1} deg^{-1} for $\bar{S}^\circ(25°)$ of HS$^-$(aq), yielded a value of -4.1 ± 2 cal mol^{-1} deg^{-1} for the entropy of S^{2-}(aq) at 25°.

A value of 13.1 ± 0.4 kcal mol^{-1} for the standard heat of dissociation of HS$^-$(aq) at 25° was calculated from the standard heat of ionization of water,[16] 13.345 kcal mol^{-1}, and ΔH_r°. The value obtained for the standard free energy of dissociation of HS$^-$(aq) was 18.8 ± 0.2 kcal mol^{-1}. Values of 8.9 ± 0.4 kcal mol^{-1} for $\Delta H_f^\circ(25°)$ and 21.7 ± 0.2 kcal mol^{-1} for $\Delta F_f^\circ(25°)$ of S^{2-}(aq) were calculated from the above values of $\Delta H_d^\circ(25°)$ and $\Delta F_d^\circ(25°)$, and values[16] of -4.2 and 2.88 kcal mol^{-1} for ΔH_f° and ΔF_f°, respectively, of HS$^-$(aq). A summary of the thermodynamic functions calculated for sulfide and bisulfide is given in Table VI.

It must be noted that the thermodynamic properties calculated above are based on the set of independent measurements of K_2^0 given in Table III. However, it can be shown that if each value of K_2^0 in the set is in error by as much as ±60%, $\Delta C_{p_d}{}^\circ|_{25}^{100}$ for the dissociation of HS$^-$(aq) will change by only ±10 cal mol^{-1} deg^{-1}, $\Delta S_d^\circ(25°)$ by ±1.5 cal mol^{-1} deg^{-1}, and $\Delta F_d^\circ(25°)$ by ±0.28 kcal mol^{-1}.

---

(27) W. D. Powers and G. C. Blalock, U. S. Atomic Energy Commission, ORNL-1653, 1954.

(28) C. M. Kriss and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5390 (1964).

TABLE VI

SUMMARY OF THERMODYNAMIC FUNCTIONS

	$\Delta F_f°(25°)$, kcal mol^{-1}	$\Delta H_f°(25°)$, kcal mol^{-1}	$S°(25°)$, cal mol^{-1} deg^{-1}	$\bar{C}_p°\|_{25}^{100}$, cal mol^{-1} deg^{-1}
KHS(c)	...	−63.08	$(19 \pm 1)^a$	$(17 \pm 2)^a$
KHS(aq)	−64.58	−64.24	39.5	-13.8 ± 2
HS^-(aq)	2.88^b	-4.2^b	15.0^b	-48.8 ± 2
S^{2-}(aq)	21.7 ± 0.2	8.9 ± 0.4	-4.1 ± 2	-105 ± 9
H^+(aq)	0	0	0	31^c

[a] Estimated quantities. [b] Reference 16. [c] Reference 28.

Even though various values for the heats and free energies of formation of the aqueous sulfide ion have been reported from time to time, the adopted values for the entropy of the ion have remained rather constant. For example, during the last 30 years values ranging from −3.5 to −6.4 cal mol^{-1} deg^{-1} have been reported[9,16,29,30] and these are essentially reconfirmed by the results of this research. One of the objectives of the present work was to try to resolve the apparent discrepancy between the predicted[31] entropy of −20 cal mol^{-1} deg^{-1} for S^{2-}(aq) and the more positive experimentally determined values. The present research on the heat capacity of S^{2-}(aq) is in a similar situation, in that the predicted value[28] of $\bar{C}_p°|_{25}^{100} = -58$ cal mol^{-1} deg^{-1} is considerably different from our experimental value of $\bar{C}_p°|_{25}^{100} = -105$ cal mol^{-1} deg^{-1}. In fact, both the entropy and heat capacity function for S^{2-}(aq) closely resemble those for SO_4^{2-}(aq), which has entropy and $\bar{C}_p°|_{25}^{100}$ values of 4.8 and −108 cal mol^{-1} deg^{-1}, respectively. There is no evidence that aqueous sulfide and sulfate are structurally similar in water. However, the structurally sensitive thermodynamic functions do suggest that sulfide is either a more complex species in water than previously suspected or, alternatively, that its hydration sphere is not bound as tightly as predicted from other simple ions.

Temperature Dependence of pK_2^0 of H_2S(aq) to 250°.—Equation 18 which gives the variation of pK_2^0 as a function of temperature was derived by substituting

$$pK_2 = \frac{4500}{T} + 12.6 \log (T/298.15) - 1.29 \qquad (18)$$

the values of $\Delta F_d°(25°)$, $\Delta S_d°(25°)$, and $\Delta C_{pd}°|_{25}^{100}$ into the equation

$$\Delta F_d°(T) = \Delta F_d°(25°) - \Delta S_d°(25°)\Delta T + a(T)\Delta C_{pd}°|_{25}^{95}$$

recognizing that

$$\Delta F_d°(T) = 2.303RT pK_2^0 \qquad (19)$$

Because of the importance of H_2S in high-temperature aqueous processes, it is of interest to estimate K_2^0 for this species above 100°. For the dissociation of HSO_4^-(aq), $\Delta C_p°$ was reported not to change very rapidly above 90°. Assuming that $\Delta C_p°$ for the dissociation of HS^-(aq) behaves similarly, an extrapolation of pK_2^0, according to eq 18, can be made to 250°.

Comparison of the thermodynamic properties for the dissociation of HS^-(aq) and H_2O shows a remarkable similarity in the two weak acids. The value of pK_2^0 for H_2S(aq) is only 0.2 unit lower than pK_w^0 at 25°. This difference remains almost constant to 100° because of the nearly identical values of $\Delta S_d°(25°)$ for the dissociation reactions. Aqueous bisulfide does become slightly more acidic with increasing temperature than H_2O, as the values of $\Delta C_{pd}°|_{25}^{100}$ indicate. This means that significant concentrations of sulfide in solutions of moderate hydroxide concentration will be obtained only at temperatures much higher than 100°.

---

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

(30) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(31) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

The Vibrational Spectrum and Force Field of Osmium Tetroxide[1]

BY ROBIN S. McDOWELL* AND MAXWELL GOLDBLATT

Received June 15, 1970

Infrared spectra of the vapor and infrared and Raman spectra of CCl_4 solutions are reported for $Os^{16}O_4$ and $Os^{18}O_4$. Particular attention was given to measurement of the isotopic frequency shifts and the band contours, from which the Coriolis interaction constants are obtained. Anharmonicity corrections are estimated and the resulting harmonic frequencies are used to determine the general quadratic force constants of this molecule. The relative effectiveness of Coriolis constants and frequency shifts in determining the force field is compared. The valence stretching force constant, f_r = 8.32 mdyn/Å, supports the assumption of appreciable double-bond character for the Os–O bond. Standard-state thermodynamic functions for OsO_4 vapor are calculated for the temperature range 273–600°K.

Introduction

The vibrational spectrum and force constants of osmium tetroxide present a surprisingly vexing problem for such a simple molecule. OsO_4 has been shown to be tetrahedral (point group T_d) by electron diffraction of the vapor[2a] and by X-ray diffraction of the solid.[2b] The distribution of vibrational fundamentals for such

---

[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. M. Seip and R. Stølevik, *Acta Chem. Scand.*, **20**, 385 (1966); (b) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **19**, 157 (1965).