[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRIGHAM YOUNG UNIVERSITY]

Thermodynamic Properties of Silver Sulfide[1]

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By means of electromotive force measurements on cells of the types

$$\text{Ag, Ag}_2\text{S}\ \left|\ \begin{array}{c}\text{H}_2\text{S}\\ (1\ \text{atm.})\end{array}\ \right|\ \begin{array}{c}\text{HCl}\\ (0.1\ \text{molal})\end{array}\ \left|\ \begin{array}{c}\text{HCl}\\ (0.1\ \text{molal})\end{array}\ \right|\ \begin{array}{c}\text{H}_2\text{, Pt}\\ (1\ \text{atm.})\end{array}$$

and

$$\text{Ag, Ag}_2\text{S}\ |\ \text{S}^{=}\ \|\ \text{normal calomel},$$

various thermodynamic properties of the reactions

$$2\text{Ag(s)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{Ag}_2\text{S(s)} + \text{H}_2\text{(g)}$$

and

$$2\text{Ag(s)} + \text{S}^{=}\text{(aq)} \rightleftharpoons \text{Ag}_2\text{S(s)} + 2\text{e}$$

have been determined. From these values and data from other sources for the thermodynamic constants of sulfide ion, solid silver, hydrogen gas and hydrogen sulfide gas, the following thermodynamic constants of silver sulfide have been calculated: $\Delta F_f^\circ = -9.562$ kcal./mole, $\Delta H_f^\circ = -7.93$ kcal./mole, $S^\circ = 33.6$ e.u., and $K_{sp} = 6.2 \times 10^{-52}$.

Wide discrepancies are found in the values quoted in various standard sources for the standard free energy of formation (ΔF_f°), standard heat of formation (ΔH_f°), standard entropy (S°), and solubility product constant (K_{sp}) of many of the metal sulfides. A check on the original source of these data shows that the experimental measurements from which these values have been determined are fairly old. It seems desirable, therefore, to make a complete re-determination of the thermodynamic properties of some of the important metal sulfides. This paper is a report on the results of an electrochemical measurement of the ΔF_f°, ΔH_f°, S° and K_{sp} of silver sulfide.

Cell Type I

The first cell studied is of the type previously used by Noyes and Freed[2]:

$$\text{Ag, Ag}_2\text{S}\ \left|\ \begin{array}{c}\text{H}_2\text{S}\\ (1\ \text{atm.})\end{array}\ \right|\ \begin{array}{c}\text{HCl}\\ (0.1\ \text{molal})\end{array}\ \left|\ \begin{array}{c}\text{HCl}\\ (0.1\ \text{molal})\end{array}\ \right|\ \begin{array}{c}\text{H}_2\text{, Pt}\\ (1\ \text{atm.})\end{array}$$

the over-all reaction for which is

$$2\text{Ag(s)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{Ag}_2\text{S(s)} + \text{H}_2\text{(g)}$$

This cell has the desirable features of its electromotive force being independent of the acid concentration, independent of pressure, and free from liquid junction potential. The Nernst equation for the cell reaction is

$$\epsilon = \epsilon^\circ - (RT/n\mathbf{F}) \ln \left[(a_{\text{Ag}_2\text{S}} \cdot f_{\text{H}_2})/(a_{\text{Ag}}^2 \cdot f_{\text{H}_2\text{S}})\right]$$

Since the silver and silver sulfide are both solids, and since calculations show the ratio of $f_{\text{H}_2}/f_{\text{H}_2\text{S}}$ at one atmosphere pressure to be so near to unity that the result of any corrections for deviation of this quantity from unity is within the limits of the experimental error, the measured electromotive force (ϵ) may be taken as the standard electromotive force (ϵ°).

Experimental.—The cell containers were 100-ml. Berzelius beakers fitted with rubber stoppers through which openings were made for inserting the electrode housing, the hydrochloric acid bridge connecting the half cells, and the outlet tube for the hydrogen and hydrogen sulfide gases, which entered through side arms in the electrode housing. Internal contact between half cells at the time of taking a reading was made through a capillary bridge containing hydrochloric acid solution of the same concentration as that present in the cells. Siphoning across the bridge during the readings was prevented by allowing the solutions to siphon to the same level previous to beginning the flow of gases through the system. The bridge was withdrawn after each reading, and was rinsed and refilled just before being inserted for the next reading in order to prevent diffusion through the connection.

The silver–silver sulfide electrodes were prepared by electroplating silver from a 4% silver nitrate solution onto a spiraled platinum wire, and then forming the sulfide coating either by anodic precipitation of the sulfide from a one molar solution of sodium sulfide or simply by bubbling hydrogen sulfide gas over the electrodes for several minutes. Electrodes prepared either way required 6 to 8 hours to reach an equilibrium voltage.

The hydrogen sulfide gas that was used with these electrodes was obtained from the Matheson Co., Joliet, Illinois. Minimum purity of 99.9%, with possible traces of metallic chlorides as impurities, was claimed by the manufacturers. This gas was washed and brought to the desired temperature in a train consisting of two 500-ml. flasks of saturated barium hydroxide solution, two flasks of distilled water, and one flask of hydrochloric acid of the same concentration as the acid in the cells.

The hydrogen half cells were prepared in the conventional way.[3] The electromotive force of the cells was read with a Leeds and Northrup type K-2 potentiometer. A recently calibrated Eppley cell was used as the standard cell. Measurements of temperatures were made with an N.B.S.-calibrated mercury-in-glass thermometer. Constant temperatures were maintained to within 0.05°, of the desired temperature.

Results.—Table I records the results of electromotive force measurements on six cells of the type described above. Average deviation from the mean electromotive force values reported in the table is 0.0001 volt. The ΔF° values are calculated from the relationship $\Delta F^\circ = -n\mathbf{F}\epsilon^\circ$, using the value of 23,061 cal. abs. v.$^{-1}$ g. equiv.$^{-1}$ for Faraday's constant.

TABLE I

$$2\text{Ag(s)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{Ag}_2\text{S(s)} + \text{H}_2\text{(g)}$$

T, °C.	5.00	25.00	45.00
ϵ, abs. v.	0.0382	0.0362	0.0340
ΔF°, kcal.	−1.762	−1.670	−1.568

The arithmetical average of $\Delta\epsilon^\circ/\Delta T$ measured from 5° to 25° and from 25° to 45° was found to be -1.05×10^{-4} volts/degree. The ΔS° of the cell reaction at 25°, calculated from this value by means of the expression $\Delta S^\circ = n\mathbf{F}(\partial\epsilon^\circ/\partial T)_p$, was found to be −4.8 e. u. The ΔH° of the cell

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[1] Presented at the Pacific Division Meeting of the American Association for the Advancement of Science, June, 1950.

[2] A. A. Noyes and E. S. Freed, THIS JOURNAL, **42**, 476 (1920).

[3] F. Daniels, J. H. Mathews, J. W. Williams, and Staff, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 198–199.

reaction at 25°, calculated from the expression $\Delta H^\circ = -n\mathbf{F}\epsilon^\circ + n\mathbf{F}T(\partial\epsilon^\circ/\partial T)_p$, was found to be −3.11 kcal. These values for the cell reaction, together with ΔF_f°, ΔH_f° and S° data from other sources for hydrogen gas, hydrogen sulfide gas, and solid silver make possible a calculation of the ΔF_f°, ΔH_f° and S° of silver sulfide. Table II records these data.

Table II

Thermodynamic Properties of Silver Sulfide at 25° and the Data[4] Used in Calculating These Values

	H_2(g)	H_2S(g)	Ag(s)	Ag_2S(s)
ΔF_f°, kcal.	0.000	−7.892	0.000	−9.562
S°, e.u.	31.211	49.15	10.206	33.6
ΔH_f°, kcal.	0.000	4.815	0.000	−7.93

Cell Type II

To provide a check on the free energy of formation value of silver sulfide, measurements were made on a second type of cell

$$\text{Ag, Ag}_2\text{S} \mid \text{S}^{=}(x\text{ molal}) \parallel \text{normal calomel}$$

the half cell reaction of which is

$$2\text{Ag(s)} + \text{S}^{=} \rightleftarrows \text{Ag}_2\text{S} + 2\text{e}$$

The electromotive force of the Ag, Ag_2S, $S^=$ half cell is given by the Nernst equation as

$$\epsilon = \epsilon^0 + (RT/n\mathbf{F}) \ln a_{\text{S}^=}$$

This type of cell lacks some of the advantages of the cell previously described in that there is some uncertainty as to junction potential, and the measured electromotive force is a function of the activity of the sulfide ion in the cell.

Sodium sulfide solutions were used as the source of sulfide ions in these experiments, and the activity of the sulfide ion was calculated from its hydrolysis constant. Of the two steps in the hydrolysis

$$\text{S}^{=} + \text{H}_2\text{O} \rightleftarrows \text{HS}^- + \text{OH}^-$$

and

$$\text{HS}^- + \text{H}_2\text{O} \rightleftarrows \text{H}_2\text{S} + \text{OH}^-$$

only the first needed to be considered, since the hydrolysis constant of the second step is of the order of 10^{-7}, and has, therefore, a negligible effect on the sulfide ion concentration of the basic solutions of sodium sulfide. The hydrolysis constant of the first step, $K_{h_1} = (a_{\text{HS}^-})\cdot(a_{\text{OH}^-})a_{\text{S}^=} = 10$ was calculated from the relationship $K_{h_1} = K_w/K_i$, using the value of 1.0×10^{-14} for K_w and 1.0×10^{-15} for K_i. The activity of the sulfide ion was found by substituting the activities of the hydroxyl and bi-sulfide ions into this expression. The activities of these ions were obtained from their analytically determined concentrations and Debye–Hückel theory. Since considerable hydrogen sulfide gas is lost when sodium sulfide is first added to water, the concentration of the bi-sulfide and hydroxyl ions are not the same, and it was necessary, therefore, to make separate determinations of the concentrations of these ions.

The hydroxyl ion concentration was obtained in terms of the sulfide ion and bisulfide ion concentrations from the relationship

$$[\text{OH}^-]_{\text{present}} = [\text{OH}^-]_{\text{total}} - [\text{HS}^-] - 2[\text{S}^=]$$

in which the brackets refer to molal concentrations. The total hydroxyl ion concentration is the hydroxyl ion produced by complete hydrolysis of sodium sulfide, and was determined by back-titrating an aliquot of the solution that had been treated with an excess of acid and heated to drive off all hydrogen sulfide.

The bi-sulfide ion concentration was expressed as the difference between the concentration of total sulfides (sulfide plus bi-sulfide) and the unknown sulfide ion concentration. The concentration of total sulfides was determined volumetrically by oxidation with calcium hypochlorite.[5]

Results.—The standard electromotive force of the Ag, Ag_2S, $S^=$ electrode determined from measurements on eight cells at four sodium sulfide concentrations (0.1 molal to 0.005 molal) is 0.7125 ± 0.0004 absolute volt, from which the value of the ΔF° of the half cell reaction is found to be −32.87 kcal. From this information and the value of 23.42 kcal. for the ΔF_f° of the sulfide ion, we obtained −9.45 kcal./mole for the ΔF_f° of silver sulfide.

Discussion

Measurements of the ΔF_f° of silver sulfide from the two types of cells are in agreement within the limits of accuracy of the value obtained from the second type cell. Estimates of accuracy, based chiefly upon temperature control, reproducibility of electromotive force readings, and accuracy of the thermodynamic constants used in the calculations are indicated by the number of significant figures reported.

Solubility Product Constant.—The solubility product constant of silver sulfide may be calculated from the standard free energy change of the reaction

$$\text{Ag}_2\text{S} \rightleftarrows 2\text{Ag}^+ + \text{S}^=$$

by means of the expression $\ln K = -\Delta F^\circ/RT$. Using our value of −9.562 kcal. for the ΔF_f° of silver sulfide and 18.43 kcal. and 23.42 kcal. for the ΔF_f° of the silver and sulfide ions, respectively, we calculated K_{sp} of silver sulfide at 25° to be 6.2×10^{-52}.

Acknowledgment.—The authors are grateful to Dr. F. D. Rossini for supplying us with a copy of "Selected Values of Chemical Thermodynamic Properties" previous to its publication. We wish also to express appreciation to Professor J. K. Nicholes for suggesting this investigation and for his interest in it.

Provo, Utah Received July 24, 1950

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(4) The thermodynamic constants for hydrogen, hydrogen sulfide and silver were taken from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, to be published by the U. S. Govt. Printing Office later this year.

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1938, p. 558.