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An electrochemical determination of the free energy of formation and solubility product constant of silver and mercury sulfides

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AN ELECTROCHEMICAL DETERMINATION OF THE FREE ENERGY OF FORMATION AND SOLUBILITY PRODUCT CONSTANT OF SILVER AND MERCURY SULFIDES

A Thesis
Presented to
The Faculty of the Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
Earl L. Gray
May 1950

This thesis by Earl L. Gray is accepted in its present form by the Department of Chemistry as satisfying the thesis requirement for the degree of Master of Science.

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CHAPTER I

INTRODUCTION TO THE PROBLEM

In the chemical literature there exist many discrepancies in the values reported for such useful thermodynamic properties as the standard free energy of formation and solubility product constant of many of the important metal sulfides. (See Table 1). A review of the development of solubility product constant data makes clear how such inconsistencies have arisen. The early work in this field was done just after the turn of the nineteenth century. Two papers during this period, one by Weigel[1] and one by Bruner and Zawadski[2], are especially significant. Their data were quoted in nearly all textbooks of inorganic chemistry and qualitative analysis until 1931, at which time Kolthoff[3] made a critical study of the available solubility product constant data of metal sulfides and completely discredited their results. Kolthoff obtained a better set of constants by correcting the results of various other early investigations for hydrolysis of the sulfide ion. Although Kolthoff's paper in 1931 made a big step forward by eliminating ridiculous values for the constants of

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[1] O. Weigel, Z. physik. Chem., 58, 294 (1907).

[2] L. Bruner and J. Zauadski, Z. anorg. Chem., 65, 136 (1909).

[3] I. M. Kolthoff, J. Phys. Chem., 35, 2711 (1931).

TABLE I

SOLUBILITY PRODUCT CONSTANTS OF METALLIC SULFIDES FROM VARIOUS SOURCES

Source	Solubility Product Constant				
	Bi_2S_3	SnS	MnS	NiS	ZnS
Handbook of Chem. and Phys. Chem. Rubber Pub. Co., 1947	-----	-----	1.4×10^{-15}	1.4×10^{-24}	1.2×10^{-23}
Oxidation Potentials Latimer	1.6×10^{-72}	8×10^{-29}	5.6×10^{-16}	3×10^{-22}	4×10^{-24}
Quant. Inorganic Anal. Kolthoff and Sandell	1.6×10^{-72}	-----	7×10^{-16}	1.1×10^{-27}	7×10^{-26}
The Theory and Practice of Semimicro Qual. Anal. Heisig	1.6×10^{-72}	-----	5.6×10^{-16}	3×10^{-21}	4.5×10^{-24}
General Inorganic Chemistry, Sneed and Maynard	-----	-----	5.6×10^{-16}	3×10^{-21}	-----
Introduction to Qual. Anal. Walton and Sorum	-----	-----	1.4×10^{-15}	1.4×10^{-24}	1.2×10^{-23}

several sulfides, he made no new experimental measurements and admitted the need for more reliable experimental data.

In 1936 Ravitz,[4] with the aid of new activity data, made a number of recalculations of old electromotive force measurements to obtain a new set of values for the solubility product constants of several metal sulfides. The use of activities in his recalculations resulted in an improvement over Kolthoff's values, but Ravitz, like Kolthoff, made no new experimental measurements.

Solubility product constant and free energy of formation data for the metal sulfides were again reviewed in 1938 by Latimer[5] in his book Oxidation Potentials. Best values were chosen by Latimer from all work reported previous to 1938. Latimer's book also contains some new data on free energies of formation calculated by combining available heat of formation data with somewhat questionable estimates of entropy data in the Third-Law calculation. A detailed criticism and evaluation of all work previous to the study described in this thesis are presented in Chapter II.

Because present data on free energy of formation and solubility product constants of the metal sulfides are both inconsistent and based on very old experimental data, a new

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[4] S. F. Ravitz, J. Phys. Chem., 40, 67 (1936).

[5] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, 1938, p. 178.

study using modern techniques is amply justified. Because metal sulfide precipitates are often colloidal[6] and because the solubility of these sulfides is so low, ordinary physical and analytical methods are not applicable to a direct determination of the solubility product constant. Therefore, a more reliable thermodynamic approach was undertaken in this study. The standard free energy of formation of silver and mercury sulfide was determined from electromotive force measurements of suitable galvanic cells, and the solubility product constants calculated from the free energy measurements. This study is part of a large program extending to other metal sulfides and to other thermodynamic properties.

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[6] *Ibid.*

CHAPTER II

REVIEW OF THE LITERATURE

Three general methods of approach have been used by past investigators for obtaining the free energy of formation and the solubility product constant of the metal sulfides. These three general methods are Third-Law calculations, equilibrium studies, and electromotive force determinations. They will be discussed in this order for silver and mercury sulfides.

SILVER SULFIDE

Standard Free Energy of Formation. Latimer[1] calculated the standard free energy of formation of silver sulfide using a Third-Law calculation. In this calculation he used 5,500 cal/mole as the standard heat of formation of silver sulfide, reported by Bichowsky and Rossini[2], and 35 e.u. as the entropy value of silver sulfide, reported by Kelley[3]. Latimer obtained -7600 cal/mole as the standard free energy of formation of silver sulfide from this Third-Law calculation. In a like manner, using Thomsen's[4] value for the standard heat of formation and the same entropy value (35 e.u.), he calculated the standard free energy of formation of silver sulfide

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[1] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, 1938, p. 178.

[2] R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936, p. 78.

[3] K. K. Kelley, U.S. Bur. Mines Bull., 406, 63 (1937).

[4] Thomsen, "Thermochemische Untersuchungen," vol. IV, (1886).

to be -9,000 cal/mole.

These Third-Law calculations are in poor agreement with each other because of the inconsistency of heat of formation data listed for silver sulfide. However, these calculations are ridiculous, even if reliable heat of formation data had been used, because Kelley calculated his entropy value from the equation $\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ$ which contains the free energy of formation of silver sulfide as one of its terms. It is obvious that any calculation of the free energy of formation of silver sulfide involving Kelley's entropy value will be no more correct than the free energy value Kelley used in determining the entropy value.

Kelley in his entropy calculation used -8,580 cal/mole for the free energy of formation of silver sulfide, which is a weighted mean of the work of Jellinek and Zakowski,[5] Watanabe,[6] and Keyes and Felsing.[7] These investigators independently studied the equilibrium involved in the reduction of silver sulfide with hydrogen gas at high temperatures (above 450°K). From their measurements they calculated the equilibrium constants for the reaction $Ag_2S + H_2 = H_2S + 2Ag$

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[5] K. Jellinek and J. Zakowski, Z. anorg. Chem., 142, 1 (1925).

[6] M. Watanabe, Science Reports Tohoku Imp. Univ., 22, 902 (1933).

[7] F. S. Keyes and W. A. Felsing, J. Am. Chem. Soc., 42, 246 (1920).

at various temperatures.

According to Kelley,[8] two forms of silver sulfide exist: the low temperature or αform existing below 448° K and the high temperature or βform existing above 448° K. Jellinek and Zakowski, Watanabe, and Keyes and Felsing all made their equilibrium studies above the transition point and were therefore working with the high temperature form and not the low temperature form encountered in qualitative analysis. The absence of very detailed heat capacity data makes calculation of the standard free energy of formation of silver sulfide at 25° from these high temperature data not completely reliable.

Kokichi[9] also studied the reaction $Ag_2S + H_2 = 2Ag + H_2S$ at various temperatures between 490° and 660° K. From his equilibrium measurements he calculated the free energy of the reaction $2Ag + S_{(rhombic)} = Ag_2S$ at 25° to be -9,736 cal/mole. Kokichi's value for the free energy of formation of silver sulfide would also be for the high temperature form. The same criticism as was applied to the data of Jellinek and Zakowski, Watanabe and Keyes and Felsing could be applied to Kokichi's data also.

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[8] Kelley, *op. cit.*, p. 64.

[9] K. Sano, *Science Reports Tohoku Imp. Univ., First Sec.*, *25*, 187-96 (1936).

The standard free energy of formation of silver sulfide was determined by Noyes and Freed[10] by measuring the equilibrium constant of the reaction:

$Ag_2S_{(s)} + 2H^+, I^-_{(in\ water)} = 2AgI + H_2S_{(in\ water)}$ at 25° C. The standard free energy change of the reaction is related to the equilibrium constant by the equation $\Delta F^\circ = -RT \ln K$. The mean equilibrium constant, as derived from their experimental data, was 964. Using this value for K in the equation, the free energy change of the reaction was calculated. From this free energy change and from the known free energies of formation of the other compounds involved in the reaction, the free energy of formation of silver sulfide was calculated to be -9,425 cal/mole. It should be remembered that the relationship between the standard free energy change of a reaction and the equilibrium constant of this reaction is valid only when the equilibrium constant is determined by using activities and not concentrations. Noyes and Freed in their calculations of the equilibrium constants used concentrations and not activities.[11] For this reason, their value of the free energy of formation of silver sulfide should not be weighted too heavily.

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[10] Noyes and Freed, J. Am. Chem. Soc., 42, 476 (1920).

[11] Arthur Cole, "Electrochemical Determination of the Thermodynamic Properties of Silver and Mercury Sulfides," Master's Thesis, Brigham Young University, Provo, Utah, 1949, p. 7.

Noyes and Freed[12] also determined the standard free energy of formation of silver sulfide by electromotive force measurements of a galvanic cell. They found the free energy of formation by this electrochemical method to be -9,558 cal/mole for silver sulfide. This electrochemical method will be discussed in more detail in a later chapter.

Kapustinsky and Makolkin[13] repeated the electrochemical determination of Noyes and Freed and reported the standard free energy of formation to be -9,510 cal/mole.

The electrochemical method of Noyes and Freed was also repeated by Kimura[14] who listed -9,542 cal/mole as the standard free energy of formation of silver sulfide.

Jellinek and Czerwinski[15] calculated the free energy of formation of silver sulfide from electromotive force measurements of a galvanic cell of the type M,MS $|$ Na_2S $||$ Reference electrode to be -8,160 cal/mole. This method, also, will be discussed in more detail in a later chapter.

Jellinek and Czerwinski's determinations were all carried

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[12] Noyes and Freed, _op_. _cit_., p. 476.

[13] Kapustinsky and Makolkin, _Acta_. _Physicochim_. _U_. _R_. _S_. _S_., _X_, _No_. _2_, 259 (1939).

[14] G. Kimura, _Science Reports Tohoku Imp_. _Univ_., _1_, _24_, 259 (1935).

[15] K. Jellinek and J. Czerwinski, _Z_. _physik_, _Chem_., _102_, 438 (1936).

out at 10° and not at the more conventional 25° C. Also, as pointed out by Ravitz,[16] the concentrations of the sulfide ion used in their calculations were probably incorrect. Jellinek and Czerwinski's calculations may be further criticized because they used concentrations and not activities in their calculation of the free energy change of the cell reaction.

Ravitz[17] recalculated the results of these investigators by correcting the sulfide ion concentrations, using the ionization constants of hydrogen sulfide and water to make these corrections. He also made use of more recent activity data in his recalculation. However, since Jellinek and Czerwinski's data were all at 10° C., Ravitz had to convert his results to 25° by use of the Van't Hoff equation $\ln \frac{K_2}{K_1} = \frac{\Delta H\ (T_2 - T_1)}{R\ (T_1 T_2)}$. This calculation involved an assumption that ΔH is constant over the 15° temperature range. From this calculation Ravitz reported -9,930 cal/mole for the standard free energy of formation of silver sulfide.

<u>Solubility Product Constant</u>. Latimer[18] reported the solubility product constant of silver sulfide as 1×10^{-51}. This value corresponds to -9,500 cal/mole as the standard

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[16] S. F. Ravitz, <u>J</u>. <u>Phys</u>. <u>Chem</u>., <u>40</u>, 65 (1936).

[17] <u>Ibid</u>., p. 67.

[18] Latimer, <u>op</u>. <u>cit</u>., p. 315.

free energy of formation of silver sulfide, which was selected by him as the best value for the free energy of formation of silver sulfide. He selected this value from a survey of all the available data, but gave more weight to values obtained from electromotive force measurements.

Weigel[19] attempted to measure the actual solubility of a number of metal sulfides, including silver sulfide, by electrical conductance measurements. He reported 5.5 X 10^{-7} as the solubility of silver sulfide in water. Kolthoff,[20] commenting on Weigel's solubility measurements, said:

> Weigel's work on the electrical conductance of saturated solutions of metallic sulfides cannot be correct. The solubility of most sulfides in water is so small that in many cases the conductivity of the saturated solution is much smaller than that of the purest (ultra pure) conductivity water. At such extremely small solubilities, the conductance measured in the saturated solution in contact with the solid body must be mainly attributed to slight impurities, which are very hard to wash out from precipitates of a colloidal nature, and to surface conductance of the solid particles. Another factor which has to be considered is that sulfides are easily oxidized by the oxygen of the air. In Weigel's work no indication is found that he performed his experiments in the absence of oxygen and, therefore, it is quite possible that he measured the conductance of the metal hydroxides formed by oxidation of the sulfides.

Weigel, in his calculations, assumed that hydrolysis of the sulfide ion was complete, as shown here:

$$S^{=} + H_2O = H_2S + 2OH^{-}$$

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[19] O. Weigel, Z. physik. Chem., 58, 294 (1907).

[20] I. M. Kolthoff, J. Phys. Chem., 35, 2711 (1931).

This assumption is greatly in error because nearly all the sulfide is hydrolyzed by water only to the bisulfide.[21] It is evident from the foregoing discussion that no weight should be given to values listed by Weigel for the solubility of the various metal sulfides.

Bruner and Zawadski[22] attempted to measure the solubility of silver sulfide by studying the equilibrium of the reaction

$$Ag_2S \rightleftarrows 2Ag^+ S^=$$

at a known acidity and hydrogen sulfide concentration. They reported 3.4×10^{-17} moles/liter as the solubility of silver sulfide in water. The difficulty involved in measuring low concentration in solution makes this method not very useful and susceptible to large error for very slightly soluble metal sulfides such as silver sulfide. Results obtained by this method are based on concentrations rather than activities, and thus further error is introduced.

Biltz[23] determined the solubility of silver sulfide by the use of the ultramicroscope. In his determination he mixed very dilute solution of silver ions and sulfide ions together very slowly while looking through the ultramicroscope to observe at what concentration the first particles of

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[21] Ibid.

[22] L. Bruner and J. Zawadski, Z. anorg. Chem., 65, 136 (1909).

[23] W. Biltz, Z. physik. Chem., 57, 288 (1907).

the precipitate formed. He assumed the water to be saturated with silver ions and sulfide ions when he could see the first particles of precipitate with the ultramicroscope. He listed 9.0×10^{-7} mole/liter as the solubility of silver sulfide in water.

This direct method of measuring the solubility of slightly soluble metal sulfides can certainly be questioned. First, there must be a minimum number of particles formed to be visible with the ultramicroscope and this minimum number is not a constant, but depends on the particle size.[24] Second, it is entirely possible that supersaturation may have taken place. Third, hydrolysis of the sulfide ion was completely ignored. Biltz's value should be disregarded because of these errors.

Jellinek and Czerwinski[25] reported 5.7×10^{-51} and 1.2×10^{-50} as values for the solubility product constant of silver sulfide. These values are based on calculations from free energy of formation data, as determined by these investigators from measurements of the electromotive force of galvanic cells.

Ravitz[26] used the experimental data of Jellinek and

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[24] Kolthoff, <u>op</u>. <u>cit</u>., p. 2711.

[25] Jellinek and Czerwinski, <u>op</u>. <u>cit</u>., p. 438.

[26] Ravitz, <u>op</u>. <u>cit</u>., p. 67.

Czerwinski to calculate the free energy of formation of silver sulfide at 25°, as discussed under standard free energy of formation of silver sulfide at the beginning of this chapter. From this free energy value and the known free energies of silver ion and sulfide ion, he calculated the free energy change of the reaction:

$$Ag_2S = Ag^+ + S^= .$$

Then from the free energy change of the reaction, he calculated the equilibrium constant of the reaction which is the solubility product constant. He listed 3.28×10^{-52} as the solubility product constant of silver sulfide by these calculations.

Benfeld,[27] Lucas,[28] and Knox,[29] each independently determined the solubility product of silver sulfide by electromotive force measurements similar to those of Jellinek and and Czerwinski,[30] and obtained the following values respectively: 1.8×10^{-50}, 2.2×10^{-51}, and 3.9×10^{-50}.

Kapustinsky and Makolkin[31] calculated the solubility

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[27] I. Benfeld, Z. physik. Chem., 25, 46 (1898).

[28] R. Lucas, Z. anorg. Chem., 41, 193 (1904).

[29] J. Knox, Z. Electrochemie, 12, 477 (1906).

[30] Jellinek and Czerwinski, op. cit., p. 438.

[31] Kapustinsky and Makolkin, op. cit., p.259.

product constant of silver sulfide from its free energy of formation as determined by electromotive force measurements of a galvanic cell of the type used by Noyes and Freed.[32] They reported 5.9 X 10^{-52} as the solubility product constant of silver sulfide.

Using the free energy of formation value of silver sulfide that was obtained from electromotive force measurements of a Noyes and Freed[33] type galvanic cell, Kimura[34] calculated 6.0 X 10^{-52} as the solubility product constant of silver sulfide.

MERCURIC SULFIDE

<u>Standard</u> <u>Free</u> <u>Energy</u> <u>of</u> <u>Formation</u>. Latimer[35] lists -8,800 cal/mole as the standard free energy of formation of mercuric sulfide. He obtained this value from a Third-Law calculation by using -10,700 cal/mole as the heat for formation of mercuric sulfide, as reported by Bichowsky and Rossini,[36] and by using an estimated entropy change of -6.3 e.u. Latimer's value for the free energy of formation of mercuric sulfide can be criticized because of the uncertainty

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[32] Noyes and Freed, *op. cit.*, p. 476.

[33] Noyes and Freed, *op. cit.*, p. 478.

[34] Kimura, *op. cit.*, p. 77.

[35] Latimer, *op. cit.*, p. 305.

[36] Bichowsky and Rossini, *op. cit.*, p. 70.

of the heat of formation value used and because the entropy change used is a questionable estimate.

Rinse[37] made extensive equilibrium measurements, involving mercuric sulfide in the reaction

$$HgS = Hg_{(g)} + \frac{1}{X} S_{x(g)} \quad .$$

His study showed the existence of two forms of mercuric sulfide, the transition point for the two forms being at 659° K. He reported -12,340 cal/mole as the free energy of formation of the low temperature form.

Pelabon,[38] and Jellinek and Zakowski[39] independently studied the reaction

$$HgS + H_2 = Hg + H_2S$$

at temperatures above 600°. Kelley,[40] in discussing the measurements of these investigators, said:

> No reasonably reliable calculations may be made from these measurements, but they indicate even lower values of the heat and free energy of formation of mercuric sulfide than do the figures of Rinse.

Kelley[41] calculated the free energy of formation of mercuric sulfide from the solubility product constant reported

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[37] J. Rinse, <u>Rec</u>. <u>trav</u>. <u>chim</u>., <u>47</u>, 28, (1928).

[38] Pelabon, <u>Bull</u>. <u>soc</u>. <u>chim</u>. <u>Belg</u>., <u>ser</u>. <u>3</u>, <u>Vol</u>. <u>25</u>, 777 (1901).

[39] Jellinek and Zakowski, <u>op</u>. <u>cit</u>., p. 1.

[40] Kelley, <u>op</u>. <u>cit</u>., p. 63.

[41] <u>Ibid</u>.

by Knox,[42] and from the known free energies of silver, silver ion, sulfur, and sulfide ion. Knox calculated his solubility product constant from electromotive force measurements. Kelley's calculated value for the free energy of formation of mercuric sulfide was reported as -10,330 cal/mole.

Makolkin[43] determined the free energy of formation of mercuric sulfide electrochemically by using a galvanic cell of the type:

$$Pt,H_2 \mid KCl_{(0.01 mole)} \mid KCl_{(0.01 mole)} \mid H_2S \mid HgS,Hg\ .$$

The chemical reaction of the cell is

$$HgS + H_2 \rightarrow Hg^{\circ} + H_2S\ .$$

From the standard electromotive force of this cell, it is possible to calculate the free energy of the above chemical reaction. It is then possible to calculate the standard free energy of formation of mercuric sulfide, using the free energy change of the reaction and the known free energies of the other substances involved in the reaction. He reported -10,470 cal/mole as the standard free energy of formation of mercuric sulfide.

Solubility and Solubility Product Constant. The solubility of mercuric sulfide was listed by Weigel[44] as

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[42] Knox, *op. cit.*, p. 477.

[43] I. A. Makolkin, *J. Phys. Chem. U. S. S. R.*, *16*, 18 (1942).

[44] Weigel, *op. cit.*, p. 294.

5.4×10^{-8} mole/liter, and by Bruner and Zawadski[45] as 6.3×10^{-27} mole/liter. The work of these investigators has been discussed in connection with the solubility of silver sulfide, and will not be discussed further at this point.

Treadwell and Schaufelberger[46] studied the equilibrium of the reduction of cinnabar and metacinnabar with hydrogen gas at temperatures between -100° and 400° K. They reported 0.7×10^{-52} as the solubility product constant of mercuric sulfide as cinnabar, and 0.3×10^{-51} as the solubility product constant for mercuric sulfide as metacinnabar.

Knox[47] reported 3×10^{-54} as the solubility product constant of mercuric sulfide calculated from the free energy of formation of mercuric sulfide, as determined from electromotive force measurements.

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[45] Bruner and Zawadski, op. cit., p. 136.

[46] W. D. Treadwell and F. Schaufelberger, Helv. Chim. Acta., 29 (1946).

[47] J. Knox, Z. Electrochemie, 12, 477 (1906).

CHAPTER III

THEORY OF THE ELECTROCHEMICAL METHOD SELECTED

The method selected for use in this study consists of the accurate measurement of the electromotive force of various simple galvanic cells. From this measured potential the standard electromotive force was calculated, and from this standard electromotive force the standard free energy change of the cell reaction was obtained. The free energy of formation of the metal sulfide was calculated using the standard free energy change of the reaction, and the solubility product constant was determined from the free energy of formation of the metal sulfide. The thermodynamic equations relating these different values will be developed below from fundamental definitions.

DERIVATION OF EQUATIONS

Derivation of Equation Relating the Standard Free Energy Change and the Equilibrium Constant of a Reaction. The thermodynamic property F, known as the free energy, is defined by the expression

$$F = H - TS, \tag{1}$$

in which H is the heat content, S the entropy, and T the temperature of the system.

The free energy, F, is a function of the temperature, pressure and components of the system, or mathematically stated is

$$F = f(T, P, n, n_2, - - - n_i - - -),$$

in which n_1 is the first component, n_2 the second component, and n_1 is the "ith" component. Taking the total differential of F gives

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P, n_1, n_2 ---} dT + \left(\frac{\partial F}{\partial P}\right)_{T, n_1, n_2 ---} dP + \left(\frac{\partial F}{\partial n}\right)_{T, P, n_2 ---} dn$$

$$+ \left(\frac{\partial F}{\partial n_2}\right)_{T, P, n_1 ---} dn_2 + \left(\frac{\partial F}{\partial n_i}\right)_{T, P, n \neq i} dn \; . \qquad (2)$$

The term $\left(\frac{\partial F}{\partial n_i}\right)_{T, P, n = i}$ is known as the partial molar free energy of the ith constituent and is represented by the symbol $\bar{F}$. The partial molar free energy, $\bar{F}$, for the "ith" component is equal by definition to the chemical potential, μ_i, for this same component; therefore,

$$\left(\frac{\partial F}{\partial n_i}\right)_{T, P, n \neq i} = \bar{F} = \mu_i \, . \qquad (3)$$

Substituting the chemical potential, μ, into equation (2) results in the expression

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P n_1, n_2 ---} dT + \left(\frac{\partial F}{\partial P}\right)_{T, n_1, n_2} dP + \mu_1 dn_1 + - - - . \qquad (4)$$

If the system is held at constant temperature and pressure, equation (4) now becomes

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + - - - - ,$$

and if the system is at equilibrium, the free energy change is zero, so that

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + - - - = 0 \qquad (5)$$

Consider a perfectly general reaction represented by

$$\nu_1 A + \nu_2 B + --- \rightleftharpoons \nu_3 C + \nu_4 D + ---$$

taking place in a closed system at a given temperature and pressure and having been allowed to reach a state of equilibrium. Now suppose an infinitesimal change is allowed to take place in the system so that the reaction goes just slightly toward completion. During this infinitesimal change dn_A moles of A and dn_B moles of B are transformed into dn_C moles of C and dn_D moles of D. The free energy change accompanying this transformation will be given by equation (5) as

$$dF = (\mu_C dn_C + \mu_D dn_D + ---) - (\mu_A dn_A + \mu_B dn_B + ---).$$

Now writing $\nu_1, \nu_2, ---, \nu_3, \nu_4, ---$ for the quantities $dn_A, dn_B --- dn_C\ dn_D ---$ — the expression becomes

$$dF = (\nu_3 \mu_C + \nu_4 \mu_D + ---) - (\nu_1 \mu_A + \nu_2 \mu_B + ---) = 0. \quad (6)$$

Then the free energy change at constant temperature, pressure, and composition of a reaction at equilibrium is given by the equation:

$$\Delta F_{T,P,N} = \left(\sum \nu_i \mu_i \right)_{eq} = 0 \quad (7)$$

the heat constant, H, is defined by the expression

$$H = E + PV. \quad (8)$$

Combining equation (1) with the equation defining heat content gives

$$F = E - TS + PV.$$

Differentiating this equation gives the expression

$$dF = dE - TdS - SdT + PdV + VdP ,$$

and for an infinitesmal stage in a reversible process involving only work of expansion,

$$dF = VdP - SdT .$$

Then at constant temperature

$$dF_T = VdP_T$$

and

$$\left(\frac{\partial F}{\partial P}\right)_T = V$$

Differentiating this with respect to n_i gives the expression

$$\frac{\partial^2 F}{\partial P \partial n_i} = \frac{\partial V}{\partial n_i} = \bar{V}_i . \qquad (9)$$

Equation 3 defined the chemical potential as

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n \neq i} = \mu_i .$$

Differentiating this equation with respect to pressure gives

$$\frac{\partial^2 F}{\partial n_i \partial P} = \frac{\partial \mu_i}{\partial P} . \qquad (10)$$

Comparing this result with equation (9) one may see that

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \bar{V}_i \qquad (11)$$

The equation of state for any constituent, i, of a mixture of ideal gases may be written as

$$P_iV = n_iRT , \qquad (12)$$

in which P_i is the partial pressure due to n_i moles of the ith constituent. Equation (12) may be rearranged into the form

$$V = \frac{n_i RT}{P_i} \quad ,$$

and then differentiating with respect to n_i at constant temperature and pressure gives

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P} = \bar{V}_i = \frac{RT}{P_i} \, . \qquad (13)$$

If all the pressure change is due to the "ith" constituent, P in equation (11) may be replaced by P_i. Then combining (11) and (13) gives

$$\left(\frac{\partial \mu_i}{\partial P_i}\right)_{TN} = \frac{RT}{P_i} \, ,$$

or upon rearranging

$$d\mu_i = RT \, \frac{dP}{P_i} = RT \, d \ln P_i \, .$$

On integration this gives

$$\mu_i = \mu_i^* + RT \ln P_i \, , \qquad (14)$$

in which μ^* is the integration constant. For real gases P_i may be replaced by F_i, the fugacity of the "ith" constituent. This modification would change the value of the integration constant:

$$\mu_i = \mu_i' + RT \ln f_i \qquad (15)$$

Then since the fugacity is proportional to the activity, the expression could be written:

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \qquad (16)$$

in which A_i represents the activity of the component "i", which can be a substance other than a gas. Combining with equation (7) and (16) gives

$$\sum \nu_i \mu_i = \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln a_i = 0 .$$

Then upon rearrangement,

$$- \sum \nu_i \mu_i^0 = RT \sum \nu_i \ln a_i .$$

Dividing through by RT gives

$$\frac{\sum \nu_i \mu_i^0}{RT} = \sum \nu_i \ln a_i . \tag{17}$$

For the general reaction

$$\nu_1 A + \nu_2 B + --- \rightleftharpoons \nu_3 C + \nu_4 D + ---$$

the equilibrium constant K is defined by the expression

$$\frac{a_C^{\nu_3} \times a_D^{\nu_4}}{a_A^{\nu_1} \times a_B^{\nu_2}} = \sum a_i^{\nu_i} = K . \tag{18}$$

Equation (18) expressed in logarithmic form is

$$\sum \nu_i \ln a_i = \ln K \tag{19}$$

Combining equations (17) and (19) gives

$$\frac{\sum \nu_i \mu_i^0}{RT} = \ln K$$

which upon rearrangement gives

$$- \sum \nu_i \mu_i^0 = RT \ln K . \tag{20}$$

Combining equation (7) and (20) gives

$$\Delta F^0 = - RT \ln K . \tag{21}$$

This equation makes possible the calculation of the equilibrium constant of a reaction if the standard free energy change accompanying the reaction is known.

Derivation of Equation Relating the Standard Electromotive Force and the Standard Free Energy Change. The term A, called the work function, is defined by

$$A = E - TS, \qquad (22)$$

in which E is the internal energy, T the temperature, and S the entropy of the system.

Consider a change at constant time from an initial state, indicated by subscript 1, to the final state, indicated by 2,

$$A_2 - A_1 = E_2 - E_1 - T(S_2 - S_1)$$

$$\Delta A_T = \Delta E_T - T\Delta S \qquad (23)$$

By definition,

$$\Delta S = \frac{Q_{rev.}}{T}, \qquad (24)$$

where $Q_{rev.}$ is the heat taken up when the change is carried out reversibly.

Combining equations (23) and (24) gives

$$\Delta A_T = \Delta E_T - Q_{rev.} \qquad (25)$$

According to the first law of thermodynamics

$$\Delta E = Q_{rev.} - W_{rev.}, \qquad (26)$$

in which $W_{rev.}$ is the total reversible work obtainable in the given change.

Combining equations (25) and (26) gives

$$-\Delta A_T = W_{rev.} \qquad (27)$$

Combining equations (1) and (8) gives

$$F = E - TS + PV \cdot \qquad (28)$$

Combining equations (22) and (28) gives

$$F = A + PV \cdot \qquad (29)$$

For a process taking place at constant pressure the equation can be written

$$\Delta F_p = \Delta A_p + P \Delta V , \qquad (30)$$

and if the process is carried out at constant temperature, also, the equation takes the form

$$- \Delta F_{PT} = W_{rev.} - P \Delta V .$$

The term $W_{rev.} - P \Delta V$ represents the reversible work, other than pressure volume work. This quantity is referred to as the net work, and is represented by $W'_{rev.}$

$$- \Delta F_{PT} = W'_{rev.} \qquad (31)$$

In general, the work done, regardless of its form, is equal to the product of a generalized force, frequently referred to as the <u>intensity factor</u>, and a generalized displacement, frequently referred to as the <u>capacity factor</u>. The net work, or the work other than pressure volume work, of a reversible galvanic cell at constant temperature and pressure is equal to the electromotive force of the cell times the quantity of electricity that passes through the cell, or mathematically:

$$W_{rev.} = n \mathcal{F} \mathcal{E} \qquad (32)$$

in which $\mathcal{E}$ is the electromotive force of the cell, n the number of Faradays, $\mathcal{F}$ the Faraday, and $W'_{rev.}$ is the work other than pressure volume work. The potential $\mathcal{E}$ is the generalized force or intensity factor, and the quantity of electricity passing through the cell, $n\mathcal{F}$, is the generalized displacement or capacity factor.

If $\mathcal{E}$ is expressed in int. volts, and if is expressed in int. coulombs, the work done, $W_{rev.}$, will have the dimensions of int. volt-coulombs or int. joules.

Combining equations (31) and (32) gives

$$F = -n\mathcal{F}\mathcal{E}^\circ \tag{33}$$

This equation makes possible the calculation of the standard free energy change accompanying the cell reaction if the standard electromotive force of the cell is known.

<u>Derivation of Equation Relating the Measured Electromotive Force and the Standard Electromotive Force.</u> Combining equations (16) and (7) gives

$$\sum \nu_i \mu_i = \sum \nu_i \mu_i^\circ + RT \sum \nu_i \ln a_i$$

Therefore,

$$\Delta F = \Delta F^\circ + RT \sum \nu_i \ln a_i \tag{34}$$

Considering the general chemical reaction

$$\nu_1 A + \nu_2 B + \cdots \rightleftharpoons \nu_3 C + \nu_4 D + \cdots$$

and referring to equations (18) and (19) one can write

$$\sum V_i \ln a_i = \ln K = \ln \frac{a_C^{V_3} \times a_D^{V_4}}{a_A^{V_1} \times a_B^{V_2}}.$$

Combining this expression and equation (34) gives

$$\Delta F = \Delta F^\circ + RT \ln \frac{a_C^{V_3} \times a_D^{V_4}}{a_A^{V_1} \times a_B^{V_2}}. \qquad (35)$$

Combining equations (33) and (35) and rearranging terms gives

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln \frac{a_C^{V_3} \times a_D^{V_4}}{a_A^{V_1} \times a_B^{V_2}}. \qquad (36)$$

This equation makes possible the calculation of the standard electromotive force of a reaction taking place in a galvanic cell, if the measured electromotive force is known.

Derivation of Equation Relating the Free Energy Change of a Reaction and the Free Energy of Formation of the Substances Involved in the Reaction. Equation (6), which has been previously derived, gives the relationship between the free energy change of a chemical reaction and the free energy of formation of the substances involved. This equation could be expressed in the form

$$\Delta F_{(reaction)} = \sum \Delta F_{(products)} - \sum \Delta F_{(reactants)}. \qquad (37)$$

DISCUSSION OF CELLS OF THE FIRST TYPE

The first cell selected for study was a cell of the type

$$\mathrm{PT, H_2}_{(P\ atm.)} \Big| \mathrm{HCl}_{(X\ mol.)} \Big| \mathrm{HCl}_{(X\ mol.)} \Big| \mathrm{H_2S}_{(P\ atm.)}, \mathrm{MS, M}$$

which had been previously employed by Noyes and Freed,[1] Kimura,[2] and Kapustinsky and Makolkin.[3] The chemical reaction taking place in this cell is

$$MS_{(s)} + H_2{}_{(P\ atm.)} = H_2S_{(P\ atm.)} + M_{(s)}\ .$$

The symbol M as used here represents any metal.

This particular cell is an ideal one experimentally for three reasons: First, the cell reaction is independent of pressure because the same number of moles of gas appear on both sides of the equation. Second, the electromotive force of the cell is independent of the concentration of hydrochloric acid because the concentration of the acid solution is the same in both half-cells. Third, using the same concentration of hydrochloric acid solution in both half-cells precludes any possibility of a liquid junction potential between the two half-cells.

CALCULATIONS FOR CELLS OF THE FIRST TYPE

Standard Electromotive Force. The relationship between the standard electromotive force and the measured electromotive force of this cell is given by equation (36)

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[1] Noyes and Freed, J. Am. Chem. Soc., 42, 476 (1920).

[2] G. Kimura, Science Reports Tohoku. Imp. Univ., ser. 24 1, 77 (1935).

[3] A. F. Kapustinsky and I. A. Makolkin, Acta Physicochim. U. R. S. S., X, No. 2, 259 (1939).

$$\mathcal{E} = \mathcal{E}^{0} - \frac{RT}{n\mathcal{F}} \ln \frac{f_{H_2S} \times A_{(M)}}{f_{H_2} \times A_{(MS)}}$$

which was previously derived on page 25. The activities of the pure solids, metal and metal sulfide, are taken as unity by convention. The equation then reduces to

$$\mathcal{E} = \mathcal{E}^{0} - \frac{RT}{n\mathcal{F}} \ln \frac{f_{H_2S}}{f_{H_2}} \qquad (38)$$

To calculate the standard electromotive force from the measured electromotive force it is now necessary to know the fugacities of hydrogen and hydrogen sulfide gases under the conditions of the experiment. Using the critical temperature and pressure values listed in International Critical Tables[4] for these gases and the temperature (298.1° K) and pressure (650 mm.) at which the experiment was carried out, one can calculate the reduced temperature and pressure. These values used, together with generalized fugacity curves, show the activity coefficients of both gases to be very nearly unity. The ratio of the fugacities, as calculated by the above method, is close enough to unity to make any correction due to slight differences in fugacity less than experimental error. If the ratio $\frac{f(H_2S)}{f(H_2)}$ is unity, the term $\frac{RT}{n\mathcal{F}} \ln \frac{f(H_2S)}{f(H_2)}$ in equation (38) become zero, and the standard electromotive force is equal to the measured electromotive force of the cell.

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[4] International Critical Tables, vol. III, (1928), p. 248.

Standard Electrode Potential. The standard electromotive force of a cell is equal to the algebraic sum of the standard electrode potentials of the two electrodes. Then, since the standard electrode potential of the hydrogen electrode (the electrode used as a reference electrode in this particular cell) is equal to zero by definition, the standard electromotive force of the cell is equal to the standard electrode potential of the electrode M, MS, H_2S.

Standard Free Energy of Formation. The standard electromotive force of a chemical reaction taking place in a cell is related to the free energy change of the reaction by equation (33): $\Delta F^\circ = - n\mathfrak{F}\mathcal{E}^\circ$.

Using this equation and the calculated standard electromotive force, one can calculate the standard free energy change of the reaction. The free energy change of the reaction is related to the free energy of formation of the metal sulfide by the expression:

$$\Delta F^\circ_{(\text{reaction})} = \Delta F^\circ_{(H_2S)} + \Delta F^\circ_{(M)} - \Delta F^\circ_{(MS)} - \Delta F^\circ_{(H_2)} .$$

The free energy of hydrogen gas and of the free metal are taken as zero by convention. The equation then reduces to

$$\Delta F^\circ_{(MS)} = \Delta F^\circ_{(H_2S)} - \Delta F^\circ_{(\text{reaction})} .$$

The free energy change of the reaction is calculated from standard electromotive force data, and the free energy of formation of hydrogen sulfide is known accurately and listed in the chemical literature.[5] Having these two values it is possible to calculate the free energy of formation of the metal sulfide from the above equation.

Solubility Product Constant. The very slightly soluble metal sulfides dissolve in water to give a saturated solution, according to the equation:

$$MS = M^{++} + S^{=} \ .$$

The free energy change of this reaction is given by the expression:

$$\Delta F^{\circ}_{(reaction)} = \Delta F^{\circ}_{(M^{++})} + \Delta F^{\circ}_{(S^{=})} - \Delta F^{\circ}_{(MS)} \ .$$

The free energy of formation of the MS can be calculated as was shown under the section on standard free energy of formation. The free energies of formation of the metal ion and the sulfide ion are reliably listed in tables.[6] These values, when substituted into the above equation, make possible the calculation of the free energy change of the reaction. The equilibrium constant of the reaction is related to the free energy change of the reaction by equation (21)

$$\Delta F^{\circ} = - RT \ln K \ .$$

With the free energy change of the reaction known, the equilibrium constant can be calculated. This equilibrium constant is the thermodynamic solubility product constant

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[5] W. M. Latimer, "Oxidation Potentials", Prentice-Hall Corporation, New York, 307 (1938).

[6] Latimer, *op. cit.*, pp. 305-307.

based on the activities of the ions.

DISCUSSION OF CELLS OF THE SECOND TYPE

The second cell selected for study was a cell of the type

$$\text{M, MS} \Big/ S^{=}_{(a=\text{variable})} \Big\| \text{Normal calomel.}$$

The chemical reaction taking place in the M, MS $S^{=}_{(a=\text{variable})}$ half=cell is

$$M + S^{=} = MS + 2e ,$$

in which M represents any metal and e represents an electron. This particular type of cell was previously studied by Jellinek and Czerwinski[7] as well as a number of other investigators.

This second type cell is not as desirable as a cell of the first type because this cell involves the use of a salt-bridge, which does not leave the cell entirely free of liquid junction potential. Another disadvantage of the second type cell, as is obviously seen below under the section on calculations, is that the calculation of the standard electromotive force from the measured electromotive force of the cell is much more complicated. For these reasons results obtained from cells of the first type should be weighted higher than those of cells of the second type; however, the calculations on the second type cell involve no unreasonable assumptions

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[7] K. Jellinek and J. Czerwinski, <u>Z</u>. <u>physik</u>, <u>Chem</u>., <u>102</u>, 438 (1936).

and should produce a fairly good check on the first type cell.

CACLULATIONS ON CELLS OF THE SECOND TYPE

Standard Electromotive Force. The relationship between the standard electromotive force and the measured electromotive force of this type cell is given by equation (36):

$$\mathcal{E} = \mathcal{E}^{0} + \frac{RT}{n\mathcal{F}} \ln \frac{A_{(MS)}}{A_{(M^{+})} \times A_{(S^{=})}}$$

Then since the activities of the pure solids, metal and metal sulfide, are unity by convention, the equation reduces to

$$\mathcal{E} = \mathcal{E}^{0} + \frac{RT}{n\mathcal{F}} \ln A_{(S^{=})} .$$

In order to calculate the standard electromotive force from the measured electromotive force, one must know the activity of the sulfide ion.

The sulfide ion in this second type cell was provided by sodium sulfide solutions of varying concentrations. Determinations on silver sulfide were made in sodium sulfide solutions of the following concentrations expressed in moles per liter: 0.1, 0.05, 0.01, and 0.005. At concentrations lower than 0.005 molar the observed electromotive force of the cell was very erratic, probably due to the large internal resistance of the cell. Solutions of higher concentrations were not used because they fall outside the limit of application of the Debye-Hückel theory, which will be applied in a number of subsequent calculations. In determinations made on mercuric sulfide, the concentration range was more restricted because the sulfide coating on the Hg, HgS | $S^=$ electrode would not persist in sodium sulfide solutions more concentrated than 0.01 molar. The lack of stability of the Hg, HgS | $S^=$ electrode in concentrated sodium sulfide solutions is probably due to the fact that these solutions are very strongly basic because of the hydrolysis of the sulfide ion. This hydrolysis will be discussed in more detail below.

Determinations were made on mercuric sulfide in the following approximate concentration of sodium sulfide solution: 0.01, 0.0075, 0.0050, and 0.0025 moles per liter.

When the salt, sodium sulfide, is dissolved in water, hydrolysis takes place according to the reactions:

(First Hydrolysis) $Na_2S + H_2O = Na^+ + OH^- + Na^+ + HS^-$

(Second hydrolysis) $HS^- + H_2O = H_2S + OH^-$

(Total hydrolysis) $Na_2S + 2H_2O = 2Na^+ + 2OH^- + H_2S$

The equilibrium constants of these reactions, which are the hydrolysis constants, can be written:

(First hydrolysis) $K_{h_1} = \dfrac{A_{OH^-} \times A_{HS^-}}{A_{S^=}}$

(Second hydrolysis) $K_{h_2} = \dfrac{A_{H_2S} \times A_{OH^-}}{A_{HS^-}}$

(Total hydrolysis) $K_H = \dfrac{A_{OH^-}^{\,2} \times A_{H_2S}}{A_{S^=}}$

where K_{h_1}, K_{h_2}, and K_H represent the first, second, and total hydrolysis constants respectively, and A represents the activity of the various subscripted ions and molecules. Any substance that appears unchanged on both sides of the hydrolysis reaction has been omitted from the above hydrolysis expressions, and the activity of the water term is taken as unity in accordance with the chosen standard state.

It has already been stated that it is necessary to know the exact activity of the sulfide ion in the cell in order to convert measured electromotive force to standard electromotive force. If the hydroxide and bisulfide ion activities of the sodium sulfide solution could be obtained, it would then be possible to calculate the activity of the sulfide ion by substituting these activity values and the known value of the first hydrolysis constant, K_{h_1},[8] into the expression given above for the first hydrolysis. This procedure was the one followed in calculating the sulfide ion activity. The hydroxide and bisulfide ion activities of the sodium sulfide solution were calculated from data obtained from two separate titrations, and by use of the Debye-Hückel theory.

The sodium sulfide solutions were not made up to an exact molality because the sodium sulfide crystals ($Na_2S \cdot 9H_2O$) were very hygroscopic and could not be weighed exactly. If sodium sulfide is made to undergo a complete hydrolysis by the addition of hydrogen ions, there will be two hydroxide

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[8] Latimer, op. cit., p. 65.

ions formed for every molecule of sodium sulfide hydrolyzed. The hydroxide ion concentration of the completely hydrolyzed sodium sulfide solution was determined by the following neutralization titration: A definite amount of sodium sulfide solution was measured out in a pipette and transferred to a beaker. An excess, but measured amount of sulfuric acid, was added to this solution from a burette. The solution was boiled carefully for five minutes to expel any hydrogen sulfide gas in the solution. Then phenolphthalein was added as an indicator, and the acid back titrated with standard sodium hydroxide solution. This titration gave the concentration of the hydroxide ion when the sodium sulfide was completely hydrolized and the concentration of the sodium sulfide solution, which is half as much as the hydroxide ion if the salt is hydrolized completely.

There is only a very minute amount of sulfide ion in the sodium sulfide solution. However, this small amount of sulfide ion is in equilibrium with the bisulfide ion and if this sulfide is removed from the scene of action, more bisulfide will change into sulfide until finally all the bisulfide will be changed over.

The bisulfide ion concentration was determined by an oxidation-reduction titration on the sulfide ion. A definite amount of sodium sulfide solution was measured out in a pipette and transferred to a beaker. An excess, but measured amount of approximately one per cent solution of calcium hypochorite was added from a pipette. The mixture was made acid and an excess of potassium iodide was added. This solution was back titrated with standard sodium thiosulfate solution; no indicator was needed. A blank determination was then made. The chemistry involved in this determination will be illustrated by the reactions:

$$S^{=} + 4\ OCl^{-} \rightarrow SO_4^{=} + 4\ Cl^{-}$$

$$OCl^{-} + 2I^{-} + 2H^{+} \rightarrow I_2 + Cl^{-} + H_2O$$

$$2S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2I^{-}.$$

This titration makes possible the calculation of the bisulfide ion concentration.

Recalling the equations for the hydrolysis of sodium sulfide, one can see that the hydroxide ion concentration from the first hydrolysis is equal to the bisulfide ion concentration, which is equal to the amount of sodium sulfide that will undergo just the primary hydrolysis. There is, however, a certain amount of the sodium sulfide that will undergo complete or total hydrolysis. This amount can be calculated by subtracting the amount that will undergo just the primary hydrolysis from the total amount present. Now, since each mole of sodium sulfide that hydrolizes completely will give two moles of hydroxide ion, the hydroxide ion concentration formed from the complete hydrolysis can be calculated. The total hydroxide ion concentration of the solution can now be calculated by adding the hydroxide ion concentration obtained from the first hydrolysis to that obtained from the complete hydrolysis.

Through reasoning of this kind the total hydroxide ion concentration of the solution was calculated. With the hydroxide and bisulfide ion concentrations known, it now becomes necessary to know the activity coefficient of these ions in order to calculate their activities. (The ratio of the activity of a substance to its concentration is the activity coefficient). The Debye-Hückel limiting law equation was employed to calculate the activity coefficient of these ions. The limiting law equation is[9]

$$\log \gamma_{\pm} = \frac{A z^{+} z^{-} \sqrt{\mu}}{1 + \mathring{a} B \sqrt{\mu}}$$

where $\gamma_{\pm}$ is the mean activity coefficient, A is a known constant, equal to 0.509 for water as solvent at 25° C, μ is the ionic strength, $\mathring{a}$ is the mean distance of closest approach of the ions in the solution and B is a constant involving universal constants together with the dielectric constant and the temperature. B is equal to 0.33×10^8 in water as a solvent at 25° C, and by taking an average value of $\mathring{a}$ as

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[9] S. Glasstone, "Thermodynamics For Chemists," D. Van Nostrand Co., New York, 1947, p. 418.

3×10^{-8},[10] the product $\overset{\circ}{a}B$ is approximately unity. The limiting law equation for water as a solvent at 25° may be written

$$\log \gamma_{\pm} = \frac{A z^{+} z^{-} \sqrt{\mu}}{1 + \sqrt{\mu}} .$$

The ionic strength, μ, must now be known in order to calculate the mean ionic activity coefficient of the ions. The ionic strength is half the sum of the terms obtained by multiplying the molality of each ion present in the solution by the square of its valence.[11] Since all the concentrations of the various ions in solution are known from the two titrations discussed above, the ionic strength can be calculated. Then, by the use of this ionic strength value and by the use of known constants, the limiting law equation can be employed to calculate the activity coefficients of the ions.

The product of the activity coefficient and the concentration of the hydroxide ion is equal to the activity of the hydroxide ion, and the product of the activity coefficient and the concentration of the bisulfide ion is equal to the activity of the bisulfide ion. The equilibrium expression for the first hydrolysis of sodium sulfide is

$$K_{h_1} = \frac{A_{OH^-} \times A_{HS^-}}{A_{S^=}} .$$

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[10] <u>Ibid.</u>

[11] <u>Ibid.</u>, p. 420.

Using this expression, and the calculated activities of hydroxide and bisulfide ions, and by the known hydrolysis constant,[12] the activity of the sulfide ion may be calculated.

The appropriate form of equation (36) for this particular half-cell reaction is

$$\mathcal{E} = \mathcal{E}^{\circ} + \frac{RT}{n} \ln A_{(S^{=})} \ .$$

Using this equation and the calculated sulfide ion activity, it is possible to convert measured electromotive force to standard electromotive force.

Standard Electrode Potential. As has already been stated, the standard electromotive force of a cell is equal to the algebraic sum of the standard electrode potentials of the two electrodes. Then, since the electromotive force of the half-cell reaction,

$$S^{=} + M \rightarrow MS + 2e \ ,$$

was the only electromotive force considered in the conversion of measured electromotive force to standard electromotive force, the standard electrode potential of the electrode $M, MS \mid S^{=}$ is equal to the standard electromotive force calculated above.

Standard Free Energy of Formation. The free energy of formation of the metal sulfide can be calculated from the

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[12] Latimer, op. cit., p. 65.

free energy change of the cell reaction, and the free energy change of the cell reaction can be calculated from the standard electromotive force by the same general procedure as was employed in making similar calculations on a cell of the first type.

Solubility Product Constant. The calculation of the solubility product constant of the metal sulfide from its free energy of formation is identical with that used for a cell of the first type.

DISCUSSION OF CELLS OF THE THIRD TYPE

The third cell selected for study was a cell of the type

$$Ag,\ Ag_2S \mid S^{=} \mid S^{=} \mid MS, M\ .$$

The chemical reaction taking place in the cell is

$$2Ag_{(S)} + MS_{(S)} = M_{(S)} + Ag_2S_{(S)}\ ,$$

where M, as used here, represents any metal. This third type cell is an original cell, and has not been reported in the chemical literature as being used to determine the free energy of formation of any metal sulfide.

This particular type cell is theoretically desirable because all the substances involved in the cell reaction are pure solids. Also, the concentration of the sulfide ion in each half-cell is the same and thereby eliminates any chance of liquid junction potential.

CALCULATIONS ON CELLS OF THE THIRD TYPE

Standard Electromotive Force. The relation between the standard electromotive force and the measured electromotive force of a cell is given by equation (36):

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{A(M) \times A(Ag_2S)}{A(Ag)^2 \times A(MS)}$$

The activity of the pure solids are taken as unity by convention. Then, since all the substances involved in the cell reaction are pure solids, the term $\frac{RT}{n\mathcal{F}} \ln \frac{A(M) \times A(Ag_2S)}{A(Ag)^2 \times A(MS)}$ equal to zero and the measured electromotive force becomes equal to the standard electromotive force, or

$$\mathcal{E} = \mathcal{E}^\circ .$$

Standard Electrode Potential. The standard electromotive force of a cell is equal to the algebraic sum of the standard electrode potentials of the two electrodes. The standard electromotive force of the cell can be calculated, as shown above, and the standard electrode potential of the electrode $Ag, Ag_2S | S^=$ can be obtained from calculations made for a cell of the second type. The standard electrode potential of the electrode $M, MS | S^=$ could be calculated by taking the algebraic difference of these two potentials.

Standard Free Energy of Formation. The free energy of formation of the metal sulfide can be calculated from the free energy change accompanying the cell reaction, and the free energy change of the cell reaction can be calculated from the standard electromotive force by the same general method used to calculate these values in cells of the first two types. However, the free energy of formation of silver sulfide must be known in order to make these calculations. The free energy of formation of silver sulfide could be determined by one of the first two type cells discussed above.

Solubility Product Constant. The solubility product constant of the metal sulfide can be calculated from its free energy of formation by the identical method used to calculate this value in cells of the first two types.

CHAPTER IV

SOLUBILITY FROM SOLUBILITY PRODUCT CONSTANT DATA

From a practical point of view, it is of interest to the chemist to know the solubility in water of the slightly soluble metal sulfides. An attempt will be made in this chapter to point out the difficulties involved in calculating the amount of dissolved metal sulfide from the solubility product constant and to suggest methods of improving this calculation.

Consider a slightly soluble substance of the type AB which dissolves in water, according to the reaction

$$AB \rightleftarrows A^{++} + B^{=} ,$$

whose solubility product constant expression is

$$K = A_{A^{++}} \times A_{B^{=}} .$$

The usual method of calculating the solubility is to take the square root of the solubility product constant. The solubility is equal to the square root of the solubility product constant in this case because for each molecule of AB that dissolves there will be one cation, A^{++}, and one anion, $B^{=}$, formed and the solubility product constant is the product of these two ions.

The above method of calculating solubility from solubility product constant data cannot be applied to a slightly soluble compound such as mercuric sulfide, which dissolves in water, according to the reaction

$$HgS \rightleftarrows Hg^{++} + S^{=}$$

because both the mercuric and sulfide ions will be hydrolyzed by water. The hydrolysis will decrease the amount of mercuric and sulfide ions, and as a result more mercuric sulfide will dissolve. At equilibrium, the concentration of the mercuric and sulfide ions in solution will not be the same, and as a result the solubility <u>will</u> <u>not</u> be equal to the square root of the solubility product constant.

In order to calculate the solubility from the solubility product constant, the hydrolysis of this salt must be taken into account. If a special case is considered in which the solution is distinctly acid, the hydrolysis of the mercuric ion will be negligible, but the hydrolysis of the sulfide ion will be appreciable. The sulfide ion hydrolyzes according to the reactions:

(First hydrolysis) $S^{=} + H_2O = HS^{-} + OH^{-}$

(Second hydrolysis) $HS^{-} + H_2O = H_2S + OH$

(Total hydrolysis) $S^{=} + 2H_2O = 2OH^{-} + H_2S$

The hydrolysis constant for the first hydrolysis, K_{h_1}, is defined by

$$K_{h_1} = \frac{A_{HS^-} \times A_{OH^-}}{A_{S^=}} ,$$

the hydrolysis constant for the second hydrolysis, K_{h_2}, is defined by

$$K_{h_2} = \frac{A_{H_2S} \times A_{OH^-}}{A_{HS^-}} ,$$

and the hydrolysis constant for the total hydrolysis, K_H, is defined by

$$K_H = \frac{A_{OH^-}^{\,2} \times A_{H_2S}}{A_{S^=}} ,$$

in which A is the activity of the various subscripted ions. The water terms have been omitted from these expressions because the activity of the water is taken as unity by convention. The product of the two constants K_{h_1} and K_{h_2} is another constant K_H, as shown by the following equation:

$$K_{h_1} K_{h_2} = \frac{A_{HS^-} \times A_{OH^-}}{A_{S^=}} \, \frac{A_{H_2S} \times A_{OH^-}}{A_{HS^-}} = \frac{A_{OH^-}^{\,2} \times A_{H_2S}}{A_{S^=}} = K_H \, . \quad (39)$$

Solving the expression for the sulfide ion activity gives

$$A_{S^=} = \frac{A_{OH^-}^{\,2} \times A_{H_2S}}{K_H} \, . \quad (40)$$

Recalling the solubility product constant expression for mercuric sulfide,

$$K_{S.P.} = A_{Hg^{++}} \times A_{S^=} ,$$

and solving this expression for the mercuric ion activity gives

$$A_{Hg^{++}} = \frac{K_{S.P.}}{S^=} \, . \quad (41)$$

The activity of the mercuric ion is equal to the solubility of mercuric sulfide because for each molecule of mercuric sulfide that dissolves one mercuric ion goes into solution. Now, combining equations (40) and (41) gives

$$A_{Hg^{++}} = \text{solubility of HgS} = \frac{K_{S.P.}\ K_H}{A_{OH^-}^{2} \times A_{H_2S}} \quad . \qquad (42)$$

By definition,

$$K_w = A_{H^+} \times A_{OH^-} \quad .$$

in which K_w is the dissociation constant for water. Solving for the activity of the hydroxide ion gives

$$A_{OH^-} = \frac{K_w}{A_{H^+}} \quad .$$

Then combining this expression with equation (42) gives

$$A_{Hg^{++}} = \text{solubility of HgS} = \frac{K_{S.P.}\ A_{H^+}^{2}\ K_H}{K_w^{2}\ A_{H_2S}} \quad . \qquad (43)$$

Hydrogen sulfide dissociates in water solution according to the reactions:

$$H_2S \rightleftarrows H^+ + HS^- \qquad (2)$$

$$HS^- \rightleftarrows H^+ + S^= \qquad (1)$$

and the ionization constants of these reactions are

$$K_{i_2} = \frac{A_{H^+} \times A_{HS^-}}{A_{H_2S}}$$

$$K_{i_1} = \frac{A_{H^+} \times A_{S^=}}{A_{HS^-}} \quad .$$

The relationship between K_{h_1}, K_i, and K_w is given by the equation:

$$\frac{K_w}{K_{i_1}} = \frac{A_{H^+} \times A_{OH^=}}{\frac{A_{H^+} \times A_{S^=}}{A_{HS^-}}} = \frac{A_{HS^-} \times A_{OH^-}}{A_{S^=}} = K_{h_1} \quad ,$$

or

$$K_{h_1} = \frac{K_w}{K_{i_1}} \qquad (44)$$

The relationship between K_{h_2}, K_i and K_W is given by the equation:

$$\frac{K_W}{K_{i_2}} = \frac{A_{H^+} \times A_{OH^-}}{\frac{A_{H^+} \times A_{HS^-}}{A_{H_2S}}} = \frac{A_{H_2S} \times A_{OH^-}}{A_{HS^-}} = K_{h_2} \; . \qquad (45)$$

Comparing equations (39), (44) and (45) one can write the following equation:

$$K_H = \frac{K_W^2}{K_{i_1} \, K_{i_2}} \; . \qquad (46)$$

Solving this expression for K_{W_2} and combining with equation 43 gives

$$A_{Hg^{++}} = \text{solubility of HgS} + \frac{K_{S.P.} \, A_{H^+}^2}{K_{i_1} \, K_{i_2} \, A_{H_2S}} \; . \qquad (47)$$

The equation makes possible calculations of the solubility of a slightly soluble metal sulfide of the mercuric sulfide type at any given pH and partial pressure of hydrogen sulfide from the solubility product constant of the metal sulfide and the two dissociation constants of hydrogen sulfide. The equation is developed on the assumption that the cation does not hydrolyze, and therefore is applicable only to acid solutions.

Consider another slightly soluble substance of the type A_2B which dissolves in water, according to the reaction

$$A_2B \rightleftarrows 2A^+ + B^= \; ,$$

and whose solubility product constant expression is

$$K_{S.P.} = A_{A^+}^2 \times A_{B^=} \; .$$

The usual method of calculating the solubility of the substance, A_2B, is as follows: Let X equal the amount of $B^=$ that is in solution; then the amount of A^+ in solution is equal to 2x. Substituting X into the solubility product constant expression gives

$$K_{S.P.} = (2X)^2 X = 4X^3 \quad .$$

The solubility of the substance A_2B is equal to the amount of $B^=$ going into solution, and therefore equal to X. The solubility would be given by

$$X = \sqrt[3]{\frac{K_{S.P}}{4}}$$

The above method of calculating solubility from solubility product constant data cannot be applied to slightly soluble compounds such as silver sulfide, which dissolves in water, according to the reaction

$$Ag_2S \rightleftharpoons 2Ag^+ + S^=$$

because of the hydrolysis of the cation and anion.

In order to calculate the solubility of silver sulfide from the solubility product constant, a special case will be considered in which the solution is distinctly acid. In acid solution the hydrolysis of the silver ion will be negligible, but the hydrolysis of the sulfide ion will be appreciable.

Recalling the solubility product constant expression for silver sulfide, solving it for the activity of the silver ion, and combining this expression with equation (40) gives

$$A_{Ag^+}^2 = \frac{K_{S.P.}\, K_H}{A_{OH^-}^2 \times A_{H_2S}} \quad . \qquad (48)$$

By definition,

$$K_W = A_{H^+} \times A_{OH^-} \quad .$$

Solving for the activity of hydroxide ion gives

$$A_{OH^-} = \frac{K_W}{A_{H^+}} \quad .$$

Combining this expression with equation (48) gives

$$A_{Ag^+} = \sqrt{\frac{K_{S.P.}\, A_{H^+}^2\, K_H}{K_w^2\, A_{H_2S}}} \qquad (49)$$

Recalling equation (46) and combining it with equation (49) gives

$$A_{Ag^+} = \sqrt{\frac{K_{S.P.}\, A_{H^+}^2}{K_i\, K_i\, A_{H_2S}}}$$

Then, since for every molecule of silver sulfide that dissolves two silver ions go into solution, the solubility of silver sulfide is given by the expression:

$$\text{solubility} = \frac{A_{Ag^+}}{2} = \frac{1}{2}\sqrt{\frac{K_{S.P.}\, A_{H^+}^2}{K_i\, K_{i_2}\, A_{H_2S}}}$$

The equation makes possible a calculation of the solubility of a slightly soluble metal sulfide of the silver sulfide type. In order to carry out the calculation, the solution must be acid, at a specific pH, and at a particular partial pressure of hydrogen sulfide.

CHAPTER V

EXPERIMENTAL TECHNIQUES

APPARATUS

The electromotive force of the various cells was measured with a Leeds and Northrup type K-2 potentiometer. A mirror type Leeds and Northrup (2620-C) galvanometer was used. The combination of potentiometer and galvanometer was sensitive to a potential of one microvolt. An Eppley standard cell, calibrated by the U. S. Bureau of Standards on March 15, 1949, was used as a primary standard. The cells being studied were maintained at constant temperature by immersion in a water bath. The bath was heated with an electric heater which was controlled by a mercury filled regulator. The temperature of the water bath was controlled to within five-hundredths of a degree centigrade. A mercury-in-glass thermometer graduated in tenths of a degree was used to measure temperature. The thermometer was calibrated by the National Bureau of Standard, March 10, 1949.

The cell containers were one-hundred milliliter Berzelius beakers fitted with two-holed rubber stoppers, one hole for the electrode or electrode housing and the other for the bridge during readings. An additional hole was bored and fitted with a gas outlet tube when cells of the first type involving hydrogen sulfide gas were under observation. The beakers were airtight except for a small interval of time during which readings were made; it was then necessary to have the bridge hole open in order to insert the bridge. A cell of the first type is shown in figure I. The bridge for cells of the first and third types was made from capillary glass tubing. This bridge was rinsed and filled with the same concentration of solution as that in the cells before inserting into the half-cells. For cells of the first type the bridge was never left in place longer than twenty seconds without being removed, washed, and refilled. For cells of the second type the bridge was a salt bridge attached to the normal calomel electrode. (See figure II).

REAGENTS

The hydrogen for the hydrogen electrodes used was commercial hydrogen. It was purified before entering the cell by bubbling through a purifying train consisting of two bottles of alkaline pyrogallic acid, two bottles containing concentrated sulfuric acid saturated with potassium dichromate, two bottles of distilled water, and one bottle of acid of the same concentration as contained in the cells.

The hydrogen sulfide for the M, MS, H_2S electrode was commercial hydrogen sulfide, 99.9 per cent pure. This gas was further purified by passing through a purifying train consisting of two bottles of saturated barium hydroxide solution, two bottles of distilled water, one bottle of acid of the same concentration as that contained in the cells.

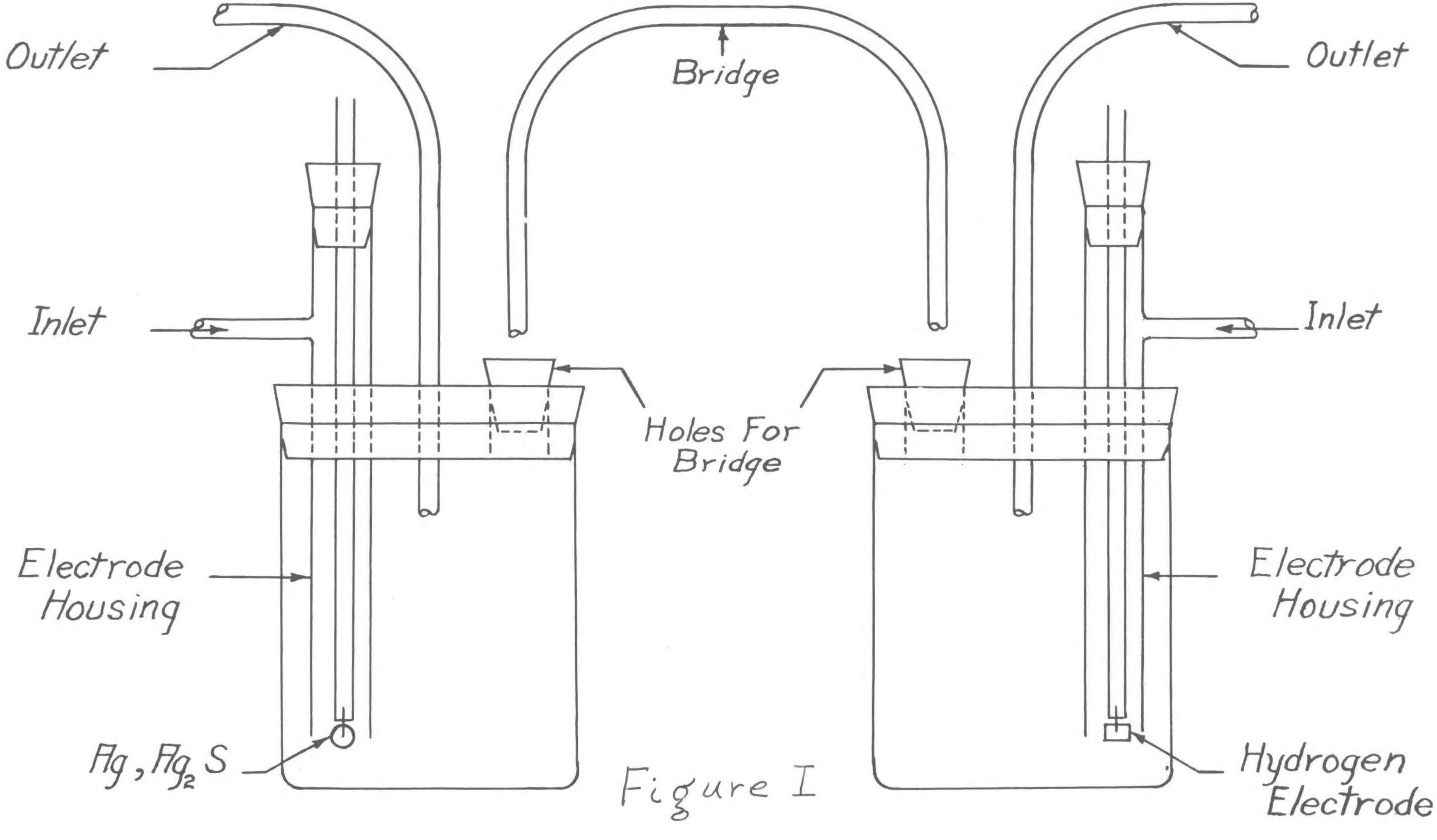
Outlet
Bridge
Outlet
Inlet
Inlet
Holes For Bridge
Electrode Housing
Electrode Housing
Ag, Ag_2S
Hydrogen Electrode

Figure I

The sodium sulfide solutions used in cells of the second and third types were prepared from $Na_2S \cdot 9H_2O$ crystals conforming to the specifications of the American Chemical Society Committee on Guaranteed Reagents. The maximum amount of impurities are ammonium compounds 0.002 per cent and sulfite and thiosulfate 0.10 per cent.

PREPARATION OF ELECTRODES

Hydrogen. The hydrogen electrodes were prepared by electroplating an even coat of platinum black onto clean platinum metal strips. These electrodes were stored in test tubes of distilled water until they were needed. The measurement of one hydrogen electrode against another showed whether the electrodes were prepared correctly.

Silver Sulfide. The silver, silver sulfide electrodes were prepared by electroplating silver on clean platinum wires from a four per cent solution of silver nitrate, then forming a coating of silver sulfide on the outside of the silver by electrolysis of a solution of sodium sulfide for a short time. Electrodes that produced the best results were obtained by electroplating the silver on the platinum wire as heavily as possible and plating the sulfide from a one molar solution of sodium sulfide for twenty-five seconds using about three hundredth ampere of current. Electrodes used without previously being coated with a silver sulfide coating were much slower reaching equilibrium than those

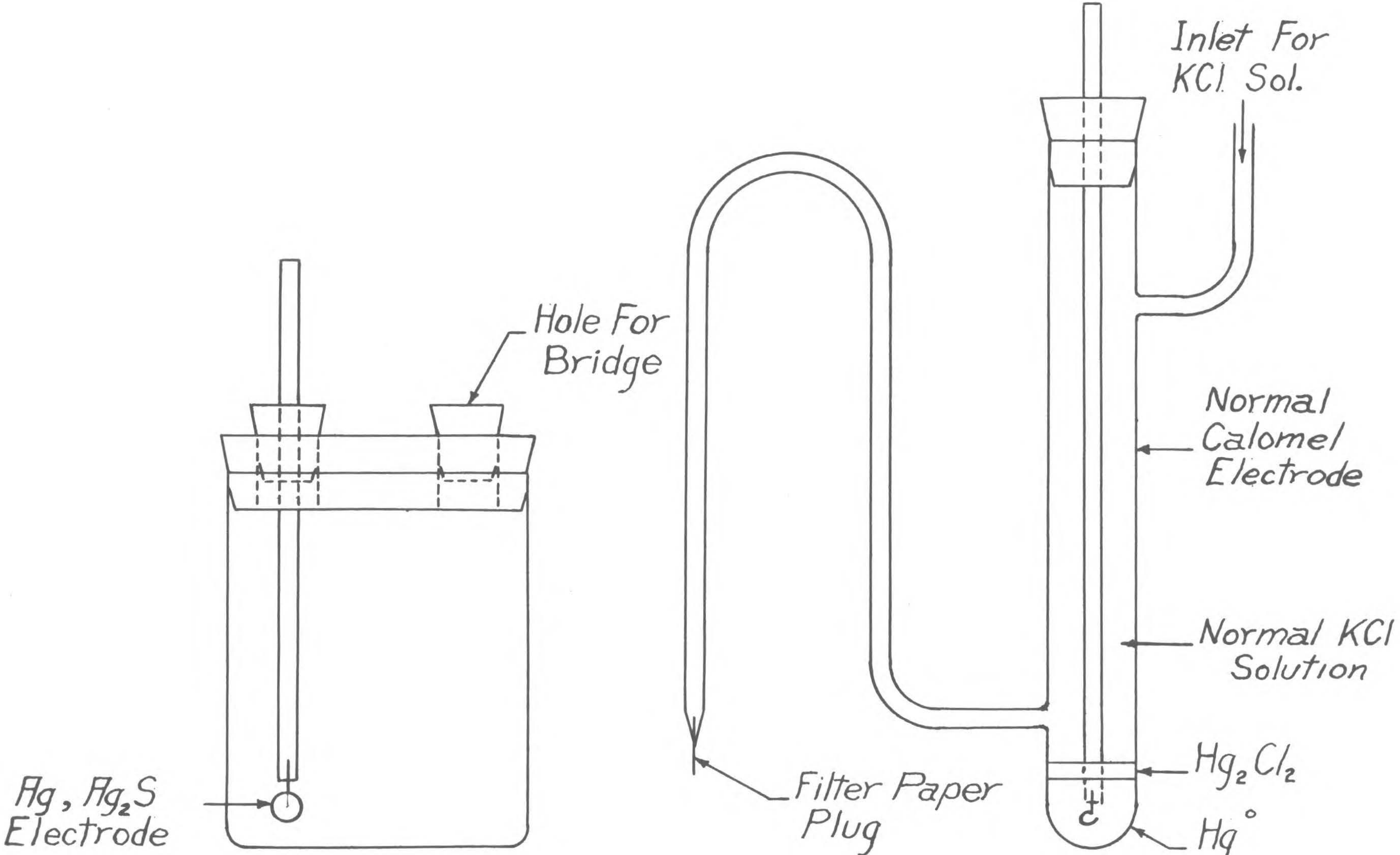
Inlet For KCl Sol.
Hole For Bridge
Normal Calomel Electrode
Normal KCl Solution
Hg_2Cl_2
Hg°
Filter Paper Plug
Ag, Ag_2S Electrode

Figure II

having a preliminary coating of silver sulfide.

Mercury Sulfide. The mercury-mercuric sulfide electrodes for cells of the second and third types in which no gas is involved were prepared as follows: A small dish was filled with re-distilled mercury and placed inside a Berzelius beaker. Contact was made by means of platinum wire fused in the end of a glass tube partially filled with mercury into which the leads from the potentiometer could be dipped. This platinum wire was completely immersed in the mercury of the dish. The beaker was partly filled with one hundredth molar sodium sulfide solution, and a coating of mercuric sulfide was electroplated on top of the mercury. The sodium sulfide solution was siphoned off and the beaker filled about two thirds full with sodium sulfide solution of the desired molality. The electrode in coming to equilibrium changes the concentration of the sulfide ion in the solution. This changed solution was removed by siphoning and re-placed by fresh sodium sulfide solution of the same desired molality. This procedure of filling the half-cell with a solution of sodium sulfide at a specific concentration, allowing the electrode to reach equilibrium, then refilling the half-cell with more solution of the original concentration was repeated until the electrode was in equilibrium with the solution at the original specified concentration.

The mercury-mercuric sulfide electrodes for cells of the first type were prepared by placing mercury filled dishes directly below the usual electrode housing. (See figures 8). Contact was made by a platinum wire fused in the end of a glass tube which was partially filled with mercury. This platinum wire was immersed completely in the mercury of the dish. The hydrogen sulfide gas was forced through the electrode housing so that the electrode was alternately covered by hydrochloric acid and hydrogen sulfide gas. A black coating of mercuric sulfide was formed on the surface of the electrode very quickly.

Lead Sulfide. A lead, lead sulfide electrode was prepared by electroplating lead metal on a clean platinum wire from a four per cent solution of lead nitrate, then forming a coating of lead sulfide on the outside of the metal by the electrolysis of sodium sulfide solution.

Nickel Sulfide. Nickel metal was electroplated on a platinum wire from a concentrated solution of nickelous nitrate. A layer of nickel sulfide was formed on the outside of this electrode by the electrolysis of sodium sulfide solution.

Cobalt Sulfide. Cobalt metal was electroplated on a platinum wire from a concentrated solution of cobalt nitrate. A coating of cobalt sulfide was formed by the electrolysis of sodium sulfide solution.

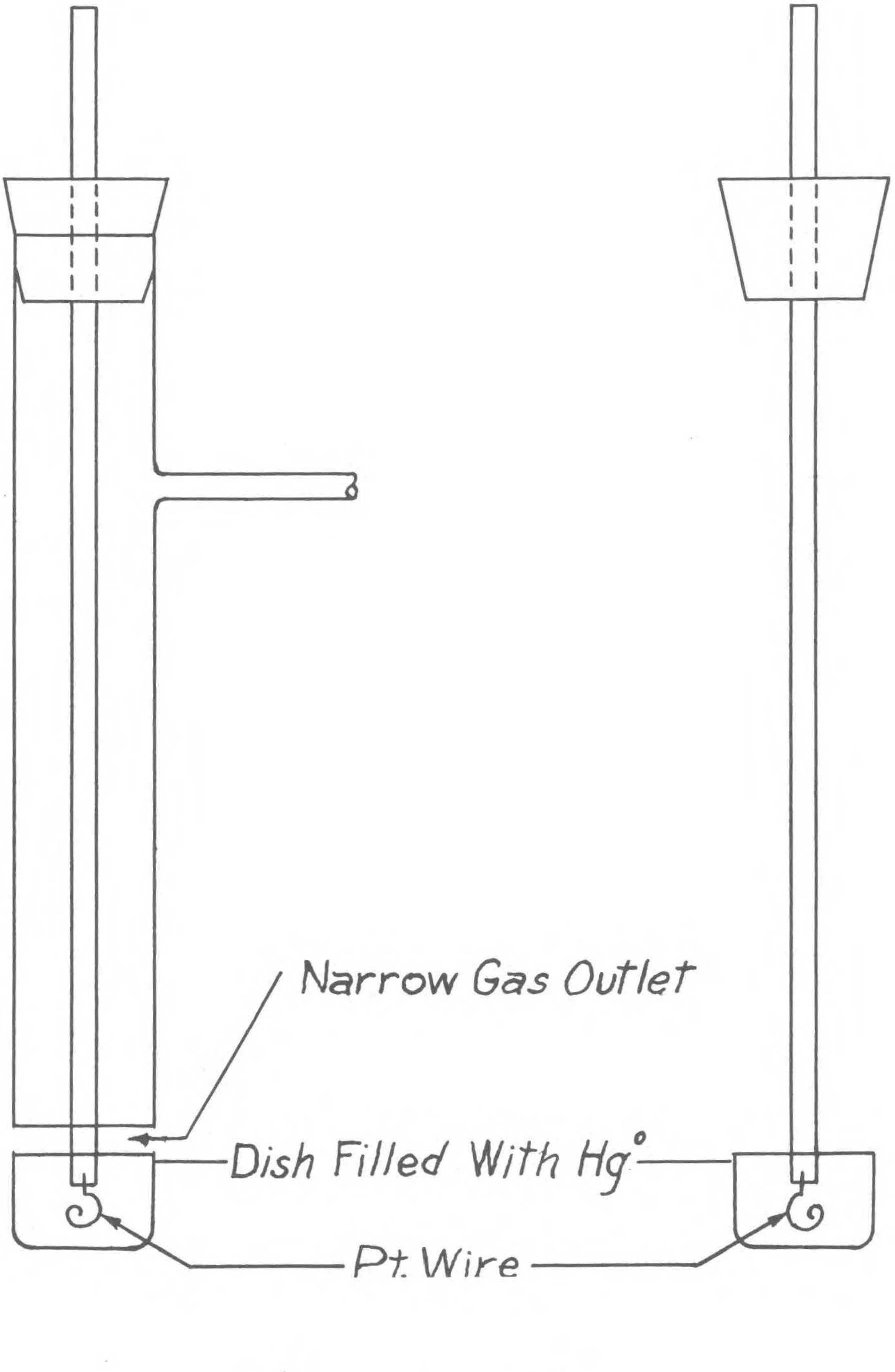

Figure III

Bismuth Sulfide. A bismuth-bismuth sulfide electrode was prepared by electroplating bismuth metal on a platinum wire from an acid solution of bismuth nitrate, and then forming a sulfide coating by electrolysis of sodium sulfide solution.

A second type of bismuth-bismuth sulfide electrode was prepared by dipping a clean platinum wire in molten bismuth metal, removing any bismuth oxide that might have formed on the electrode by dipping it in concentrated hydrochloric acid solution, and then forming a sulfide coating by electrolysis of sodium sulfide solution.

Cadmium Sulfide. Cadmium metal was electroplated from an acid solution of cadmium chloride. A cadmium sulfide coating was formed by the electrolysis of sodium sulfide solution.

Tin Sulfide. Long crystals of metallic tin were plated on a platinum wire from an acid solution of stannous chloride. A layer of sulfide was then coated by electrolysis of sodium sulfide solution.

READING TECHNIQUES

Cells of the First Type. Three identical cells were studied on each run. The hydrogen electrodes were usually platinized the night before a run was to be made. The metal-metal sulfide electrodes, with the exception of the mercury-mercuric sulfide electrodes, were prepared about one-half hour before they were to be placed in the cells. Both the hydrogen and the metal-metal sulfide electrodes were stored in test tubes of distilled water until needed. The mercury-mercuric sulfide electrodes were prepared immediately before use, as described above. (See section on Preparation of Electrodes).

The half-cells were filled half full with hydrochloric acid solution and placed in the temperature bath. Bridges made of small bore glass tubing and filled with the same concentration of acid as used in the cells were used to connect each half-cell with each other half-cell. This arrangement allowed the acid in each half-cell to siphon to the same level. This was done to prevent siphoning of solution through the contact bridge during readings, which would contaminate the electrodes.

After all the half-cells reached the same level the siphon bridges were removed, stoppers placed in the holes, and the hydrogen and hydrogen sulfide gases started. The gases were allowed to flow through the system for one-half hour before the electrodes were placed in the cells.

After the electrode had been in the cells for about three hours with the gases flowing, readings were taken between hydrogen electrodes, and then between metal-metal sulfide electrodes. If all these readings were zero, all electrodes were assumed to have reached equilibrium and readings were taken between the hydrogen and the metal-metal sulfide electrodes. The readings were made as rapidly as possible to minimize the possibility of contaminating the hydrogen electrodes by diffusion of hydrogen sulfide gas. Readings on the same cell were taken at least twenty minutes a part to allow the cell to reach equilibrium again before reading.

Cells of the Second Type. During each run measurements were made on duplicate cells at four different concentrations of sodium sulfide solution. The sodium sulfide solutions were made up at least forty-eight hours before they were used in a run. This allows the solution to reach a hydrolysis equilibrium.

The half-cells are filled with the various sodium sulfide solutions and placed in the constant temperature bath. The metal-metal sulfide electrodes, which were prepared as desribed above, were placed in the cells. The electrodes were allowed to attain equilibrium with the desired solution by using the siphoning procedure previously discussed.

The electodes are in equilibrium with the desired solution after about one-half hour and the voltage is measured using a normal calomel as a reference electrode. The cells are allowed to rest for at least thirty minutes between readings.

After all readings are taken, the various sodium sulfide solutions are analyzed as described in chapter III.

Cells of the Third Type. Ten cells were measured during each run. Silver-silver sulfide electrodes were used as reference electrodes against other metal-metal sulfide electrodes in these runs. The preparation of these electrodes was described above.

The cells filled with sodium sulfide solution and fitted with electrodes are placed in the constant temperature bath. Both electrodes are allowed to come to equilibrium by the procedure described previously. Readings are made no oftener than once every half hour to give the cells a chance to regain their equilibrium.

CHAPTER VI

EXPERIMENTAL RESULTS

CELLS OF THE FIRST TYPE

SILVER SULFIDE

Electromotive Force Measurements. The electromotive force of the cell

$$\mathrm{Pt, H_2} \left| \mathrm{HCl_{(x\ mol)}} \right| \mathrm{HCl_{(x\ mol)}} \left| \mathrm{H_2S} \right| \mathrm{Ag_2S, Ag}$$

as measured at 25° C is -0.0362 international volts. Duplicate determinations agreed within ± 0.0001 international volts. The measured standard electrode potential of the electrode Ag, Ag_2S, H_2S is 0.0362 international volts since the standard electrode potential of the hydrogen electrode is zero by definition.

Standard Free Energy of Formation. The free energy change of the reaction

$$Ag_2S + H_2 = 2Ag^\circ + H_2S$$

was calculated from the standard electromotive force using equation (33), and found to be 1,670 cal/mole.

The free energy of formation of silver sulfide at 25° C was calculated from the appropriate form of equation (37), and found to be -9,430 cal/mole.

Latimer's[1] value for the free energy of formation of hydrogen sulfide was used in this calculation.

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[1] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, 1938, p. 307.

Solubility Product Constant. The reaction taking place when slightly soluble silver sulfide dissolves in water is

$$Ag_2S \rightleftarrows 2Ag^+ + S^= \quad .$$

The free energy change of the reaction was calculated from the appropriate form of equation (37). Latimer's[2] values for the free energy of formation of the silver and sulfide ions were used in this calculation. The solubility product constant was calculated to be 6.6×10^{-52} by the use of equation (21).

MERCURY SULFIDE

Electromotive Force Measurements. The electromotive force of the cell

$$\mathrm{PT}, H_2 \,\Big|\, HCl_{(x\ mol)} \,\Big|\, HCl_{(x\ mol)} \,\Big|\, H_2S \,\Big|\, HgS, Hg$$

as measured at 25° C is -0.051 international volts. In duplicate determinations the maximum deviation was ± 0.001 international volts. The experimental standard electrode potential of the electrode Hg, HgS H_2S is -.051 international volts since the standard electrode potential of the hydrogen electrode is zero.

Free Energy of Formation. The free energy of the cell reaction $HgS + H_2 = H_2S + Hg$, as calculated from the standard electromotive force using equation (33) is 2348 cal/mole. The standard free energy of formation of mercuric sulfide was

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[2] *Ibid.*

calculated using the appropriate form of equation (37), and found to be -10,220 cal/mole. Latimer's[3] value for the free energy of formation of hydrogen sulfide was used in this calculation.

Solubility Product Constant. The equation for the dissolving of slightly soluble mercuric sulfide is

$$HgS = Hg^{++} + S^{=} \quad .$$

The free energy change of this reaction was calculated from equation (37), using the experimental free energy of formation of mercuric sulfide and Latimer's[4] value for the free energy of formation of the mercuric and sulfide ions. The solubility product constant of mercuric sulfide was found to be 1.7×10^{-54}, using the free energy value of the reaction calculated above and equation (21).

LEAD SULFIDE

Determinations were made on lead sulfide at different concentrations of acid and it was found that the cell reaction was not independent of the concentration of the acid in the cell. Therefore no reliable results were obtained.

CELLS OF THE SECOND TYPE

SILVER SULFIDE

Electromotive Force Measurements. The electromotive

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[3] Ibid.

[4] Ibid.

force of the cell

$$Ag,Ag_2S \,|\, S^{=} \;\|\; \text{normal calomel}$$

was measured and the potential of the normal calomel electrode algebraically subtracted from the total potential to give the potential of the $Ag,Ag_2S \,|\, S^{=}$ half-cell. This measured electrode potential was converted to the standard electrode potential by using the appropriate form of equation (36)

$$\mathcal{E} = \mathcal{E}^{\circ} + \frac{RT}{n\mathcal{F}} \ln A_{S^{=}} \quad .$$

The details of calculating the activity of the sulfide ion were discussed in chapter III. The standard electrode potential was calculated to be 0.713 international volts. Duplicate determinations give results that agree within one in the third place.

Free Energy of Formation. The free energy change of the reaction was calculated using equation (33). The free energy of formation of silver sulfide was then calculated from the appropriate form of equation (37), and was found to be -9,455 cal/mole. The free energy of formation of the sulfide ion used in this calculation was 23,420 cal/mole which is the value reported by Latimer.[5]

Solubility Product Constant. The free energy of the reaction

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[5] Ibid.

$$Ag_2S = 2Ag^+ + S^=$$

was calculated from the measured free energy of formation of silver sulfide and Latimer s[6] values for the free energy of formation of the silver and sulfide ions. The solubility product was calculated from this free energy value by use of equation (21).

MERCURY SULFIDE

The electromotive force of the cell $Hg,HgS \mid S^= \parallel$ normal calomel was measured, and the potential of the $Hg,HgS \mid S^=$ half-cell calculated by subtracting the potential of the normal calomel. This measured potential was converted to standard potential by the use of the appropriate form of equation (36),

$$\mathcal{E} = \mathcal{E}^\circ + \frac{RT}{n\mathcal{F}} \ln A_{S^=} .$$

The calculation of the sulfide ion activity was described in chapter III. The standard electrode potential was found to be 0.733 international volts. Duplicate determinations checked within one in the third place.

Free Energy of Formation. The standard free energy change of the half-cell reaction was calculated from the standard electrode potential and from using equation (33). The free energy of formation of mercuric sulfide was calculated from the free energy of the reaction and Latimer's[7] value for the

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[6] Ibid.

[7] Ibid.

free energy of formation of the sulfide. The free energy of formation of mercuric sulfide at 25° C was calculated to be -10,400 cal/mole.

Solubility Product Constant. The free energy change of the reaction

$$HgS = Hg^{++} + S^{=}$$

was calculated from the free energy of formation of mercuric sulfide and from the free energy of formation of the sulfide and mercuric ion as listed in tables.[8] The solubility product constant was calculated from this standard free energy change by the use of equation (21). The calculated value of the solubility for mercuric sulfide is 2.4×10^{-54}.

BISMUTH SULFIDE

No reliable results were obtained for bismuth sulfide using this type cell. A possible explanation for this failure would be that the bismuth electrodes were reacting chemically with the strongly basic sodium sulfide solution.

CELLS OF THE THIRD TYPE

Mercury Sulfide. The cell

$$Hg,HgS \mid S^{=} \mid S^{=} \mid Ag_2S,Ag$$

was studied in an effort to obtain an additional check on the free energy of formation of mercuric sulfide assuming that the free energy of formation of silver sulfide was

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[8] *Ibid.*

known. No reliable results were obtained, however, because of the erratic nature of the electromotive force reading. The lack of a constant potential could have been due to the small differential in voltage that must exist between the two electrodes.

Other Metal Sulfides. A number of other metal sulfides such as nickel sulfide, cobalt sulfide, cadmium sulfide, and tin sulfide were tried in cells of this third type, but no reliable results were obtained. A possible explanation would be that the metals were reacting with the basic sodium sulfide solution.

CHAPTER VII

SUMMARY

Values for the standard free energy of formation and the solubility product constants of silver and mercury sulfides were determined from electromotive force measurements on galvanic cells of the types

(1) $\mathrm{Pt,H_2} \mid \mathrm{HCl}_{(x\ \mathrm{mol})} \mid \mathrm{HCl}_{(x\ \mathrm{mol})} \mid \mathrm{H_2S} \mid \mathrm{MS,\ M}$

(2) $\mathrm{M,MS} \mid \mathrm{S}^{=}_{(a=\mathrm{variable})} \parallel$ normal calomel

The weighted mean values for these thermodynamic constants are:

$\Delta F^{\circ}_{\mathrm{Ag_2S}25^{\circ}}$ - - - - - - - -9,540 cal/mole

$K_{\mathrm{S.P.Ag_2S}25^{\circ}}$ - - - - - - - 6.6×10^{-52}

$\Delta F^{\circ}_{\mathrm{HgS}25^{\circ}}$ - - - - - - - -10,310 cal/mole

$K_{\mathrm{S.P.HgS}25^{\circ}}$ - - - - - - - 2.1×10^{-54}

The generally accepted values which are quoted in most textbooks of chemistry at the present time are those reported by Latimer[1] in his book Oxidation Potentials. Latimer lists -9,500 cal/mole for the standard free energy of formation of silver sulfide and -8,800 cal/mole for the standard free energy of formation of mercuric sulfide. The value obtained in this study for the free energy of formation of silver sulfide increases the accuracy of the figure quoted in Latimer's

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[1] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Incorporation, New York, 1938, p. 305.

tables by at least one significant figure. The value obtained in this study for the free energy of formation of mercuric sulfide makes a correction of 1,500 cal/mole in the estimate made by Latimer.

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