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

Free Energy of Formation and Solubility Product Constant of Mercuric Sulfide

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By means of electromotive force measurements on cells of the types $\mathrm{Hg, HgS}\ \Big|\ \begin{matrix}\mathrm{H_2S}\\ (1\ \mathrm{atm.})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{HCl}\\ (0.1\ \mathrm{molal})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{HCl}\\ (0.1\ \mathrm{molal})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{H_2, Pt}\\ (1\ \mathrm{atm.})\end{matrix}$ and $\mathrm{Hg, HgS}\ |\ \mathrm{S^{=}}\ \|$ normal calomel, values of the standard free energy change of the reactions $\mathrm{Hg(l)} + \mathrm{H_2S(g)} \rightleftarrows \mathrm{HgS(s)} + \mathrm{H_2(g)}$ and $\mathrm{Hg(l)} + \mathrm{S^{=}(aq)} \rightleftarrows \mathrm{HgS(s)} + 2e$ have been determined. From these values the standard free energy of formation and solubility product constant of HgS (black) at 25° are calculated to be -10.22 kcal./mole and 9×10^{-52}, respectively.

The two most generally accepted values for the solubility product constant of the black form of HgS are 3×10^{-54} and 3×10^{-53}. The former was reported by Kolthoff,[1] who had recalculated electrochemical data reported by Knox[2] (1906); the latter was calculated by Latimer[3] (1938) from heat of formation and entropy data. The discrepancy of these values, which represent the most reasonable data from the very meager information on the solubility product constant of mercuric sulfide, made further investigation of this subject desirable.

The method used in the study reported in this paper was to measure the standard free energy of formation of HgS ($\Delta Ff^0_{\mathrm{HgS}}$) and calculate the solubility product constant from the free energy data. Values of $\Delta Ff^0_{\mathrm{HgS}}$ were obtained from electromotive force measurements on two types of cells which had proved successful in a similar study with $\mathrm{Ag_2S}$.[4]

Cell type I was

$$\mathrm{Hg, HgS}\ \Big|\ \begin{matrix}\mathrm{H_2S}\\ (1\ \mathrm{atm.})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{HCl}\\ (0.1\ \mathrm{molal})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{HCl}\\ (0.1\ \mathrm{molal})\end{matrix}\ \Big|\ \begin{matrix}\mathrm{H_2, Pt}\\ (1\ \mathrm{atm.})\end{matrix}$$

the over-all reaction for which is

$$\mathrm{Hg(l)} + \mathrm{H_2S(g)} \rightleftarrows \mathrm{HgS(s)} + \mathrm{H_2(g)}$$

The Nernst equation for the cell reaction is

$$E = E^0 - (RT/n\mathfrak{F}) \ln\left[(a_{\mathrm{HgS}} \cdot f_{\mathrm{H_2}})/(a_{\mathrm{Hg}} \cdot f_{\mathrm{H_2S}})\right]$$

Calculations of the fugacity of $\mathrm{H_2}$ and $\mathrm{H_2S}$ gases at one atmosphere pressure by means of the Berthelot equation of state show the value of $\ln(f_{\mathrm{H_2}}/f_{\mathrm{H_2S}})$ to be negligible. Since the other substances involved in the reaction are in their standard states, the measured electromotive force was taken as the standard electromotive force.

Experimental.—The Hg, HgS electrodes were very simply prepared by making gas outlet holes one cm. from the bottom of 1.6×13 cm. glass tubes sealed at the lower end. The one cm. of the tubes below the holes was filled with mercury and the tubes immersed in the electrolyte of the cell. $\mathrm{H_2S}$ gas was led into the cell through side arms in the electrode tubes and bubbled gently over the surface of the Hg, which formed a black coating within a few minutes after contact with the gas. The mercury used was triply distilled reagent grade. The remainder of the experimental details is the same as was used in the study of $\mathrm{Ag_2S}$.[4]

Results.—The arithmetical mean of the standard electromotive force of a total of 12 cells at 2 acid concentrations (0.1 and 0.5 *N* HCl) was 0.0504 absolute volt, with average deviation from the mean of ±0.0009 volt. The value of the standard free energy change of the half cell reaction calculated from the relationship $\Delta F^0 = -n\mathfrak{F}E^0$, using the value of 23,063 cal. abs. $\mathrm{v.}^{-1}$ g. $\mathrm{equiv.}^{-1}$ for the faraday is -2.33 kcal. This value together with the value of -7.892[5] for $\Delta Ff^0_{\mathrm{H_2S}}$ results in -10.22 kcal. for $\Delta Ff^0_{\mathrm{HgS}}$ at 25°.

Cell type II was

$$\mathrm{Hg, HgS}\ |\mathrm{S^{=}}\|\ \text{normal calomel}$$

the sulfide half cell reaction for which is

$$\mathrm{Hg(l)} + \mathrm{S^{=}(aq)} \rightleftarrows \mathrm{HgS(s)} + 2e$$

This cell will not give results as accurate as the cell previously described because of the uncertainty of the assumption of complete elimination of liquid junction potential by a saturated KCl salt bridge. However, within the limits of the accuracy of this assumption, the results obtained with this cell can act as a check on the results of cell type I. The study of Bjerrum and Unmack,[6] shows that the error involved in the above assumption may be as high as 1–2 millivolts. A 2 millivolt error in the value of E results in slightly less than a 1% error in the value of $\Delta Ff^0_{\mathrm{HgS}}$.

The liquid junctions with the KCl solution were formed inside a glass tube 4 mm. in diameter. The reproducibility of the junctions as determined by measuring the electromotive force of each Hg, HgS, $\mathrm{S^{=}}$ half cell against two different calomel half cells was good to within 0.3 millivolt.

The free energy of formation of HgS was obtained from measurements of the electromotive force of cell type II through the relationship

$$\Delta Ff^0_{\mathrm{HgS}} = \Delta Ff^0_{\mathrm{HS^-}} - n\mathfrak{F}E + RT \ln\,(a_{\mathrm{HS^-}} \cdot a_{\mathrm{OH^-}}/K_{\mathrm{w}}) \quad (1)$$

in which E refers to the electromotive force of the Hg, HgS, $\mathrm{S^{=}}$ half cell, $a_{\mathrm{HS^-}}$ and $a_{\mathrm{OH^-}}$ refer to the activities of the $\mathrm{HS^-}$ and $\mathrm{OH^-}$ ions in the solution of $\mathrm{Na_2S}$ used as the electrolyte of the half cell, and K_{w} is the ion product of water, 1.008×10^{-14}.

This equation is derived from the following reasoning: The standard free energy change of the Hg, HgS, $\mathrm{S^{=}}$ half cell reaction is

$$\Delta F^0 = \Delta Ff^0_{\mathrm{HgS}} - \Delta Ff^0_{\mathrm{S^{=}}} = n\mathfrak{F}E^0 \quad (2)$$

The Nernst equation for the same reaction is

$$E = E^0 + (RT/n\mathfrak{F}) \ln a_{\mathrm{S^{=}}} \quad (3)$$

Solving for E^0 in (3) and substituting into (2) gives

$$\Delta Ff^0_{\mathrm{HgS}} - \Delta Ff^0_{\mathrm{S^{=}}} = -n\mathfrak{F}E + RT \ln a_{\mathrm{S^{=}}} \quad (4)$$

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

[2] J. Knox, *Z. Elektrochem.*, **12**, 366 (1906).

[3] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Corp., New York, N. Y., 1938.

[4] J. Rex Goates, Arthur G. Cole, Earl L. Gray and Neal D. Faux, THIS JOURNAL, **73**, 707 (1951).

[5] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Natl. Bur. Standards Circ.* 500, U. S. Government Printing Office, Washington, 1950.

[6] Bjerrum and Unmack, *Kgl. Danske. Vid. Selsk. Mat. Fys. Med.*, **9**, 1 (1929).

The activity of the sulfide ion may be expressed in terms of a_{HS^-}, a_{OH^-}, and the hydrolysis constant (K_w/K_i) of the $S^=$ ion. Only the first hydrolysis to the HS^- ion needs be considered, the effects of the second step of the hydrolysis being negligible in solutions of Na_2S; hence,

$$a_{S^-} = a_{HS^-} \cdot a_{OH^-} \cdot K_i/K_w \qquad (5)$$

Substituting the value of a_{S^-} in (5) into (4) gives

$$\Delta Ff^0_{HgS} - \Delta Ff^0_{S^-} = -n\mathfrak{F}E + RT \ln (a_{HS^-} \cdot a_{OH^-} \cdot K_i/K_w) \qquad (6)$$

K_i refers to the reaction $HS^- \rightleftarrows H^+ + S^=$, the standard free energy change for which is

$$\Delta Ff^0_{S^-} - \Delta Ff^0_{HS^-} = -RT \ln K_i \qquad (7)$$

Substitution of (7) into (6) gives (1).

The activities of the HS^- and OH^- ions were obtained from the following relationships, in which parentheses denote molal concentrations.

$$a_{HS^-} = (HS^-)\gamma_{HS^-} = [(A) - (S^=)]\gamma_{HS^-} \qquad (8)$$

$$a_{OH^-} = (OH^-)\gamma_{OH^-} = [(B) - (HS^-) - 2(S^=)]\gamma_{OH^-} \qquad (9)$$

The symbol (A) represents the concentration of total sulfides ($HS^- + S^=$), which was determined volumetrically by oxidation with calcium hypochlorite.[7] The symbol (B) is the hydroxyl ion concentration produced by complete hydrolysis of the Na_2S solution, 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 H_2S.

The molality of the $S^=$ ion, which is required in equations (1) and (2), was calculated from the relationship

$$[[\gamma_{S^-} \cdot K_h/\gamma_{HS^-} \cdot \gamma_{OH^-}] + (B)](S^=) - (S^=)^2 = (A)(B) - (A)^2 \qquad (10)$$

This equation results from substituting the expressions given for a_{HS^-} and a_{OH^-} in equations (8) and (9) into

$$a_{S^=} = a_{OH^-} \cdot a_{HS^=}/K_h$$

The value of K_h was taken as 0.029, which was obtained from the relationship $K_h = K_w/K_i$, using the value of 3.5×10^{-13} for K_i. This figure was calculated from the values of the standard free energy of formation of HS^- ion (3.01 kcal.) and $S^=$ ion (20.0 kcal.) given in "Selected Values of Chemical Thermodynamic Properties."[6]

The values of γ_{HS^-} and γ_{OH^-} used in equations (8) and (9) were calculated from Debye–Hückel theory, using 3.5×10^{-8} cm. as the effective diameter of the ions. The ionic strength did not exceed 0.02 in any of the solutions.

Results.—The arithmetical mean of the value of the standard free energy of formation of HgS calculated from electromotive force measurements made on a total of 6 cells at 3 concentrations of Na_2S (0.005 − 0.01 molal) was −10.5 kcal., the average deviation from the mean being ±0.07 kcal.

Discussion

Measurements of the free energy of formation of mercuric sulfide from the two types of cells are in fair agreement (−10.22 and −10.5 kcal.) Estimates of accuracy based chiefly upon reproducibility of electromotive force readings, analytical data, accuracy of the thermodynamic constants used in the calculations, and estimates of error from liquid junctions are indicated by the number of significant figures reported.

Solubility Product Constant.—The solubility product constant of HgS may be calculated from the ΔF^0 of the reaction

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

by means of the relationship $\ln K = -\Delta F^0/RT$. Using the value of −10.22 kcal. for the standard free energy of formation of HgS, and 39.38[5] and 20.0[5] kcal. for the standard free energy of formation of the Hg^{++} and $S^=$ ions, respectively, we calculated the solubility product constant of HgS at 25° to be 9×10^{-52}. If the value reported by Kolthoff[1] is corrected for the latest values of the free energy of formation of Hg^{++} and $S^=$ ions,[5] it becomes 8×10^{-52}, which is in fair agreement with the value obtained in this investigation.

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(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1937.