A Study of the Effect of Dissolved Ag₂SO₄ on the Activity of H₂SO₄ Solutions by Means of E.M.F. Measurements[1]

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E.M.F. measurements of the cell Pt, PbO₂, PbSO₄, H₂SO₄$_{(m)}$, Ag₂SO₄, Ag have been used to demonstrate the effect of Ag₂SO₄ on the activity of H₂SO₄ solutions. It is pointed out that care must be used in the interpretation of data involving the use of a Ag₂SO₄ electrode in H₂SO₄ solutions. It is necessary to refer the thermodynamic functions of the H₂SO₄ to a Ag₂SO₄ solution, the concentration of which may be by no means inappreciable.

Introduction

In a previous paper[2] the solubility of Ag₂SO₄ in H₂SO₄ solutions was described as a function of H₂SO₄ concentration and temperature. It was shown that the solubility increased with H₂SO₄ concentration and that this effect became very pronounced at higher temperatures. Hence when the Ag, Ag₂SO₄ electrode is used in H₂SO₄ solutions account must be taken of the solubility of the Ag₂SO₄ in these solutions. For example, the thermodynamic functions of H₂SO₄ are not those of H₂SO₄ in pure aqueous solution but are referred to a Ag₂SO₄ solution, the concentration of which may be by no means inappreciable. In the present paper it will be shown how e.m.f. measurements of the cell Pt, PbO₂, PbSO₄, H₂SO₄$_{(m)}$, Ag₂SO₄, Ag can be used to determine the effect of dissolved Ag₂SO₄ on the activity of H₂SO₄ solutions.

Experimental

Two types of Pt, PbO₂, PbSO₄ electrodes were used in the present work.

(1) Electrodes were prepared according to the method suggested by Vosburgh and Craig[3] and used by Hamer.[4] Essentially, this type of electrode consisted of a platinum wire covered with a slurry of PbO₂ and PbSO₄. The PbO₂ was prepared by electrolysis of a solution of Pb(NO₃)₂ in HNO₃. After being treated in hot H₂SO₄ the PbO₂ was mixed with PbSO₄ and slurried in H₂SO₄ of the concentration to be studied.

(2) Electrodes were also prepared by plating onto platinum a hard, tightly adhering deposit of PbO₂ from a 35% HNO₃ solution saturated with Pb(NO₃)₂. The electrodeposition was carried out at reflux temperature (ca. 111°). In the course of the investigation the time of deposition was varied from a few seconds to several hours and the current from 10 milliamperes to one ampere. In all cases the electrode base consisted of a spatula of platinum made by flattening a 25 mm. length of 18 gage wire on one end. The platinum was sealed in a soft glass tube for support so that the average dimensions of the exposed part were 15 × 2 × 0.25 mm. Connection to the platinum was accomplished by soldering stranded insulated copper wire to the end within the glass tube. In the first experiments the electrode was surrounded with PbSO₄ slurried in H₂SO₄ of the concentration to be studied. The slurry was held in place with a loose sleeve of Fiberglas or a wad of glass wool. In the later experiments this practice was abandoned and the hot, freshly plated electrode was placed directly in the sulfuric acid cell-medium. Solid PbSO₄ was added to the excess Ag₂SO₄ in the cell to maintain a saturated solution with respect to both components.

The Ag, Ag₂SO₄ electrode consisted of a spiral of silver wire spotted to a platinum wire which was sealed into a soft glass tube. Connection with the silver electrode was accomplished in the same fashion as with PbO₂, PbSO₄ elec-

trode. The silver spiral was surrounded with crystals of Ag₂SO₄ prepared by the method described by Archibald.[5] A sufficient amount of Ag₂SO₄ was used so that the H₂SO₄ solution was saturated with Ag₂SO₄ at all temperatures. The electrodes and solution were sealed into a Fischer and Porter tube provided with the necessary flanges to hold the Teflon ends in place. This type of apparatus was suitable for use to about 140°.

The electrode assembly was heated in an electric oven provided with a circulating fan. The temperature was controlled to ±1° and was measured by means of an iron–constantan thermocouple.

Electrode and thermocouple e.m.f.'s were measured by means of a Rubicon Portable Precision Potentiometer.

Results and Discussion

In the course of the work an attempt was first made to use the type of Pt, PbO₂, PbSO₄ electrode described by Hamer (type 1 above). It was observed, however, that different e.m.f. values were obtained from two different platinum wires immersed in the same PbO₂, PbSO₄ slurry when measured against a Ag, Ag₂SO₄ electrode. Although new platinum wires were used which showed no difference in potential between each other in H₂SO₄ solutions, they sometimes showed a difference of at least 100 mv. when immersed in the PbO₂, PbSO₄ slurry. The same phenomenon was observed with old platinum wires that had been in contact with lead solutions. No explanation for this behavior is available, although it may be due in some way to adsorption of lead or a lead compound on the platinum.

It was possible to bring two platinum electrodes in PbO₂, PbSO₄ slurry to the same e.m.f. vs. a Ag, Ag₂SO₄ electrode by connecting them together for a short time. The agreement was temporary, however, and an e.m.f. between them returned on standing. A pair of platinum wires sealed in glass and left for several weeks in a PbO₂, PbSO₄ slurry still showed a difference in potential of 1.5 mv. Even annealing the wires in a muffle furnace did not significantly reduce the potential difference. Because of the difficulty of obtaining reproducible results with this type of PbO₂, PbSO₄ electrode, attention was directed to a study of the electrode made by plating PbO₂ on platinum (type 2 above).

Hard, mechanically resistant PbO₂ for electrode purposes has been prepared by others.[6] While not all these modifications have been investigated in the present work, the method of preparation described as type 2 seemed to offer the most promise. Merely plating PbO₂ onto platinum by electrolysis of Pb(NO₃)₂–HNO₃ solutions without regard to

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) M. H. Lietzke and R. W. Stoughton, This Journal, 78, 3023 (1956).

(3) W. C. Vosburgh and D. N. Craig, ibid., 51, 2009 (1929).

(4) W. J. Hamer, ibid., 57, 9 (1935).

(5) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

(6) K. Suzino, Bull. Chem. Soc. Japan, 23, 115 (1950).

the concentrations and temperature given did not produce a satisfactory electrode. Besides variability in initial potential from sample to sample the electrodes tended to suffer a decrease in potential with age. This and other possible sources of error in work involving the use of the PbO$_2$, PbSO$_4$ electrode have been considered by Brown and Zimmer.[7]

Figure 1 shows the e.m.f. values obtained with the cell Pt, PbO$_2$, PbSO$_4$ (type 2), H$_2$SO$_{4(m)}$, Ag$_2$SO$_4$-(sat.), Ag as a function of temperature and concentration. The various points on the graph were obtained in the course of several different runs at each concentration (6 in the case of 1 m H$_2$SO$_4$). A new Pt, PbO$_2$, PbSO$_4$ electrode was used in each run. The mean values of the e.m.f. (in millivolts) for the system at each concentration of H$_2$SO$_4$ as a function of temperature are given by the equations 1a to 1d obtained by the method of least squares.
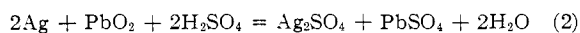
$$E_{(0.3\ m\ H_2SO_4)} = 838.8 + 0.1041t \qquad (1a)$$

$$E_{(0.5\ m\ H_2SO_4)} = 850.8 + 0.2723t \qquad (1b)$$

$$E_{(1.0\ m\ H_2SO_4)} = 891.9 + 0.3406t \qquad (1c)$$

$$E_{(2.0\ m\ H_2SO_4)} = 928.7 + 0.6126t \qquad (1d)$$

Equations 1a to 1d were solved to give mean e.m.f. values at 25° intervals from 0 to 125°.

When the Ag, Ag$_2$SO$_4$ electrode is measured against the Pt, PbO$_2$, PbSO$_4$ electrode in H$_2$SO$_4$ the cell reaction is

$$2Ag + PbO_2 + 2H_2SO_4 = Ag_2SO_4 + PbSO_4 + 2H_2O \qquad (2)$$

Hence the e.m.f. of the cell can be expressed by the Nernst equation in the form

$$E = E^0 - \frac{RT}{2F}\ln\frac{a_w{}^2}{a^2{}_{H_2SO_4}} \qquad (3)$$

Therefore

$$E = E^0 - \frac{RT}{F}\ln a_w + \frac{RT}{F}\ln a_{H_2SO_4} \qquad (4)$$

where $a_{H_2SO_4}$ represents the activity of H$_2$SO$_4$ in a solution saturated with Ag$_2$SO$_4$. In the present work it was not possible to obtain reproducible e.m.f. values over the entire temperature range at H$_2$SO$_4$ concentrations much below 0.3 m. If all e.m.f. measurements are referred to the values at 0.3 m and substituted into equation 4, it *follows that*

$$E_m - E_{(0.3)} = \frac{RT}{F}\ln\frac{a_{w(0.3)}}{a_{wm}} + \frac{RT}{F}\ln\frac{a_{H_2SO_4 m}}{a_{H_2SO_4(0.3)}} \qquad (5)$$

Equation 5 can be rearranged to give

$$\log\frac{a_{H_2SO_4 m}}{a_{H_2SO_4(0.3)}} = \frac{F}{2.303RT}(E_m - E_{(0.3)}) - \log\frac{a_{w(0.3)}}{a_{wm}} \qquad (6)$$

Values of $a_{H_2SO_4(m)}/a_{H_2SO_4(0.3)}$ were then calculated at 25° intervals from 0 to 125°. For convenience in representing the data and in order to facilitate comparison of $a_{H_2SO_4(m)}/a_{H_2SO_4(0.3)}$ ratios at different molalities values of the ratios were multiplied at each concentration by a constant $k_m{}^{-1}$, where $k_m = [a_{H_2SO_4(m)}/a_{H_2SO_4(0.3)}]_0$. This process normalized all the plots to unity at 0°. Values of k_m as a function of concentration both for pure H$_2$SO$_4$ solutions and for H$_2$SO$_4$ solutions saturated with Ag$_2$SO$_4$ are shown in Table I.

The a_w's in equation 6 represent the activity of

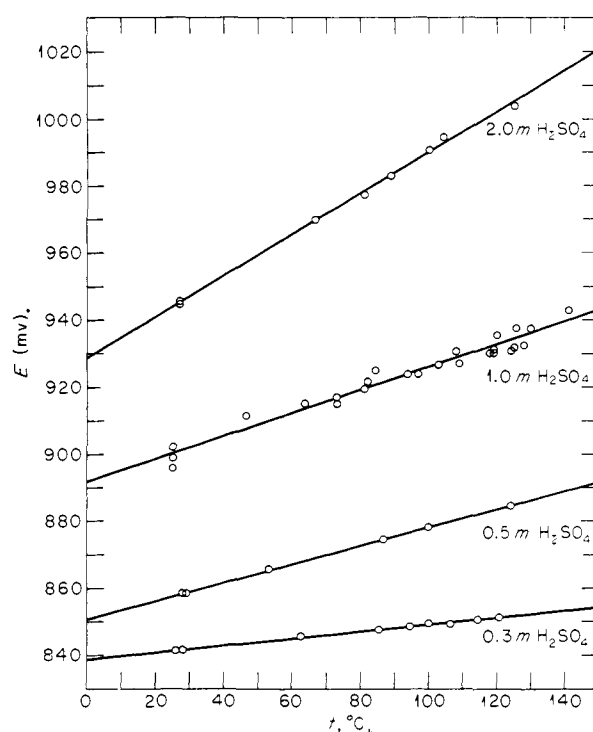(7) D. J. Brown and J. C. Zimmer, THIS JOURNAL, **52**, 1 (1930).

Fig. 1.—E.m.f. of the cell Pt, PbO$_2$, PbSO$_4$, H$_2$SO$_4$(m), Ag$_2$SO$_4$, Ag as a function of temperature and H$_2$SO$_4$ concentration.

TABLE I

VALUES OF $k_m = [a_{H_2SO_4(m)}/a_{H_2SO_4(0.3)}]_0$ AS A FUNCTION OF CONCENTRATION

$m_{H_2SO_4}$	0.5	1.0	2.0
$k_{H_2SO_4}$	2.8690	14.423	109.48
$k_{H_4SO_4 + Ag_2SO_4}$	1.652	9.270	41.93

water in H$_2$SO$_4$ solutions saturated with Ag$_2$SO$_4$. Since these data were not available a_w's in pure aqueous H$_2$SO$_4$ solutions were used in the calculations.[8] Since the terms log $a_{w(0.3)}/a_{wm}$ are small compared to the $F/2.303$ $(E_m - E_{(0.3)})$ terms this introduces no very large error in the calculations. Values of a_w above 60° were derived by a linear extrapolation of the values measured between 0 and 60°.

In order to compare the values of $a_{H_2SO_4}/a_{H_2SO_4(0.3)}$ measured in H$_2$SO$_4$ solutions saturated with Ag$_2$SO$_4$ with values of the same ratio measured in H$_2$SO$_4$ solutions containing no Ag$_2$SO$_4$ equation 7 was integrated over the desired temperature range.

$$\frac{\partial \ln a_m/a_{(0.3)}}{\partial T} = \frac{\bar{L}_2(T)_{(0.3)} - \bar{L}_2(T)_m}{RT^2} \qquad (7)$$

In this equation a_m and $a_{(0.3)}$ refer to activities of H$_2$SO$_4$ in water and $\bar{L}_2(T)_m$ and $\bar{L}_2(T)_{(0.3)}$ to the corresponding partial molal heat content values of the H$_2$SO$_4$ which are functions of the temperature. The $\bar{L}_2(T)$ values have been determined by Hamer and can be expressed as quadratic functions of the temperature as shown in equations 8 and 8a.

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 436.

$$\bar{L}_2(T)_{(.3)} = \bar{L}_2(0)_{(0.3)} + \alpha_{(0.0)}t + \beta_{(0.3)}t^2 \qquad (8)$$

and

$$\bar{L}_2(T)_m = \bar{L}_2(0)_m + \alpha_m t + \beta_m t^2 \qquad (8a)$$

When these equations are substituted into equation 7 and the integration performed equation 9 is obtained

$$\ln \frac{[a_{H_2SO_4m}/a_{H_2SO_4(0.3)}]_t}{[a_{H_2SO_4m}/a_{H_2SO_4(0.3)}]_0} = \left[\frac{\bar{L}_2(0)_{(0.3)} - \bar{L}_2(0)_m - 273.16(\alpha_{0.3} - \alpha_m) + 273.16^2(\beta_{(0.3)} - \beta_m)}{273.16RT}\right](T - 273.16)$$

$$+ \left[\frac{(\alpha_{(0.3)} - \alpha_m) - 2(273.16)(\beta_{(0.3)} - \beta_m)}{R}\right]\ln T/273.16 + \left[\frac{(\beta_{(0.3)} - \beta_m)(T - 273.16)}{R}\right] \qquad (9)$$

Using the partial molal heat content data of Harned and Hamer[9] values of $a_{H_2SO_4m}/a_{H_2SO_4(0.3)}$ were calculated for H_2SO_4 in water over the same range of temperature and concentration as in the previous calculation.

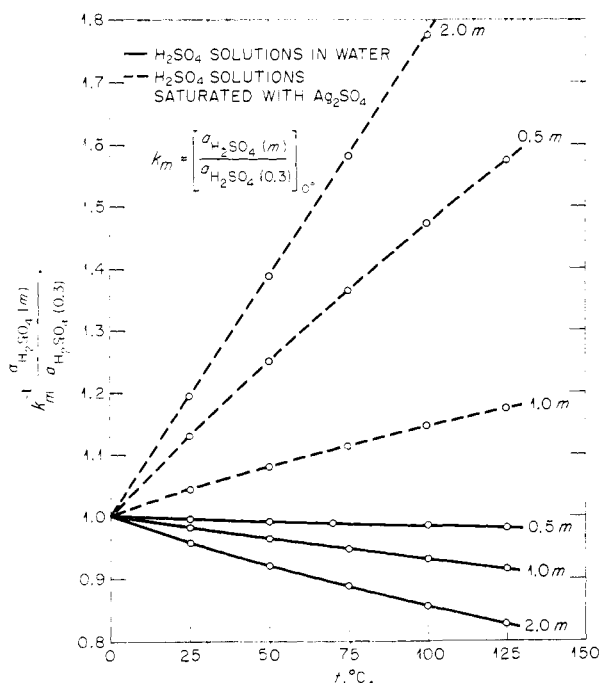Fig. 2.—The variation of $k_m^{-1}(a_{H_2SO_4m}/a_{H_2SO_4(0.3)})$ as a function of temperature and H_2SO_4 concentration both in the presence and absence of Ag_2SO_4.

Figure 2 shows the variation of k_m^{-1} ($a_{H_2SO_4m}/a_{H_2SO_4(0.3)}$) as a function of temperature and H_2SO_4 concentration both in the presence and absence of Ag_2SO_4. It is seen that in the absence of Ag_2SO_4 the values of the normalized ratios decrease as the temperature is raised and that values of the ratios at higher concentrations of H_2SO_4 decrease more than those at lower concentrations. In the presence of Ag_2SO_4 values of the activity ratio function increase with temperature at all the concentrations studied. However, when the H_2SO_4 is saturated with Ag_2SO_4 the plot of the $2.0m/0.3m$ ratios lies above the other two plots, while the $1.0m/0.3m$ plot lies below that for $0.5m/0.3m$. Although the activity ratios vary almost linearly with temperature in the presence of Ag_2SO_4, no simple relationship between activity and molality could be found based only on the assumption that H_2SO_4 acts like a 1–1 electrolyte and that the only important ionic species in solution are H^+, HSO_4^-, $SO_4^=$ and Ag^+. This is not surprising, however, since HSO_4^- is slightly dissociated in the concentration range studied, the dissociation being larger at the lower concentrations of H_2SO_4. Moreover, the enhanced solubility of Ag_2SO_4 in the H_2SO_4 means a further change of species in solution, while the effect of ionic strength on the second dissociation constant of H_2SO_4 provides an additional complication. No completely satisfactory explanation of the inversion in order of the plot of k_m^{-1} ($a_{H_2SO_4(2m)}/a_{H_2SO_4(0.3)}$) in the presence of Ag_2SO_4 could be obtained, although it may be tied in with the fact that the change of solubility of Ag_2SO_4 with H_2SO_4 concentration goes through a maximum in this range.[10]

(9) H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 27 (1935).

(10) G. Åkerlöf and H. C. Thomas, ibid., **56**, 593 (1934).