The Behavior of the Silver–Silver Sulfate and the Mercury–Mercurous Sulfate Electrodes at High Temperatures[1]

By M. H. Lietzke and R. W. Stoughton

In an attempt to develop a high temperature reference electrode, a series of measurements of the potential of the silver–silver sulfate and mercury–mercurous sulfate electrode combination has been made. In these experiments the temperature was varied from 25 to 250° and the acid concentration from 0.5 to 0.05 M sulfuric acid. The potentials obtained at given temperatures were compared with those predicted on the basis of thermodynamic calculations for the cell combination used. A possible explanation is given for the high temperature behavior of the silver–silver sulfate and mercury–mercurous sulfate electrode pair.

Introduction

No suitable reference electrode has been reported for use in solutions at temperatures above 100°. Hence it seemed of interest to study the high temperature behavior of two electrodes which have been used as reference electrodes at room temperature to determine whether their useful range could be extended above 100°. The two electrodes chosen for this study were the silver–silver sulfate and the mercury–mercurous sulfate electrodes. The potential of the electrode pair was measured as a function of temperature from 25 to 250° in 0.05, 0.2 and 0.5 M sulfuric acid. The measured potentials were then compared with potentials predicted on the basis of thermodynamic calculations.

Theoretical

When the Ag–Ag$_2$SO$_4$ electrode is used in conjunction with the Hg–Hg$_2$SO$_4$ electrode, the cell reaction is

$$2Hg + Ag_2SO_4 \longrightarrow Hg_2SO_4 + 2Ag$$
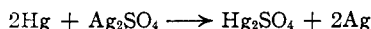
If saturated electrodes are used, the potential for the cell combination, calculated from the ΔF for the reaction, should be +42.3 mv. at 25°. This means that the silver sulfate electrode is 42.3 mv. more noble than the mercurous sulfate electrode at 25°. ΔS for the cell reaction at 25° is -16.4 e.u., hence dE/dT (the temperature coefficient of the potential) is -0.36 mv./degree at 25°.

In order to evaluate the potential of the cell combination at higher temperatures it is necessary to calculate ΔF for the reaction at several temperatures in the range of interest. This can be done by integration of the expression

$$\left(\frac{\partial \frac{\Delta F}{T}}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

where $\Delta H = \Delta H° + \int \Delta C_p dT$.

The equations giving C_p for each substance as a function of temperature are

$$C_p(Ag) = 5.09 + 2.04 \times 10^{-3}T + 0.36 \times 10^5(T^{-2})^2$$
$$C_p(Hg_2SO_4) = 13.13 + 64.0 \times 10^{-3}T^4$$
$$C_p(Hg) = 7.010 - 1.092 \times 10^{-3}T^3$$
$$C_p(Ag_2SO_4) = 23.1 + 27.9 \times 10^{-3}T^2$$

When ΔC_p is expressed with these equations and the integration performed, the following equation is obtained for the free energy of the reaction as a function of temperature

$$\Delta F = -4358 + 31.9T \log T - 21.2 \times 10^{-3}T^2 - \frac{0.36 \times 10^5}{T} - 64.3T$$

Then E may be evaluated at any desired higher temperature, since $E = -\Delta F/nF$.

Experimental

The silver–silver sulfate and mercury–mercurous sulfate electrodes were contained in small fused silica compartments 1.5 to 2″ long. The electrode compartments were sealed in a steel bomb which was fitted with electrically insulated leads. The quartz electrode compartments were sealed at one end and fitted at the other end with Teflon plugs through which passed platinum wires. The wires leading to the electrodes were coated with Teflon paint to insulate them from the solution in the bomb proper. The solution in the electrode compartment communicated with the solution in the bomb by means of a quartz capillary sealed to the side of the quartz compartment. The bomb itself was fitted with a silica liner to prevent attack on the steel by the sulfuric acid. The potential measurements were made with a vibrating reed electrometer and recorded on a Brown recording potentiometer.

The bomb containing the electrodes was surrounded by a heating jacket controlled to ±2° at the higher temperatures. This amounted to about ±0.6 mv. in the potential reading, which was sufficiently precise for the present work.

In a typical experiment the electrodes were prepared and sealed in the bomb. Potential measurements were continued until equilibrium was reached at room temperature. Then the temperature was raised to an appropriate value and measurements again made until a steady value was obtained. The time necessary for the electrodes to come to equilibrium depended upon the acid concentration. In the 0.5 M H$_2$SO$_4$ equilibrium was established almost immediately, while in the 0.2 M H$_2$SO$_4$ equilibrium was established overnight. It was necessary to wait several days for the electrodes to come to equilibrium in 0.05 M H$_2$SO$_4$.

The silver sulfate was prepared by precipitation from a solution of silver nitrate and washed by decantation. The mercurous sulfate was Baker and Adamson reagent grade.

Results and Discussion

Figure 1 shows the potentials obtained with the silver sulfate and the mercurous sulfate electrodes as a function of acid concentration and temperature. The potentials as measured in 0.5 M H$_2$SO$_4$ corresponded almost exactly with the theoretical line for the cell reaction $2Hg + Ag_2SO_4 \rightarrow 2Ag + Hg_2SO_4$. As the acid concentration was decreased, the potentials became more negative than expected.

The fact that Hg$_2$SO$_4$ hydrolyzes to form a greenish basic sulfate Hg$_2$O·Hg$_2$SO$_4$·H$_2$O has been reported. According to Mellor,[5] approximately

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

(2) K. K. Kelley, Bulletin 476, U. S. Dept. of the Interior, Bureau of Mines, U. S. Government Printing Office, Washington, D. C., 1949.

(3) Derived from data in T. B. Douglas, A. F. Ball and D. C. Ginnings, J. Research Natl. Bur. Standards, 46, 334 (1951).

(4) Derived from data in "Handbook of Chemistry and Physics," Thirty-Fourth Edition, Chemical Rubber Publishing Company, Cleveland, Ohio. 1952.

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., London, 1923, p. 966.

0.0008 M H$_2$SO$_4$ is sufficient to prevent formation of the basic salt at room temperature. Hence a mercurous sulfate electrode in 0.05 M H$_2$SO$_4$ should attain the theoretical potential against a silver sulfate electrode. This was observed in the present work. To check on the behavior of mercurous sulfate solutions at higher temperatures an aliquot of saturated mercurous sulfate solution in 0.05 M H$_2$SO$_4$ was sealed in a small Pyrex tube and heated to 250°. Small yellow crystals of what appeared to be HgO formed on the side of the tube. They were probably formed by the reaction

$$Hg_2SO_4 + H_2O \longrightarrow Hg + HgO + H_2SO_4$$
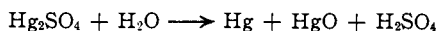
In the case of Ag$_2$SO$_4$ no basic hydrolytic product has been reported. To check on this, a quantity of Ag$_2$SO$_4$ and water was sealed in a silica tube and heated to 250°. Visual observation revealed no change in the appearance of the Ag$_2$SO$_4$ crystals up to 250°, and the crystals contained the 2:1 ratio between Ag$^+$ and SO$_4^=$ after cooling. Hence, it does not hydrolyze appreciably under the conditions of the experiment.

If the mercurous sulfate disproportionates and hydrolyzes at higher temperatures the cell reaction becomes, in the limit

$$Hg + Ag_2SO_4 + H_2O \longrightarrow 2Ag + HgO + H_2SO_4$$
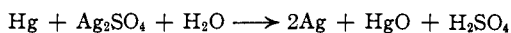
ΔF for this reaction is about $+12,560$ cal., which gives a value for E of -272 mv. ΔS for the reaction is -41.0 e.u., hence $dE/dT = -0.89$ mv./degree. Examination of the equation indicates that higher sulfuric acid concentrations will tend to repress this reaction and hence favor the simple reaction 2Hg + Hg$_2$SO$_4$ → 2Ag + Hg$_2$SO$_4$. This is what was observed experimentally. In 0.5 M H$_2$SO$_4$ the experimental plot coincided with the calculated plot over the temperature range studied, while in the lower acid concentrations the potential of the Ag$_2$SO$_4$ electrode was more negative than predicted.

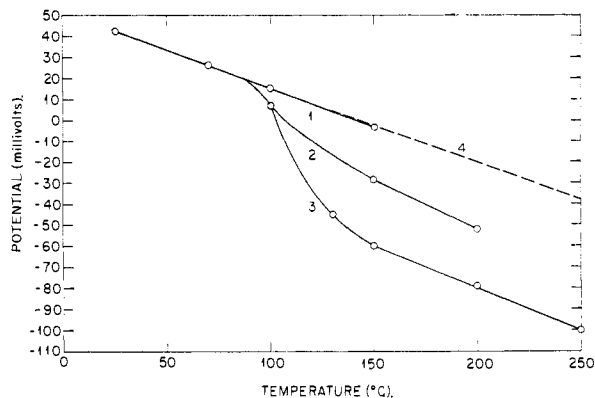It was not possible to extend the runs in 0.5 and

Fig. 1.—The potentials obtained with the silver–silver sulfate and the mercury–mercurous sulfate electrodes as a function of temperature: 1, electrodes in 0.5 M H$_2$SO$_4$; 2, electrodes in 0.2 M H$_2$SO$_4$; 3, electrodes in 0.05 M H$_2$SO$_4$; 4, theoretical plot for the electrodes with no hydrolysis.

0.2 M H$_2$SO$_4$ to higher temperatures because the H$_2$SO$_4$ attacked the silver above 150 and 200°, respectively, and destroyed the electrodes. The run in 0.05 M H$_2$SO$_4$ was not extended above 250° because the Teflon used as a plug and as an insulating coating on the wires is known to soften just above 250°.

It is proposed that at 25 and up to about 100° the potential of the electrode pair corresponds to the reaction 2Hg + Ag$_2$SO$_4$ → 2Ag + Hg$_2$SO$_4$. Above 100° this is also the cell reaction in sufficiently high H$_2$SO$_4$ concentrations. In lower acid concentrations it is proposed that the potential corresponds to a combination of this reaction and the reaction

$$Hg + Ag_2SO_4 + H_2O \longrightarrow 2Ag + HgO + H_2SO_4$$
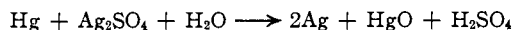
It is probable that as the temperature is raised this reaction is approached as a limit after perhaps several stages of basic salt formation.

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Catalytic Activity and Electrical Conductivity of Chromic Oxide Catalysts

By Sterling E. Voltz and Sol Weller

A study has been made of the electrical conductivity and catalytic activity of chromia and chromia–alumina catalysts. The catalysts were pretreated with hydrogen or oxygen at high temperature and evacuated at various temperatures before measurement. In agreement with literature reports, the conductivity was found to be much higher in the oxidized than in the reduced state. The activation energy for conduction was about 10 kcal./mole in the oxidized state and 40 kcal./mole in the reduced state. Hydrogen–deuterium exchange at low temperatures (-78 or $-195°$) was used as a measure of catalytic activity; the oxidation-reduction state of the catalyst was not changed by the reaction. Contrary to what might be expected, the catalytic activity was greater in the reduced than in the oxidized state, although the concentration of "defects" leading to conductivity is greater in the latter condition.

Introduction

This report is the first of several to appear on work being done in these laboratories on the electrical, chemical and catalytic properties of certain transition metal oxides. One of the objectives has been to extend the range of experimental knowledge of semi-conducting oxides in order that current theories relating catalysis and electronic structure may be

adequately tested.[1-3] This paper is concerned primarily with the electrical and catalytic properties of chromia and chromia–alumina catalysts; a study of

(1) D. A. Dowden, J. Chem. Soc., 242 (1950).

(2) C. Wagner, J. Chem. Phys., 18, 69 (1950).

(3) W. E. Garner, T. J. Gray and F. S. Stone, Proc. Roy. Soc. (London), A197, 294 (1949); A211, 472 (1952); Discussions Faraday Soc., 8, 246 (1950).