[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE FREE ENERGY OF AURIC OXIDE AS DETERMINED FROM MEASUREMENTS OF THE GOLD-AURIC OXIDE ELECTRODE[1]

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The purpose of this investigation was to measure the potential of the gold-auric oxide electrode and to calculate the free energy of formation of auric oxide from its elements at 298° A.

The cell chosen for these measurements was H_2 (g), H_2SO_4 (x-M), Au_2O_3 (s), Au (s). A careful search of the literature showed that very little work had been done on the potential of the gold-auric oxide electrode. Jirsa and Jelinek[2] in their work on the anodic oxidation of gold arrived at a value of 1.36 volts, referred to hydrogen. The aim of the present research was to extend the accuracy of this value, if possible, by the use of cell substances of such purity and homogeneity that true equilibrium would readily be established within the cells.

Materials and Apparatus

The measurements were made with auric oxide obtained by precipitation from chloro-auric acid by means of potassium hydroxide, followed by a purification process as described in a previous paper by the authors.[3] The gold was obtained in excellent crystalline form by reduction of chloro-auric acid with ferrous sulfate. The cells were of the type devised by Lewis and Rupert,[4] modified to contain two hydrogen electrodes and three gold half-cells, to make possible a triplicate series of measurements under identical conditions. Three concentrations of sulfuric acid were employed: 1.024 *M*, 0.100 *M* and 0.0100 *M*. The auric oxide as well as the gold crystals were equilibrated with the sulfuric acid solutions for 12 hours before being introduced into the cells. Hydrogen from the electrolysis of potassium hydroxide was used in the cells. All electromotive-force measurements were made with a Type K Leeds and Northrup potentiometer. The water-bath containing the cells was maintained at 25° ± 0.1° The cells came to equilibrium promptly in most cases, the more so when the more concentrated solutions of sulfuric acid were used. The measurements are summarized in Table I.

The electromotive force is seen to be substantially independent of the concentration of the sulfuric acid, as is to be expected from the cell reaction.

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[1] Abstract of a thesis submitted by William Earl Roseveare in partial fulfilment of the requirements for the Degree of Master of Science in the University of Arizona, June, 1926.

[2] Jirsa and Jelinek, *Z. Elektrochem.*, **30**, 286 (1914); *ibid.*, 534 (1924); *Chem. Listy*, **18**, 1 (1924).

[3] Roseveare with Buehrer, THIS JOURNAL, **49**, 1221 (1927).

[4] Lewis and Rupert, *ibid.*, **33**, 229 (1911).

TABLE I

DIRECT MEASUREMENTS OF POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT 25°

Concn. H_2SO_4,	E.m.f. (volts) Cell 1	Cell 2	Cell 3	Mean
1.024	1.363_4	1.363_4	....	1.363_4
0.1000	1.362_7	1.363_0	1.364_9	1.363_5
.0100	1.363_8	1.364_2	1.363_7	1.363_9

General average = 1.364 ± 0.001 volts

These results have recently been confirmed independently by Gerke and Rourke, in an investigation[5] in which they measured the potential of the cell Hg(l), Hg_2SO_4(s), H_2SO_4(x-M), Au_2O_3(s), Au(s) and from the known value of the potential cell H_2(g), H_2SO_4(x-M), Hg_2SO_4(s), Hg(l) calculated the electromotive force of the gold-auric oxide electrode against the hydrogen electrode. Their calculated mean value was 1.362 ± 0.002 volts.

The Free Energy of Auric Oxide

To obtain the free energy of auric oxide from these measurements, it is necessary to combine the free energy of the reaction tending to take place in the above cell with the free energy of formation of 1 mole of liquid water from its elements at 298° Å., which was calculated by Lewis and Randall[6] to be —56,560 calories. We shall use the value of the e.m.f. of the gold-auric oxide electrode Au, Au_2O_3, H^+, $E^\circ = -1.363 \pm 0.001$ volts, which is the average of our result, and that of Gerke and Rourke.

$$3H_2\ (g) + Au_2O_3\ (s) = 3H_2O\ (l) + 2Au\ (s);$$
$$\Delta F = -NEF = -6 \times (+1.363) \times 23{,}074 = -188{,}800 \text{ cal.}$$
$$3H_2\ (g) + 3/2\ O_2\ (g) = 3H_2O\ (l);$$
$$\Delta F = 3 \times (-56{,}560) = -169{,}700 \text{ cal.}$$

Subtracting the first from the second of these equations, we obtain:

$$2Au\ (s) + 3/2\ O_2\ (g) = Au_2O_3\ (s);\ F^\circ_{298} = +19{,}100 \text{ cal.}$$

This high positive free energy of formation of auric oxide indicates that it must be very unstable and, therefore, have a high dissociation pressure. The auric oxide involved in the above equation is very probably not Au_2O_3, but a hydrated form of the oxide. Because of its instability, it is a question whether the true degree of hydration of auric oxide can be experimentally determined.

The Dissociation Pressure of Auric Oxide

The dissociation pressure of auric oxide as calculated by the thermodynamic equation $\Delta F = -R\,T\,ln\,K$ is found at 298° Å. to be 2.13×10^9 atmospheres.

It was also considered of interest to calculate the entropy change attending the formation of 1 mole of auric oxide from its elements at 298° Å.

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[5] Gerke and Rourke, THIS JOURNAL, **49**, 1855 (1927).

[6] Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., **1923**, p. 485.

According to Thomsen[7] the value of ΔH for this reaction is —13,200 cal. for 1 Au_2O_3 (Aq.) whence $\Delta S_{298} = (\Delta H - \Delta F)/T = (-13{,}200 - 19{,}100)/298 = -108.4$ cal./mol./degree.

The writers wish to express their appreciation to Professor G. N. Lewis, who suggested this investigation.

Summary

1. Measurements have been made on the cell: $H_2(g)$, H_2SO_4(x-M), $Au_2O_3(s)$, Au(s), at three concentrations of sulfuric acid and at 25°. The electromotive force is seen to be substantially independent of concentration of sulfuric acid, the general average value being 1.364 ± 0.001 volts.

2. The free energy of formation of auric oxide from its elements, its dissociation pressure, and entropy of formation at 298° Å. are calculated, all of which indicate that auric oxide is a very unstable compound.

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NOTES

Confirmatory Test for Aluminum.—The test suggested is a modification of that proposed by Attack.[1] It has the advantage that the reagent need not be freshly prepared each time. Further, the color absorption is greater.

The reagent consists of a saturated solution of alizarin in concd. acetic acid.

After separating the aluminum hydroxide from any chromium and zinc, it is washed, dissolved in hydrochloric acid and then reprecipitated with a slight excess of ammonium hydroxide. To this solution is added one drop of the alizarin reagent which imparts an apple-blossom pink coloration to the aluminum hydroxide. The latter will soon settle out, leaving the solution above colorless.

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Plastic Films and the Drop-Weight Method of Interfacial Tension Measurement.—The drop-weight method of measuring surface and interfacial tensions has in recent years been greatly refined by Harkins and his co-workers.[1] Not only have they improved the apparatus in a

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[7] Thomsen, "Thermochemistry," Longmans, **1908**, p. 201.

[1] Attack, *Chem. Zentr.*, [1] **82**, 176 (1916).

[1] Harkins and Brown, THIS JOURNAL, **41**, 499 (1919).