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THE POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE

By Roscoe H. Gerke and M. Dorothy Rourke

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The original purpose of this investigation was to study the properties of the gold-aurous oxide electrode. The authors, however, were entirely unsuccessful in preparing aurous oxide by duplicating the methods described in the literature or by any other methods which suggested themselves. During the course of the investigation it was observed that the potential of the gold-auric oxide electrode was about the same as that reported in the literature for the gold-aurous oxide electrode.[1] Hence, it is the purpose of this paper to present the results of the experiments on the gold-auric oxide electrode and to present briefly the experimental facts which lead to the conclusion that it is doubtful whether aurous oxide has ever been prepared.

The Gold-Auric Oxide Electrode

The cell, Hg(l), Hg_2SO_4(s), H_2SO_4, Au_2O_3(s), Au (cryst.) was employed in the measurement of the potential of the gold-auric oxide electrode. The cell consisted of two half-cells[2] with side arms dipping into a small beaker containing sulfuric acid of the same concentration as in the half-cells. Thus, the cell contained no liquid potential. The electromotive-force measurements were made with a Leeds and Northrup student potentiometer and galvanometer at room temperature, which was about 25°. With this apparatus the electromotive force could be read easily to a millivolt, which is sufficiently precise for cells containing gold electrodes.

The auric oxide was prepared by the method of Krüss.[3] The gold was

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[1] Campbell, *Chem. News*, **96**, 257 (1907).

[2] Sherrill, "Laboratory Experiments on Physico-Chemical Principles," The Macmillan Company, **1923**.

[3] Krüss, *Ann.*, **237**, 291 (1887).

precipitated by the reduction of auric chloride solution with sulfur dioxide solution. The gold appeared as thin crystals. The gold-auric oxide half-cell was constructed in the following manner. The gold crystals mixed with an equal amount of auric oxide in sulfuric acid solution were introduced into the electrode vessel. A dip electrode consisting of a glass tube with a platinum wire sealed through the end made electrical contact with the gold. The results on cells with three concentrations of sulfuric acid are given in Table I.

TABLE I

POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE AT 25°C.

Concn., H_2SO_4	Volts	Volts
0.0506	0.599 ± 0.002	1.353 ± 0.002
.1031	.629 ± .002	1.367 ± .002
1.031	.690 ± .001	1.365 ± .002

The electromotive force of the cells increased for about 24 hours and after that time it was constant within the limits given in Table I, Col. 2, whether the cells were agitated or not. The first column in Table I gives the concentration of the sulfuric acid in formula weights per 1000 g. of water. Cols. 2 and 3 are, respectively, the electromotive force of the cells, $Hg(l)$, $Hg_2SO_4(s)$, H_2SO_4, $Au_2O_3(s)$, Au (cryst.) and H_2 (1 atm.), H_2SO_4, $Au_2O_3(s)$, Au (cryst.). The values for the electromotive force[4] of the latter cell were calculated from the observed values in Col. 2, and from values of the electromotive force of the cell, H_2 (1 atm.), H_2SO_4, $Hg_2SO_4(s)$ Hg.[5]

From the average of the values in Col. 3, the potential of the gold-auric oxide electrode, Au (cryst.), $Au_2O_3(s)$ H^+ is —1.362 volts, which is somewhat larger than Campbell's value, of about —1.2 volts for the gold-aurous oxide electrode, Au, $Au_2O(s)$, H^+. This latter value is corrected neither for liquid-junction potential nor by activity coefficients.

The value 18,810 cal. for the free energy of formation of auric oxide has been computed from the electromotive force of the cell in Col. 3 for the change of state, $3H_2 + Au_2O_3(s) = 2Au \text{ (cryst.)} + 3H_2O(l)$. The dissociation pressure, 1.46×10^9 atmospheres shows that auric oxide is very unstable with respect to the elements at room temperatures.

Aurous Oxide

There is no *a priori* reason why aurous oxide can or cannot be made. The necessary conditions for its preparation are: (1) a chemical reaction with a negative free energy increase and (2) the rate of decomposition of the substance, once prepared must be slow.

The methods which were employed to prepare aurous oxide will be

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[4] The conventions as to sign of electromotive force are the same as those of Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[5] Randall and Cushman, THIS JOURNAL, **40**, 393 (1918).

mentioned very briefly. The investigators who report analyses of their product are Figuier[6] and Krüss.[7] Both of these methods of preparation were tried. Both preparations had the appearance given in the descriptions, but the microscope revealed the presence of metallic gold. The method used by Campbell[1] was tried with the same results. Furthermore, the boiling of auric chloride with potassium hydroxide solution, the direct reduction of auric oxide by sulfur dioxide solution, and the treatment of aurous iodide with acids and bases did not give a product which was free from metallic gold.

In addition, Hartung[8] has made a very thorough study of methods of preparation of aurous oxide. He observed that chemical analysis is not sufficient evidence to prove whether a given preparation is aurous oxide or not. He found that his preparations contained metallic gold and concluded that "No evidence has therefore been obtained to show that aurous oxide exists; its chemical and physical properties are those of a mixture of gold and auric hydroxide."

Finally, Buehrer[9] made a preparation by a method adapted from that of Krüss,[7] which was employed with crystalline gold as a gold-gold oxide electrode. This electrode when compared with a hydrogen electrode in sulfuric acid solution gave an initial value of about +1.1 volts. After two years the electromotive force had increased to +1.363 volts. This result can be interpreted in two ways; one in which it is assumed that aurous oxide is thermodynamically more stable than auric oxide, in which case the electrode initially consisted of Au (crystalline), Au_2O (solid), H^+; and second, which the present writers have suggested, in which it is assumed that aurous oxide did not exist in the blue-black precipitate in the electrode and that the electrode consisted initially of Au (colloidal), Au_2O_3 (solid), H^+. If the colloidal gold slowly changed to crystalline gold, the electromotive force would increase to the value 1.363 volts. The latter assumption has in its favor the fact that the blue-black precipitate has somewhat the color of the purple of Cassius, which is characteristic of colloidal gold.

In conclusion, it may be said with confidence that it is doubtful whether a pure preparation of aurous oxide has ever been prepared.

Summary

1. The potential of the gold-auric oxide electrode, Au (cryst.), Au_2O_3 (s), H^+ has been found to be —1.362 volts.

2. The free energy of formation of auric oxide at 25° has been found to be +18,810 cal. from electromotive-force measurements.

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[6] Figuier, *Ann. chem. phys.*, **11**, 339 (1844).

[7] Ref. 3, p. 279.

[8] Hartung, *J. Chem. Soc.*, **129**, 1349 (1926).

[9] Buehrer, Wartman and Nugent, THIS JOURNAL, **49**, 1271 (1927).

3. It is shown that it is doubtful if a pure preparation of aurous oxide has ever been prepared.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

LUMINESCENCE OF GRIGNARD COMPOUNDS IN ELECTRIC AND MAGNETIC FIELDS, AND RELATED ELECTRICAL PHENOMENA

BY R. T. DUFFORD, DOROTHY NIGHTINGALE AND L. W. GADDUM

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Previous work by the authors and their colleagues[1] has shown the existence of interesting and remarkable regularities in the relations between chemical structure and the brightness and spectral distribution of the light emitted when ether solutions of Grignard compounds, having the general formula RMgX, are oxidized with air or oxygen. The behavior of this group of compounds raises many questions regarding the molecular structures involved.

It seemed possible that some light in this direction might be obtained from experiments with strong magnetic and electric fields. If the radiators are electrons in orbits, as current ideas go, it seemed barely possible that the application of a strong field might bring about a uniform orientation of the molecules, or of the orbits within the molecules, and that this condition might result in polarization of the light emitted in such a field.

The experiment was therefore made of oxidizing certain of the brighter compounds in magnetic fields of about 15,000 gauss; but in every case, polarization appeared to be completely lacking. If it existed, it could not have exceeded one or two per cent. However, one effect was clearly visible; in the strongest fields, there was a distinct tendency for the most of the emission to occur in the most intense parts of the field, near the pole pieces. Immediately on applying the field, a streaming appeared in the solution, with the brightening at the sides of the crucible containing the solution. It appeared as if the effect were mechanical, either the Grignard or, more probably, the oxidation product, being sufficiently paramagnetic to be drawn to the poles. If the solution were very clear to begin with, it would soon show minute black specks being drawn to the poles with the streams. Most of the oxidation product collected near the poles. The effect is shown well by *p*-BrC_6H_4MgBr. It does not, however, appear in weak fields.

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[1] Dufford and co-workers, THIS JOURNAL, **47**, 95 (1925); **45**, 2058 (1923); **45**, 278 (1923); *J. Optical Soc. Am.*, **9**, 405 (1924); *Phys. Rev.*, **21**, 203 (1923); **27**, 247 (1926).