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The Silver-Silver Oxide Electrode; the Entropy of Mercuric Oxide

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Stable, reversible Ag–Ag_2O electrodes have been prepared by partial electrolytic reduction of Ag_2O mixed with finely divided Ag in contact with a platinum wire. There is no apparent difference in the equilibrium electrode potential for annealed and unannealed Ag_2O, provided that there is no great change in particle size. The average potential for the cell reaction:

$$2Ag + HgO \longrightarrow Ag_2O + Hg$$

is −0.2447 ± 0.001 v. at 25°. The free energy of formation of Ag_2O at 25° is −2691 ± 10 cal./mole. Limited measurements of dE^0/dT were made, and the value of −0.000201 ± 0.00001 v./deg. used to calculate $\Delta S^0 = -9.27 \pm 0.5$ cal./deg. mole for the cell reaction. This value together with the entropies of Ag, Hg and Ag_2O yields 17.4 ± 0.6 cal./deg. mole for the entropy of HgO at 298°K. Other cell data give concordant values for the entropy of HgO, but the result obtained from heat capacity data extrapolated from 15°K. is appreciably smaller.

Introduction

Attempts have been made by many workers to measure the equilibrium potential of the Ag–Ag_2O electrode. Cells composed of this electrode, a stable reference half-cell (such as Hg–HgO), and an electrolyte (*e.g.*, aqueous NaOH) quite generally gave emf values which were unstable, decreased with time, and were lower by several millivolts than the value calculated for the cell reaction

$$2Ag + HgO \longrightarrow Hg + Ag_2O \qquad (1)$$

from the standard free energies of formation of HgO and Ag_2O.

The failure to measure the equilibrium potential of the electrode was inconclusively attributed to a variety of reasons such as suboxide formation, surface films, etc. Hamer and Craig[2] were finally able to prepare and study stable Ag–Ag_2O half-cells, and their emf measurements were in reasonable agreement with the calculated value. The method of electrode preparation utilized by these authors involved partial reduction of Ag_2O to Ag at 60° by H_2. Since the reduction is exothermic, it is possible that the samples of Ag_2O were heated to well above 60°.

It has been known for some time that the previous thermal history of Ag_2O has a marked effect on the heat capacity and consequently the thermodynamic properties of this substance. Pitzer and Smith[3] noticed an anomalously high heat capacity between 20 and 40°K. in Ag_2O which had been dried at 110°. Kobayashi[4] observed an irreversible evolution of heat at about 150° amounting to 315 cal. mole^{-1} for Ag_2O. Recent measurements[5-7] have shown that the low temperature heat capacity anomaly can be modified or removed altogether depending on the crystal size and the extent of annealing above the Kobayashi temperature.

This investigation was undertaken to explore methods of preparing stable Ag–Ag_2O electrodes which did not involve heating the electrode material and to study the behavior of such electrodes when prepared from samples of Ag_2O which had been subjected to various annealing treatments.

Experimental

Preparation of Samples.—The samples were obtained from Ag_2O which had been prepared for low-temperature calorimetric measurements; the material had been prepared by precipitation from 2 *N* $AgNO_3$ solutions by concentrated NaOH. Special precautions were taken to exclude the presence of Ag_2CO_3. The samples were classified by heat treatment into three types:

I. *Unannealed:* heated only to 110° in an oxygen stream to facilitate drying,

II. *Annealed:* heated in a bomb at 180° for two days under a pressure of about 130 atm. of O_2, and

III. *Macrocrystalline:* cultured under H_2O in a bomb at 325° under 200 atm. of O_2 for 20 days.

The samples were examined by differential thermal analysis. Type I had not undergone the Kobayashi annealing; types II and III had. The appearance of types I and II were similar; type III consisted of fairly large (0.02 mm.) crystallites of a dark gray color. Analytical data on all samples showed them to be stoichiometric to within 0.2%; *i.e.*, at least 99.8% Ag_2O.

Preparation of Electrodes.—All cells were made using a Pyrex H-cell with Pt wires leading to Hg-filled arms for external contact. Preliminary experiments on mechanical mixtures of Ag and Ag_2O duplicated the results of earlier workers; the potentials were unstable and as much as 20 millivolts lower than the expected value. Electrodes prepared by cathodic reduction of Ag_2O to Ag *in situ* gave potentials which approached the calculated value very slowly.

The technique finally used involved partial electrolytic reduction of a mixture of Ag_2O and fine Ag powder in place in one arm of the cell. The mixture was prepared by shaking together approximately equal portions of Ag_2O and Ag by weight. After digesting the mixture in boiling distilled water for five minutes, approximately 15 g. was placed in one arm of the cell. Freshly prepared NaOH solution (20% by weight) was added to fill the cell, and a current of 0.03 amp. at 2.5 volts was passed through the cell for 2–8 hr. with the Ag–Ag_2O arm being the cathode. The gray color of the Ag–Ag_2O mass became somewhat lighter in shade and O_2 was liberated at the anode. Upon completion, the electrolyte was pipetted out of the cell without disturbing the Ag–Ag_2O mass. The reference electrode was then installed in the other arm; it consisted of 10 g. of triply-distilled Hg and 5 g. of reagent grade HgO (red) which had been digested for several minutes in boiling distilled H_2O. The cell was filled with freshly prepared NaOH solution, stoppered and securely fastened in place in a water constant-temperature bath which maintained the temperature at 25 ± 0.1°.

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(2) W. J. Hamer and D. N. Craig, *J. Electrochem. Soc.*, **104**, 206 (1956).

(3) K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **59**, 2633 (1937).

(4) K. Kobayashi, *Sci. Repts. Tohoku Univ.*, First Series, **35**, 173 (1951).

(5) K. S. Pitzer, R. E. Gerkin, L. V. Gregor and C. N. R. Rao, *Pure and Applied Chemistry* (IUPAC), **2**, 211 (1961).

(6) R. E. Gerkin and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2662 (1962).

(7) L. V. Gregor and K. S. Pitzer, *ibid.*, **84**, 2664 (1962).

The cells were connected to a calibrated Leeds and Northrup type K drum potentiometer capable of measurements to 0.01 millivolt. A 100-megohm shunt could be switched into or out of the measuring circuit at the potential leads to the potentiometer. The total circuit resistance of cell and connections was approximately 100 ohms.

Results

Constant e.m.f. values were obtained in 1–3 days with cells prepared as described above. Observations were continued in some cases for 45 days, and none of the cells decreased in e.m.f. by more than 0.2% (0.5 mv.) after attainment of a constant e.m.f. Altogether, 20 cells were studied using the three types of Ag_2O; eight of type I, five of type II and seven of type III. The equilibrium potentials of the cells are given in Table I.[8]

In order to check the reproducibility of the reference electrodes, two cells were made at different times composed of two Hg–HgO half-cells made in the same manner. In both cases, the cell e.m.f. was less than 0.5 millivolt. Minor variations in current, voltage and time of electrolysis had no significant effect on the potential measurements. Although no special attempt was made to study the possible variation of emf with electrolyte concentration,[2] the cell measurements did not seem to be significantly affected by changing the concentration from 20 to 2% by weight NaOH. By means of the 100-megohm shunt, all cell potentials were measured with a current flow of the order of 10^{-8} ampere as well as by the usual potentiometric null-point method, and no change in potential was observed.

Although the thermostat temperature range was limited, measurements were made on seven cells at six temperatures between 22 and 32°, allowing sufficient time at each temperature for each cell to achieve constant e.m.f. Because of the limited range, only the average value of dE/dT is given in Table I.

Table I

Summary of Data on the $Ag–Ag_2O$ Electrode (Reference Electrode, Hg–HgO; Electrolyte, Aqueous NaOH)

A. Equilibrium cell potentials at 298°K. in volts

Unannealed Ag_2O	−0.24460 ± 0.0006
Annealed Ag_2O	− .24482 ± .0006
Macrocrystalline Ag_2O	− .24308 ± .0005

B. Free energy of formation of Ag_2O at 298°K.

Type of Ag_2O	Free-energy change of cell reaction (cal./mole)	Free energy of formation of Ag_2O^a (cal./mole)
Unannealed	−11281	−2696
Annealed	−11291	−2686
Macrocrystalline	−11211	−2766

[a] Based on ΔF_{298} for HgO = − 13977 cal./mole.

C. Temperature-e.m.f. coefficient for a $Ag–Ag_2O$ *vs.* a Hg–HgO cell

$$\frac{dE}{dT} = -0.000201 \pm 0.00001 \text{ v./deg.}$$

$$\Delta S^0 = -9.27 \pm 0.5 \text{ cal./mole}$$

Discussion

The average cell potentials for type I and type II Ag_2O cells differ from each other by less than the average deviation from the mean for each type. This fact suggests that there is no inherent difference in the chemical potential of Ag_2O after undergoing the evolution of heat caused by annealing above 150°. This seems to substantiate the hypothesis of Kobayashi that the annealing effect is caused by the relief of some sort of strain associated with structural defects. Presumably the reduction of Ag_2O by electrolysis of an intimate $Ag–Ag_2O$ mixture occurs at the contact interface and preferentially reduces Ag_2O at localized sites of higher energy which are caused by strain. Thus it is not surprising that unannealed and annealed Ag_2O give the same half-cell potential.

Highly annealed Ag_2O (type III) seems, however, to give consistently lower emf values by about 0.7% (approximately 2 millivolts) based on the average of type III cells compared to types I and II. This may be a real effect, assuming that the drastic annealing of this sample gave much more perfect crystals. It seems equally likely that the difference in behavior is due to the greatly decreased surface area of type III Ag_2O, and hence greater difficulty of obtaining a large area of intimate $Ag–Ag_2O$ contact by the mild electrolysis conditions used in these experiments.

The average value of the cell potential for all type I and type II samples is −0.2447 ± 0.001 volt which agrees well with Hamer and Craig's value of −0.2440 v. The free energy change of reaction 1 is then 11286 cal./mole. Taking $\Delta F°$ for HgO at 25° to be −13977 cal./mole, the value of ΔF_0 for Ag_2O at 25° is −2691 ± 10 cal./mole.

The standard oxidation potential of the $Ag-Ag_2O$ electrode is obtained by combining the average cell potential of −0.2447 volt with the potential of the Hg-HgO electrode[2] and the standard potential of the H electrode at unit activity of OH^- ion[9]; the value is −0.3423 volt. This agrees with the value of Hamer and Craig, who give −0.342 v.

The average value of dE^0/dT given in Table I corresponds to an entropy change of −9.27 ± 0.5 cal./deg. mole for reaction 1 at 25°. This agrees rather well with previous data of Hamer and Craig,[2] whose measurements cover a wider temperature and yield −0.0001978 for dE/dT and −9.12 cal./deg. mole for ΔS. The uncertainty in their ΔS value should not exceed 0.3 cal./deg. mole. These ΔS values may be compared with the ΔS computed from the entropies of the individual substances in the cell reaction 1. The entropy values recommended by Kelley[10] for Ag and Hg may be adopted together with the value 28.91 cal./deg. mole obtained from our own heat capacity measurements on Ag_2O. The results are given in Table II as values calculated for the entropy of HgO.

Also shown in Table II is the entropy value for HgO calculated from the heat capacity measure-

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(8) For additional details see L. V. Gregor, Ph.D. Dissertation, University of California, 1961.

(9) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(10) K. K. Kelley, U. S. Bureau of Mines Bulletin 592 (1961).

TABLE II

MOLAL ENTROPY OF MERCURIC OXIDE IN CAL./DEG.

Low temp. C_p (B. and J.)[11]	16.80 ± 0.1
Ag_2O cell (H. and C.)[2]	17.56 ± .5
Ag_2O cell (G. and P.)[7]	17.4 ± .6
H_2 cell, various authors[2,10,11]	17.3 ± .3

ments of Bauer and Johnston[11] from 15 to 300°K. with a Debye function extrapolation to 0°K. In addition, several workers have studied the galvanic cell with the reaction

$$H_2(g) + HgO(s) = H_2O(l) + Hg(l) \qquad (2)$$

and the results have been reviewed recently by several authors[2,10,11] and combined with other data to yield the final value in Table II.

The entropy values from the two types of cell are quite concordant, but the presumably more precise value based on the low temperature heat capacity data is slightly outside the estimated limits of error on the low side. The structure of red or yellow orthorhombic HgO was shown by Aurivillius[12] to involve long chains –O–Hg–O–Hg–O–Hg– with 180° angles at Hg and 109° angles at oxygen. Such a structure might lead to an abnormal heat capacity curve at temperatures below 15°K. where Bauer and Johnston's measurements began. The results of our measurements below 15°K. on macrocrystalline Ag_2O indicate that substantial deviation from the Debye curve is possible for heavy metal oxides.

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[11] T. W. Bauer and H. L. Johnston, *J. Am. Chem. Soc.*, **75**, 2217 (1953).

[12] K. Aurivillius, *Acta Chem. Scand.*, **10**, 852 (1956).

[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, WEIZMANN INSTITUTE OF SCIENCE AND THE RESEARCH LABORATORIES OF THE ISRAEL ATOMIC ENERGY COMMISSION, REHOVOTH, ISRAEL]

The Chemical Behavior of Fluorine 18 Produced by the $O^{16}(H^3,n)$ Nuclear Reaction

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Fluorine 18 atoms produced by the $Li^6(n,\alpha)H^3$, $O^{16}(H^3,n)F^{18}$ nuclear reactions were found to substitute hydrogen on organic molecules. The extent of labelling of a given organic molecule was found to be proportional to the number of hydrogens per molecule. In solid lithium salts, irradiated by slow neutrons, the yield of organically bound fluorine 18 was 0.6–1.0% per aliphatic hydrogen, as compared to 0.3–0.6% per aromatic hydrogen. Compounds were also labelled in solutions and the yield was dependent on the concentration of the solute. The yield of labelling of aliphatic solutes was higher than that of aromatic. The addition of aromatic compounds to an aliphatic solvent diminished the labelling yield of the solvent, however no appreciable labelling of the aromatic solute was observed. Aliphatic solutes, on the other hand, did not affect the yield of labelling of aliphatic solvents. Formic acid and nitrite ions were found to diminish considerably the yield of labelling in aqueous or alcoholic solutions. The results suggest that the active chemical species in the fluorine labelling reactions are non-excited fluorine atoms. Interactions with electron donors are of primary importance in the behavior of fluorine atoms in organic media.

Labelling of organic compounds by radioactive halogens formed by the (n,γ) reactions has been extensively studied.[1] In a series of experiments on bromine formed by (n,γ) reactions and by isomeric transitions, the participation of positively charged bromine ions has been suggested.[2] In other cases halogen atoms were suggested as the main active species. The results of the (n,γ) recoil labelling were recently compared with the hot atom chemistry of chlorine and bromine produced by (n, α) reactions.[3]

The "hot atom" chemistry of fluorine 18 has been examined first by Aten[4] who studied the retention of F^{18} in fluorobenzene following the (n, 2n) nuclear reaction. The inorganic and organic fractions of the irradiated samples were separated and their activities were measured. The organic products were neither purified nor identified. No attempt was made to utilize the "hot" F^{18} atoms for recoil labelling of other, fluorine free, organic compounds.

The purpose of the present study was to investigate the mechanism of recoil labelling of organic compounds by fluorine generated by the $O^{16}(H^3,n)F^{18}$ nuclear reaction. The $Li^6(n,\alpha)H^3$, $O^{16}(H^3,n)F^{18}$ reactions have been previously utilized for the production of fluorine 18 in a nuclear reactor,[5] and it was of interest to evaluate the feasibility of this technique for the production of fluorine 18 labelled organic compounds.

Experimental

Materials. Organic reagents used for irradiation were of C.P. grade and were further purified by recrystallization or distillation as necessary. Each reagent was tested for purity by checking on its physical properties, *e.g.* melting point or refractive index. Organic reagents of C.P. grade were used for the preparation of derivatives without further purification. Inorganic reagents used were of analytical grade and did not undergo any further purification. Triple distilled conductivity-tested water was used as solvent.

Lithium salts of the organic reagents were prepared by neutralizing an aqueous solution of the organic acid or phenol with lithium hydroxide. The water was then evaporated under vacuum and the lithium salt was dried until constant weight. Lithium 6 salts were prepared by dissolving metallic lithium 6 (96%) in water, followed by

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[1] A. H. Gordus and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 4609 (1957); I. C. Chien and J. E. Willard, *ibid.*, **79**, 4872 (1957); J. B. Evans, J. E. Quinland, M. C. Sauer and J. E. Willard, *J. Phys. Chem.*, **62**, 1351 (1958); J. B. Evans, J. E. Quinland and J. E. Willard, *Ind. Eng Chem.*, **50**, 192 (1958).

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[5] R. B. Bernstein and I. I. Katz, "*Nucleonics*," Vol. XI, [10] 46 (1953); L. G. Stang, *et al.*, Proc. Internat. Conf. on Radio-isotopes in Sci. Research, Vol I, Paris, 1957, p. 50 (1958).