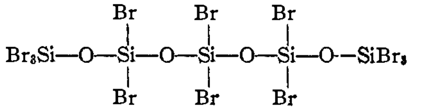
mann freezing point lowering method. Ethylene bromide (Eastman Reagent) which was used as the solvent in the molecular weight work, was dried by allowing it to stand over phosphorus pentoxide for twenty-four hours, after which it was fractionally distilled from fresh drying agent, giving a sample with a boiling point of 129.5 to 130°. The cryoscopic constant of ethylene bromide was taken as 12.50° per mole per 1000 g. of solvent.[6]

The fractions given in the following tabulation refer to those of Table I. The same weight of solvent, 54.73 g. (the contents delivered by a calibrated pipet), was used in each molecular weight determination.

The simplest conceivable oxybromide, $SiOBr_2$, like the corresponding chloride, is probably incapable of existence outside the vapor state, and in the liquid state polymerizes to $(SiOBr_2)_4$, or $Si_4O_4Br_8$. With the exception of $(SiOBr_2)_4$, the compounds are all members of the series of general formula $Si_nO_{n-1}Br_{2n+2}$, of which series $SiBr_4$ itself might be considered as the first member. Although there is evidence of a ring structure for $(SiOBr_2)_4$, the other substances are most probably straight-chain compounds, with an oxygen atom linked between each Si atom, such as



$$Br_3Si{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}SiBr_3$$

Compounds containing the terminal linkage $-\underset{\substack{|\\Br}}{Si}{=}O$, although logically to be expected, apparently are not realized.

Summary

1. The following series of silicon oxybromides was prepared: $(SiOBr_2)_4$, Si_2OBr_6, $Si_3O_2Br_8$, $Si_4O_3Br_{10}$ and $Si_5O_4Br_{12}$, definite indication of the existence of $Si_6O_5Br_{14}$ (and perhaps of higher oxybromides) also being shown. All but the first compound belong to the homologous series $Si_nO_{n-1}Br_{2n+2}$. The compounds all hydrolyze readily in the presence of moisture, the rate of hydrolysis decreasing with a decrease in volatility. They are miscible in all proportions with CS_2, CCl_4, $CHCl_3$ and $SiBr_4$.

With the exception of the first two compounds (which were prepared independently in the present work, and by independent methods) these substances have not been reported previously, nor has as complete a series of any other silicon oxyhalides been prepared.

2. With the hope of obtaining oxybromides of silicon, the following reactions were studied: A, the simultaneous reaction of oxygen and bromine, both with silicon and with calcium silicide; B, the reaction of silicon tetrabromide with oxygen; C, the oxidation of hexabromodisilane; D, the oxidation and the thermal decomposition of Si_2OBr_6; E, the reaction of silicobromoform with oxygen; F, the effect of silver oxide on silicon tetrabromide; G, the ozonization of silicon tetrabromide. The first two methods resulted in the formation of large quantities of oxybromides. In no other case were appreciable quantities of oxybromides formed, the reaction progressing all of the way to silicon dioxide.

CAMBRIDGE, MASS. RECEIVED OCTOBER 30, 1936

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(6) "International Critical Tables," Vol. IV, p. 183.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Electrode Potential of the Iodine–Iodate Electrode at 25°[1]

BY WALTER O. LUNDBERG,[2] CARL S. VESTLING[3] AND J. ELSTON AHLBERG

The purpose of the present investigation has been to gather additional data necessary to determine more closely the standard potential at 25° for the electrode reaction

$$\tfrac{1}{2}I_2(s) + 3H_2O(l) = IO_3^- + 6H^+ + 5E^-$$

The value of the standard potential available until now is based upon the work of Sammet,[4] but several experimental factors contribute to considerable uncertainty in his results. The most important of these is that he measured the potential of the iodine–iodate electrode at 25° against a normal calomel potassium chloride electrode maintained at 18°. Furthermore, the liquid potentials with which he had to deal were relatively high, ranging up to 0.034 volt. The results of Sammet have been recalculated employing the activity coefficients of hydrogen ion as given by Lewis and Randall[5] and those of iodic

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(1) In part from a dissertation submitted by Walter O. Lundberg to The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(2) Hormel Foundation Fellow in Chemistry, 1930–1934.

(3) Patrick Garvan Fellow in Chemistry, 1934–.

(4) Sammet, *Z. physik. Chem.*, **53**, 665 (1905).

(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

acid as measured by Abel, Redlich and Hersch.[6] The thermocouple effect existent in the cell (+0.005 volt) was calculated from the data of Coggeshall[7] and the proper correction applied. The liquid potentials as calculated by Sammet were employed. The voltage of the normal calomel electrode at 25° was taken to be −0.2822 volt as given by Lewis and Randall.[5] The recalculated results of Sammet are summarized in Table I. Other reviewers[5,8] of the work of Sammet have neglected to take into account the thermocouple effect.

TABLE I

EXPERIMENTAL RESULTS OF RESEARCH BY V. SAMMET[4]: ELECTRODE POTENTIAL OF THE IODINE–IODATE ELECTRODE AT 25°

Reaction: $^1/_2I_2(s) + 3H_2O(l) = IO_3^- + 6H^+ + 5E^-$

Cell employed: Pt, $I_2(s)$, HIO_3 (*xm*), KCl(*xm*), KCl(*N*), HgCl, Hg. Pt, $I_2(s)$, HIO_3(*xm*) at 25°. KCl(*N*), HgCl, Hg at 18°

Concn., mole per liter	0.1	0.01	0.001	0.001[a]
Voltage **E**, observed	−0.784	−0.710	−0.630	−0.666
Mean deviation of **E**	0.001	0.001	0.001	0.001
Liquid junction potential	−0.034	−0.034	−0.034	0.000
Standard potential **E**°	−1.187	−1.190	−1.191	−1.193

[a] For this single measurement the liquid junction was between 0.001 *m* iodic acid and 1 *N* potassium chloride.

In the present investigation the standard potential was determined using inert electrodes of platinized platinum in contact with saturated solutions of iodine in iodic acid at 0.1 and 0.01 *M* concentrations. The potential of this electrode was measured against a hydrogen electrode (both at 25°) in which the concentration of the hydrochloric acid was the same as that of the iodic acid at the other electrode. The liquid junction is of the most simple type and its potentials should be only a few millivolts.

The data presented here when combined with those available in the literature do not at present allow an ultimate evaluation of the standard electrode potential. The principal reason for being unable to do this lies in the fact that the simple expression of Lewis and Sargent[9] (later derived by MacInnes and Yeh[10]) for the potential of the liquid junction existent in the cell employed for these measurements is apparently not strictly applicable. When this expression is employed a discrepany of 0.004 volt exists between the standard potentials calculated from the measurements at 0.1 and 0.01 *M*. The activity coefficients available[6] are strictly only applicable at the freezing points of the corresponding solutions. It is of course possible that the activity coefficients are sufficiently different at 25° to account for the discrepancy. The employment of Planck's equation[11] for the liquid junction potential gives standard potentials which agree very well. However, it is not safe to assume that the expression of Planck is applicable since its derivation restricts its use to extremely dilute solutions. It is also important to note that in the calculation of the standard potential (exclusive of the liquid potentials) it is necessary to assume that the activity of the hydrogen ions at the hydrogen electrode and at the iodine–iodate electrode are the same. Fuoss and Kraus[12] have shown that the electrical conductivities of dilute solutions of iodic acid can be explained upon the basis of the interionic attraction theory (Debye–Hückel) provided one assumes that iodic acid is not completely ionized. They find that its dissociation constant (expressed in terms of activity) must be chosen to be 0.17 to give agreement with experiment. MacInnes and Yeh[10] show that the formula of Lewis and Sargent requires that the electrolytes be ionized completely and that the activities of hydrogen ion be the same in the solutions of iodic and hydrochloric acids. Calculations based upon the above equilibrium constant indicate that at 0.1 *M* the hydrogen ion activities differ to such an extent that the liquid potential cannot be calculated with exactness. However, at 0.01 *M* the equilibrium constant indicates that iodic acid may be considered almost completely ionized (hence the hydrogen ion activities almost equal) and to such an extent that the liquid potential is probably given by the equation of Lewis and Sargent with an accuracy of 0.001 volt.

On several occasions the question has been raised whether the several possible reactions of iodine and its derivatives with water might make for a number of electrode reactions which would interfere with the measurement of the potential of the main reaction in which one is interested. For that reason it is well to emphasize that as long

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[6] Abel, Redlich and Hersch, *Z. physik. Chem.*, **170A**, 112 (1934).

[7] Coggeshall, *ibid.*, **17**, 62 (1895).

[8] Gerke, *Chem. Rev.*, **1**, 377 (1925).

[9] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[10] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

[11] Planck, *Ann. Physik*, **40**, 561 (1890).

[12] Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

as all of the substances reacting at *any* electrode are in chemical equilibrium, the measured potentials for the main reaction and all other secondary reactions are the same. Furthermore, if the concentrations of the reactants and products of the secondary reactions are known, their respective standard potentials may be calculated. The above statement may be proved readily from a thermodynamic standpoint by employment of the free energy function or by the use of activities. It is important to note that the free energy changes involved when iodine is added to the iodic acid solutions used in the present measurements are such that the iodic acid concentrations are not appreciably changed. From a practical standpoint they are unchanged.

Experimental

The measurements were carried out in an air thermostat. The temperature within the thermostat, as read from an accurately calibrated mercury thermometer, could be maintained constant at 25° to within 0.02° over periods of several hours. When the thermostat was unattended in the intervals between the periods of observation, temperature deviations of 0.1° were noted. All potential measurements were made with a Leeds and Northrup type K potentiometer. The sensitivity of the galvanometer was such that with the solutions at concentrations of 0.01 *M* or greater, the potential could be easily read with an accuracy of 0.0001 volt.

The hydrogen electrode vessel was essentially the same as that described by Lewis, Brighton and Sebastian.[13] It was constructed of Pyrex glass and contained two electrodes of platinized platinum. In preparing the electrodes the platinum was thoroughly cleaned with strong chromic acid solution and hot concentrated nitric acid, and then was heated almost to white heat in the flame of a blast lamp. A thin coating of platinum black was then applied according to the procedure recommended by Clark.[14] The platinum leads were sealed into the glass, and at no time was mercury used as a seal for either the hydrogen or the iodine–iodate electrodes.

The iodine–iodate electrode vessel was so constructed that it could be filled completely with solution thus completely excluding air. It contained two electrodes of platinized platinum; the platinum coating was of such thickness that the glint of the underlying metal could be seen. In setting up the cell for a set of measurements, a saturated solution of iodine in iodic acid solution was introduced into the cell. None of the stopcocks in the iodine–iodate electrode vessel was greased.

The two electrode vessels were connected by means of an all-glass bridge containing a three-way stopcock. The third arm of the stopcock was used as a drain and also as a point of connection for the calomel cell which was used to check the hydrogen electrode.

Electrolytic tank hydrogen was used for all measurements. The hydrogen was purified by bubbling through a concentrated solution of potassium hydroxide, passed over a copper gauze heated to 450° by an electric furnace, and then through a soda lime tower.

Conductivity water was used in the preparation of all solutions. C. P. iodine was purified by treatment with potassium iodide to remove other halogens, and subsequently by several sublimations.

The iodic acid solutions used for the first set of measurements (series A-1, and A-2) were prepared from Kahlbaum best grade of iodic acid. The most concentrated (0.0950 *M*) solution (used in series A-1) was standardized with standard sodium hydroxide for its hydrogen ion concentration and with standard sodium thiosulfate for its iodate ion concentration. The values for duplicate determinations of the concentration of each ion did not differ by more than 0.1%. The average value of the concentration of each of the ions agreed exactly to the fourth decimal. The solution used for series A-2 (0.01 *M*) was made up by accurate dilution of the 0.0950 *M* solution.

The iodic acid used for the second set of measurements (series B-2) was prepared by oxidation of highly purified iodine with fuming nitric acid and hydrogen peroxide. The iodic acid was purified by several crystallizations from aqueous solutions by the addition of concentrated nitric acid. The crystals obtained were dried (for twelve hours) by vacuum desiccation at room temperature. From this white crystalline material a 0.1060 *M* solution was prepared. Triplicate analyses for hydrogen ion had a mean deviation of 0.2%. Duplicate analyses for iodate ion differed by 1.0%. The discrepancies are largely due to the fact that inadequate volumes were available for the titrations. The average value of the hydrogen ion concentration was 0.1063 *M* and that of iodate ion 0.1057 *M*. The solution used for series B-2 (0.01000 *M*) was made up by accurate dilution of the 0.1060 *M* solution.

The solid iodic acid prepared for series B-2 was further purified by recrystallization from aqueous solution by concentrated nitric acid. The crystals were dried for forty-eight hours by vacuum desiccation at room temperature. This solid (perfectly white) iodic acid was used for the third set of measurements series C-1, and C-2. A 0.0954 *M* solution was prepared. Triplicate analyses for hydrogen ion had a mean deviation of less than 0.07%. Triplicate analyses for iodate ion had a mean deviation of less than 0.02%. The average value of the hydrogen ion concentration was 0.0956 *M* and that of the iodate ion 0.0953 *M*. While this discrepancy may be due to the presence of a trace of nitric acid it has been attributed to differences in the standard reagents. The value 0.0954 *M* is a weighted average of the last two figures.

The solutions of hydrochloric acid were made up from Baker's Analyzed C. P. concentrated hydrochloric acid. These stock solutions were standardized against pure sodium carbonate and against silver chloride (gravimetrically). The concentrations given by the two methods agreed to within 0.1%.

All other chemicals used either directly or indirectly were of the highest quality.

Comparison of the hydrogen electrodes with freshly prepared calomel electrodes indicated that the hydro-

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(13) Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

(14) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1928.

TABLE II

EXPERIMENTAL RESULTS OF THIS RESEARCH (L., V. AND A.)

Electrode Potential of the Iodine–Iodate Electrode at 25°

Unit of potential, international volt

Reaction: $^1/_2I_2(s) + 3H_2O(l) = 5/2H_2(g) + H^+ + IO_3^-$

Cell employed: Pt, $I_2(s)$, $HIO_3(xM)$, $HCl(xM)$, $H_2(g)$, Pt

Series	A-1	C-1	A-2	B-2	C-2
Concn., mole per 1000 g. water	0.0950	0.0954	0.01000	0.01000	0.01000
Voltage **E** p. p. H_2 76.0 cm. Hg	−1.1621	−1.1618	−1.1425	−1.1432	−1.1429
Mean dev. of **E**	0.0001	0.0001	0.0002	0.0001	0.0003
Number of sets of voltage observations	10	11	14	4	14
Number of times solutions replaced	3	1	4	3	4
Hours allowed for equilibrium	2	6	10	10	10
Maximum hours observed	16	96	20	18	72
Standard potential $\mathbf{E}^0$ from Lewis and Sargent equation	−1.1997	−1.1994	−1.1947	−1.1954	−1.1951
Standard potential $\mathbf{E}^0$ from Planck equation	−1.1937	−1.1934	−1.1936	−1.1943	−1.1940

gen electrodes functioned properly during the measurements.

It was necessary to allow the iodine–iodate cells to stand for some time before equilibrium was established. For the 0.1 *M* solutions equilibrium was established fairly rapidly (less than two hours). For the 0.01 *M* solutions the rate of attainment of equilibrium was less rapid (less than ten hours). The periods of time that the potentials of the cells were observed and their fluctuations are given in Table I. At 0.001 *M* the cells would not give reproducible results and are consequently not reported. An attempt was made to make similar measurements on the bromine–bromate electrode but due to lack of reproducibility of potentials the investigation was discontinued.

The conditions under which the liquid junction was established were varied considerably in order to study its reproducibility. In most of the measurements the liquid junction was formed at the ungreased three-way stopcock which connected the electrode vessels. Readings were taken with the stopcock open and closed. When this stopcock was left open another stopcock in the bridge to the hydrogen electrode vessel was kept closed to prevent motion of the liquid in the bridge and to preclude the possibility of diffusion of iodine into the hydrogen electrode vessel. Readings taken with the three-way stopcock open remained constant for relatively long periods of time and were readily reproduced when the bridge was flushed and refilled with fresh solutions. Readings taken with the three-way stopcock closed changed after a few minutes, probably because of composition changes of the solutions forming a thin film in the closed stopcock. When the stopcock was again flushed the original readings were obtained.

The cell employed to measure the electromotive force of the iodine–iodate couple may be represented as

$$\text{Pt}, I_2(s), HIO_3(xm), HCl(xm), H_2(g), \text{Pt}$$

The total cell reaction is

$$^1/_2I_2(s) + 3H_2O = 5/2H_2(g) + H^+ + IO_3^- \quad \text{(A)}$$

The measured potential[15] at 25° is given by

$$\mathbf{E} = \mathbf{E}^\circ + \mathbf{E}_L - (0.05913/5) \log (H_2)^{5/2} (H^+)(IO_3^-)$$

As discussed before it is difficult to evaluate the liquid potential term. The liquid potential for such a junction is usually given by

$$\mathbf{E}_L = +0.05913 \log \frac{\Lambda_{H^+} + \Lambda_{Cl^-}}{\Lambda_{H^+} + \Lambda_{IO_3^-}}$$

Planck[11] was the first to give the theory of such a liquid junction, but his equation must be regarded as only strictly applicable at infinite dilution. Planck's expression is the same as that above, with the conductivity terms being those at infinite dilution. The liquid potential given by Planck's expression is the same (+0.0025 volt) for the 0.1 and 0.01 *M* solutions. Consequently the standard potentials calculated by Planck's equation are in excellent agreement. The Lewis and Sargent[9] equation derived by MacInnes and Yeh[10] is applicable at all concentrations provided both electrolytes are completely ionized and the activities of the common ion are the same in both solutions. The Lewis and Sargent equation is that given above with the conductivity terms being those at the concentrations employed. The equivalent conductivities employed are those given in the "International Critical Tables," 1929. When employed in the Lewis and Sargent equation these values give +0.0034 and +0.0083 volt at 0.01 and 0.1 *M* concentrations, respectively.

The products of the activities of the hydrogen ions and iodate ions were calculated from the activity coefficients of iodic acid.[6]

The experimental results are tabulated in Table II.

It is estimated that the averages of the directly measured potentials at each concentration are accurate to about 0.0005 volt. The incomplete dissociation of iodic acid at 0.1 *M* is consistent with the discrepancies noted in the standard potentials calculated from the measurements at

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[15] The conventions employed are those given by Lewis and Randall, ref. 5.

0.01 and 0.1 M concentrations. Since iodic acid may be considered almost completely dissociated at 0.01 M, it is believed that −1.195 volts should be accepted for the present as the standard potential for the iodine–iodate reaction (A). It is estimated that the probable error of this last value is about 0.002 volt.

Free Energy and Heat of Formation of Iodate Ion.—From the standard electrode potential given by this research one may calculate the standard free energy change at 298.1°K. for the reaction

$$^1/_2I_2(s) + 3H_2O(l) = 5/2H_2(g) + H^+ + IO_3^-$$

$$\Delta F^\circ_{298.1} = -5 \times 23066 \times (-1.195) = 137{,}819 \text{ calories}$$

Gordon[16] has computed the entropy of water from spectroscopic data and with the heat of formation of water[17] and the entropies of hydrogen[18] and oxygen,[19] he calculates the free energy of formation of water

$$3H_2 + 3/2\,O_2 = 3H_2O(l) \quad \Delta F^\circ_{298.1} = -170.070 \text{ calories}$$

By subtraction of the last reaction from the preceding reaction one may calculate the free energy of formation of iodate ion.

$$^1/_2I_2(s) + 3/2\,O_2 + {}^1/_2H_2 = H^+ + IO_3^- \quad \Delta F^\circ_{298.1} = -32{,}251$$

The entropies of iodine[20] and of iodate ion[21] are known in addition to those of hydrogen and oxygen. The entropy change in this reaction is 76.20 cal./deg. and combination with the value for the free energy change gives for the heat of formation of iodate ion $\Delta H^\circ_{298.1} = -54{,}966$ calories. It is well to note that this value at 298.1°K. is in good accord with the value at 291°K. given in the summary by Bichowsky and Rossini.[22]

The authors wish to thank Professor W. M. Clark and Dr. E. G. Ball of the Physiological Chemistry Department of The Johns Hopkins University for helpful advice.

Summary

The electrode potentials of the iodine–iodate electrode reaction have been measured at several concentrations and its standard electrode potential evaluated

$$^1/_2I_2 + 3H_2O = IO_3^- + 6H^+ + 5E^- \quad E^\circ_{298.1} = -1.195 \text{ volts}$$

The free energy, entropy and heat of formation of iodate ion have been evaluated.

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[16] Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

[17] Rossini, *Bur. Standards J. Research*, **6**, 1 (1933).

[18] Giauque, THIS JOURNAL, **52**, 4831 (1930).

[19] Johnston and Walker, *ibid.*, **55**, 172 (1933).

[20] Giauque, *ibid.*, **53**, 513 (1931).

[21] Ahlberg and Latimer, *ibid.*, **56**, 858 (1934).

[22] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936.

BALTIMORE, MD. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Catalytic Decomposition of Hydrogen Peroxide by Aluminum Oxyiodide Hydrosols

BY ARTHUR W. THOMAS AND BENJAMIN COHEN

The catalytic decomposition of hydrogen peroxide by aluminum oxyiodide hydrosols[1] has been investigated for the first time for the purpose of studying the changes of the iodide ion concentration in these colloidal systems under various conditions.

This particular reaction was chosen for the following reasons: (1) It has been shown by several investigators that over a large range of iodide concentration, the decomposition of hydrogen peroxide in neutral solution is strictly proportional to the iodide ion concentration. (2) Hydrous aluminum oxide itself, and also in the presence of several potassium salts used in this study, had no appreciable catalytic effect upon hydrogen peroxide. (3) The decomposition of hydrogen peroxide by the sols was homogeneous and first order.

The pH values of the hydrosols were about 5.6 and increased to a maximum of $p\mathrm{H} = 8$ upon the addition of certain potassium salts. In this range of pH, the steady state function for the iodide–iodine couple as investigated by Abel[2] and Liebhafsky[3] indicates that less than 1% of the total iodide present in our hydrosol systems will be removed to form iodine or tri-iodide ion. In

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[1] Perhaps a better name is "basic aluminum iodide" hydrosols. They are known also as "aluminum oxide" hydrosols with sorbed and contra iodide ions.

[2] Abel, *Z. physik. Chem.*, **136**, 161 (1928).

[3] Liebhafsky, THIS JOURNAL, **54**, 1792 (1932).