built is to displace the potential–layer curves up or down without altering their shape subsequent to the first three layers. The absolute magnitude of the displacement is independent of the type of film and of the magnitude of the applied voltage but the direction of displacement, up or down, depends upon the direction of the voltage. Similar shifts of potential are produced when films are immersed in the liquids under the influence of an applied voltage without the deposition of layers.

X or Y films containing lead fail to develop large contact potentials under all conditions and show certain unusual properties.

Impedance measurements at frequencies of 1 and 0.244 megacycles show no significant difference between X and Y films. They indicate a dielectric constant of about 2.5 and give evidence of power absorption. Breakdown voltages of X and Y films are the same. Breakdown voltages of films in contact with mercury increase with the thickness of the films, and correspond to fields of the order of 10^6 v./cm. Apparent breakdown voltages of films in contact with water are nearly independent of thickness and depend on the direction in which the voltage is applied. The specific d. c. resistance of both X and Y films is of the order of 10^{13} ohms.

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

The Volumetric Oxidation of Iodide and Bromide by Periodic Acid[1]

BY HOBART H. WILLARD AND LUCIEN H. GREATHOUSE

Periodic acid and periodates of the alkalies are powerful oxidizing agents in dilute aqueous solution and usually stable enough for use in volumetric analysis.

Reactions of periodates as oxidizing agents have been investigated from an early date.[2] The reaction between periodate and iodide with excess of the former

$$KI + 3KIO_4 = 4KIO_3$$

is of particular interest.[3]

The excess of periodate may be determined accurately in the presence of iodate by titrating with standard arsenite the iodine liberated from iodide in neutral solution, thus

$$KIO_4 + 2KI + 4H_3BO_3 = KIO_3 + I_2 + K_2B_4O_7 + 6H_2O$$

This principle was first stated by Péchard[4a] but the method was developed by Müller and his associates.[4b] For this purpose the solution is buffered preferably with boric acid–borax mixture.

Titrations based on these reactions have been used recently to identify polyhydric alcohols.[5]

Periodates Suitable as Reagents

Potassium Periodates.—The metaperiodate, KIO_4, commercially available, contained 79.51% of I_2O_7 compared with the theoretical value of 79.52% and was free from iodate by test with silver nitrate.[2c,6] It may be used as a primary standard for iodimetry.

The solubility of potassium metaperiodate in water was found to be as follows, in grams per 100 ml. of the saturated solutions

0°	25°	35°	45°	55°	65°
0.1546	0.5112	0.785	1.190	1.75	2.51

The specific gravity at 25° of the solution saturated at 25° was 1.00125. If the solubility at 25° as determined by Hill[7] is recalculated to grams per 100 ml. a value of 0.5106 is obtained.

The metaperiodate decomposes in solution with a strong odor of ozone. Dipotassium paraperiodate, $K_2H_3IO_6$, is much more soluble than the meta salt and more stable in solution and hence better suited for standard solutions.

Sodium Periodates.—The paraperiodates precipitated by the reaction of chlorine on iodate in alkaline solution vary in composition between $Na_3H_2IO_6$ and $Na_2H_3IO_6$.[7]

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(1) From a dissertation presented in partial fulfilment of the requirements for the degree of doctor of philosophy at the University of Michigan by Lucien H. Greathouse in 1917.

(2) (a) Ammermüller and Magnus, *Ann.*, **11**, 18–24 (1834); (b) Bengieser, *ibid.*, **17**, 254–260 (1836); (c) Langlois, *ibid.*, **83**, 153–175 (1852); (d) Selmons, *Chem. Centr.*, [3] **18**, 502–504 (1887); (e) Grützner, *Arch. Pharm.*, **234**, 634–640 (1896); (f) Péchard, *Compt. rend.*, **128**, 1101 (1899); (g) Brunner and Mellet, *J. prakt. Chem.*, [2] **77**, 33–42 (1908); (h) Willard and Greathouse, THIS JOURNAL, **39**, 2366 (1917).

(3) (a) Phillip, *Bull. soc. chim.*, [2] **12**, 350 (1869); (b) Péchard, *Compt. rend.*, **130**, 1705 (1900); (c) Garzarolli-Thurnlackh, *Monatsh.*, **22**, 955–975 (1901); (d) Müller, *Z. Elektrochem.*, **9**, 584–594, 707–716 (1903); (e) Bray, *Z. physik. Chem.*, **54**, 463–497 (1906); (f) Auger, *Bull. soc. chim.*, [4] **11**, 731 (1912).

(4) (a) Péchard, *Compt. rend.*, **128**, 1453 (1899); (b) Müller and Friedberger, *Ber.*, **35**, 2652 (1902); and Jacob, *Z. anorg. Chem.*, **82**, 308–314 (1913); and Weglin, *Z. anal. Chem.*, **52**, 755 (1913).

(5) (a) Malaprade, *Compt. rend.*, **186**, 382 (1938); *Bull. soc. chim.*, [4] **43**, 683–696 (1928); *ibid.*, [5] **1**, 833–852 (1934); (b) Fleury and Lange, *J. pharm. chim.*, [8] **17**, 107–113, 196–208, 313–326, 409–427 (1933); (c) Fleury, *ibid.*, [8] **18**, 476–481 (1933); (d) Rappaport, Reifer and Weinmann, *Mikrochim. Acta*, **1**, 290–299 (1937); Rappaport and Reifer, *ibid.*, **2**, 273 (1937).

(6) Willard and Thompson, THIS JOURNAL, **56**, 1827 (1934).

(7) Hill, *ibid.*, **50**, 2678 (1928).

The precipitate is very insoluble in excess of sodium hydroxide. The metaperiodate, $NaIO_4$, is readily soluble in water and is therefore more useful as a reagent. Analysis of a sample prepared in this work gave 85.61% of I_2O_7 as compared with the theoretical value of 85.59%. It is prepared by dissolving the paraperiodate in dilute nitric acid and recrystallizing.

Standard Solutions.—Standard arsenite was prepared in the usual way from very pure arsenious oxide and brought to a pH of approximately 7 by buffering with sodium bicarbonate saturated with carbon dioxide.

Standard tenth normal potassium paraperiodate was prepared by dissolving the meta salt in hot water and adding a 10% excess of potassium hydroxide.

The rates of decomposition of metaperiodate and paraperiodate in 0.05 M solution at about 30° are shown in Fig. 1. The sodium salt was used to obtain a metaperiodate solution of this strength. Although the paraperiodate solution gave a faint odor of ozone its loss in strength shown in Fig. 1 was probably due also to a slow precipitation by impurities extracted from the glass container by the alkaline solution.

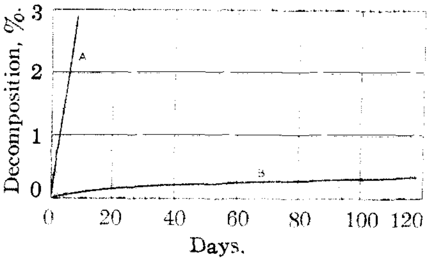

Fig. 1.—Decomposition of 0.05 M periodate solutions at 30°: A, sodium metaperiodate; B, dipotassium paraperiodate.

Standard solutions of periodic acid or of sodium metaperiodate acidified with one equivalent of sulfuric acid were found exceptionally stable. One such solution changed less than 0.1% after standing four months in the light and then two years in the dark. These acid solutions were not used because the reagents required were not commercially available at the time.

Determination of Iodide

If a neutral solution of iodide is oxidized to iodate by the addition of an excess of periodate, the latter can then be determined by titration with arsenite as already described. Since iodine is first liberated and subsequently oxidized the reaction must be carried out in a closed vessel.

Standard potassium iodide solution was prepared from a pure salt which had been recrystallized until free from chloride, bromide, and iodate. It was kept in an atmosphere of hydrogen and was standardized gravimetrically by precipitation with silver nitrate, with the following results:

Grams of iodine *in vacuo*, per gram of solution in air, 0.0125961 0.0125965 0.0125966 Av. 0.0125964

Influence of Temperature on the Reaction.—Experiments were made at 25, 35, 45 and 55°, following the reaction of 0.0025 mole of potassium iodide with 0.0075 mole of potassium paraperiodate in a volume of 250 ml. The standard periodate and iodide solutions were brought separately to the selected temperature, then mixed and diluted to volume quickly in a volumetric flask immersed in a thermostat at the same temperature. At suitable intervals 25-ml. samples were withdrawn, treated with borax and boric acid, then with an excess of potassium iodide solution, and titrated with 0.1 N arsenious acid. This titration gave residual periodate plus the oxidizing equivalent of such iodine as had been liberated but not yet oxidized to iodate. A second experiment was made at 25° but diluted to 500 ml. and 50-ml. samples withdrawn.

The results plotted in Fig. 2 indicated that at higher temperatures and with an excess of periodate the reaction would be rapid.

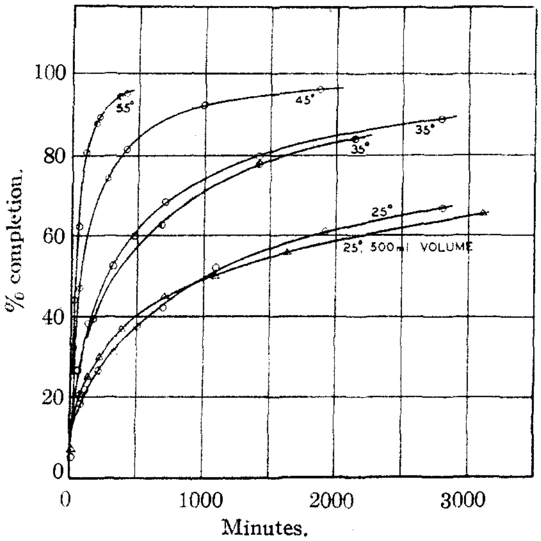

Fig. 2.—Effect of temperature on the reaction $3K_2H_3IO_6 + KI = 4KIO_3 + 3KOH + 3H_2O$: ◐, duplicate experiment; △, dilution experiment at 25°.

Determination of Iodide Alone.—One general procedure was used. Fifty milliliters of 0.1 N paraperiodate was introduced into a glass-stoppered 250-ml. Erlenmeyer flask. A flat-ended glass vial, containing 3 to 8 ml. of iodide solution, was lowered into the flask and placed upright on the bottom. Thus the two solutions were kept separate until the whole system was heated to the selected temperature. No other water was added except where noted. The flask was then stoppered and tilted to upset the vial and mix the solutions. After periods as noted in the tables, the reaction mixtures were cooled and excess periodate titrated.

In determinations 1 to 7 of Table I the oxidation was conducted at 70 to 80° and was complete in thirty-five to forty minutes when a small excess of periodate was used. In determinations 8 to 22 the reaction was conducted at 96 to 98° which reduced this period to about twenty minutes. After the iodine liberated at first had disappeared, the solution was neutralized with an excess of boric acid, the flask being opened and closed quickly.

In the determinations shown in Table I the factors of time, temperature and excess of periodate were varied to determine the limits within which the reaction would be

TABLE I

DETERMINATION OF IODIDE

No.	Iodine as KI taken, g.	Excess 0.1 *N* $K_2H_3IO_6$, ml.	Volume during oxidation, ml.	Time heated, min.	Error, mg. of iodine
1	0.0727	14.30	60	10	−0.2
2	.0767	12.41	60	7	.0
3	.0789	11.33	60	5	+ .2
4	.1004	1.16	60	30	− .1
5	.1007	1.06	60	40	− .2
6	.0964	3.12	60	35	− .2
7	.0977	2.48	60	30	.0
8	.1009	0.95	60	40	− .1
9	.1008	.96	60	40	+ .1
10	.1002	.31	60	70	.0
11	.0998	1.51	60	22	.0
12	.0996	1.64	60	21	.0
13	.0988	3.22	100	15	+ .2
14	.0985	3.38	150	15	+ .2
15	.0985	3.38	200	15	.0
16	.0987	3.28	250	15	.0
17	.0785	12.78	250	8	− .1
18	.0850	9.71	250	8	.0
19	.0923	6.33	250	8	−1.1
20	.0704	16.65	250	5	0.0
21	.0760	14.00	250	5	− .6
22	.0831	10.63	250	5	−1.7

complete. In determinations 13 to 22 the volume was increased and the time allowed for reaction progressively decreased as the excess periodate varied, until in determinations 19, 21 and 22 the reaction was incomplete.

Determination of Iodide in Presence of Bromide.—When bromide was also present, slight liberation of bromine occurred which did not affect the accuracy of the iodine determination if no bromine was lost.

The presence of bromide accelerated the reaction so that the addition of boric acid could be omitted. This avoided the procedure of opening the flask during the reaction, which would have permitted loss of bromine. In Table II, in determinations 1 and 2, 50 ml. of 0.1 *N* $K_2H_3IO_6$ was used but in the others, 25 ml. of 0.1 *N* $K_2H_3IO_6$ and 75 ml. of water were added.

TABLE II

DETERMINATION OF IODIDE IN PRESENCE OF BROMIDE

No.	Iodine taken, g.	KBr, g.	Excess $K_2H_3IO_6$, ml.	Time heated, minutes	Error, mg.
1	0.0982	0.6	1.88	15	0.0
2	.0965	.6	3.13	10	− .1
3	.0380	5.0	6.25	3	.0
4	.0382	5.0	6.15	3	+ .1
5	.0386	5.0	5.95	3	.0
6	.0415	5.0	4.69	3	− .1

The determination of small percentages of iodide in mixtures with bromides is rapid and accurate.

Recommended procedure: Measure into an Erlenmeyer flask with a ground-glass stopper standard 0.1 *N* paraperiodate in 10 to 25% excess over that required to oxidize the iodide in the sample to iodate. Dissolve the sample in 5–10 ml. of water in a small vial with a flat end, and set this upright within the flask. Place the flask in a steam-bath, heat to 97–98°, stopper it and upset the vial to mix the solutions.

After the disappearance of iodine, which should occur in less than five minutes, continue heating for ten minutes, then loosen the stopper, cool, and add an excess of powdered boric acid. If the iodine color reappears, replace the stopper, and return to the steam-bath for ten minutes. Any iodine color persisting either before or after the boric acid addition indicates insufficient periodate, in which case the determination will not be accurate.

When bromide is present, the reaction is faster. The addition of boric acid during the reaction is not required, and should be delayed until the solution, after reacting for fifteen minutes, has been cooled. With higher bromide concentrations, a faint bromine color may appear slowly, differing, however, from the iodine color which appears at once when oxidation is incomplete. After completion of oxidation, cool, add an excess of boric acid, then an excess of 5% potassium iodide solution, about 1 ml. for each milliliter of unreacted 0.1 *N* periodate being sufficient to prevent volatilization of iodine. Titrate the iodine liberated with standard arsenite. Each milliliter of 0.1 *N* periodate is equivalent to 0.0021153 g. of iodine.

Determination of Bromide

Periodic acid oxidizes bromide in acid solution to bromine. The reaction is complete if the bromine is removed by bubbling air through the solution. The excess periodate may then be titrated to determine bromide.

A standard solution by weight was prepared from potassium bromide purified for atomic weight work. It was standardized by precipitation as silver bromide with the following results:

Grams of bromine *in vacuo*, per gram of solution in air

0.0157740 0.0157731 0.0157770 0.0157730 Av. 0.0157743

Either the standard paraperiodate solution, as in the iodine determination, or the acidified sodium periodate solution described earlier, may be used. There are also required a 5 *N* sulfuric acid solution, which must be free of reducing reagents, a starch iodide indicator, and Schiff fuchsine indicator for bromine as described by Guareschi.[8]

The reaction was conducted in an Erlenmeyer flask with a ground-glass stopper, through which passed one tube connected to an aspirator and another down into the flask so that air could be drawn through the reaction mixture from several fine openings. A U-tube containing the indicator solution was connected in the suction line. The fuchsine indicator must be used instead of starch iodide if chlorine is present.

Recommended Procedure.—If iodide or other constituents oxidizable by periodate in neutral solution are present, first determine the amount of the standard reagent required for this on a separate aliquot of the solution to be analyzed. To another aliquot, placed in the reaction flask, add this amount of standard periodate, plus a volume of 10 to 35% in excess of that required for oxidation of the bromide. If much iodide is present, keep the two solutions separate until

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(8) Guareschi, *Z. anal. Chem.*, **52**, 451 (1913).

heated, then mix and oxidize as described before, which usually requires ten to fifteen minutes. Dilute to 100 ml. and acidify with 20 ml. of 5 *N* sulfuric acid in excess of that equivalent to the combined base in the bromide plus that in the standard periodate used. Heat and draw air through the solution until the bromine color disappears, then place the indicator solution in the U tube and repeat until no test for bromine is obtained. Cool, neutralize with 20 ml. of 5 *N* sodium carbonate, buffer the solution and titrate the excess of periodate.

TABLE III

DETERMINATION OF BROMIDE

No.	Bromine taken, g.	0.2 *M* KCl, ml.	Excess 0.1 *N* $K_2H_3IO_6$, ml.	5 *N* H_2SO_4, ml.	Time of heating, min.	Error bromine, mg.
1	0.3599		4.56	25	45	−0.1
2	.3600		4.54	20	55	.0
3	.3607		4.45	20	65	+ .1
4	.3401		7.48	10	90	− .6
5	.3038		11.86	10	95	+ .2
6	.2560		17.84	10	80	+ .3
7	.2001		24.84	10	55	+ .3
8[a]	.2211		22.25	18.5	150	.0
9	.3633	5	4.42	10	100	− .5
10	.3632	5	4.35	10	105	− .1
11	.3638	5	4.30	10	120	.0
12	.3621	10	4.33	10	120	+1.2
13	.3617	25	4.15	10	120	+3.1

[a] Reaction volume was 100 ml. except 300 ml. in No. 8.

Each milliliter of 0.1 *N* periodate is equivalent to 0.00792 g. of bromine.

Any considerable amount of chloride interferes but, as shown in the results of Table III, by using low acidity and a prolonged bubbling, separation from a millimole or less of chloride may be effected.

Summary

1. Potassium metaperiodate, KIO_4, can be purified readily so as to have the theoretical composition and may be used as a primary standard in iodimetry.

2. Dipotassium paraperiodate in a slightly alkaline solution, and sodium metaperiodate acidified with sulfuric acid are both stable volumetric solutions, the latter showing remarkable permanency. Metaperiodates in neutral solution decompose with noticeable rapidity.

3. Iodide may be determined in the presence of bromide, chloride, and other substances not oxidized by neutral periodate solution by oxidation to iodate with standard periodate, and titration of the excess of the latter with arsenious acid. Conditions required for a rapid reaction are shown.

4. Bromide may be determined in presence of small amounts of chloride by oxidation to bromine with standard periodate in slightly acid solution, expulsion of the bromine, and titration of the excess periodate.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 6, 1938

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Hydrogen Disulfide, Dimethyl Disulfide and Sulfur Dichloride

BY D. P. STEVENSON AND J. Y. BEACH[1]

We have investigated the structure of the gas molecules of hydrogen disulfide, dimethyl disulfide and sulfur dichloride by the electron diffraction method. The apparatus has been described elsewhere.[2] The electron wave length was 0.0590 Å., determined from transmission pictures of gold foil (*a* = 4.070 Å.). The distance from the gas nozzle to the photographic plate was 12.19 cm. The photographs were interpreted by the visual method.[3] The radial distribution method[4] and a modification[5] of the radial distribution method also were used.

Hydrogen Disulfide.—The hydrogen disulfide was prepared according to Vanino.[6] The compound was clear and colorless. The photographs were taken within an hour after the compound was made. After standing for several days at room temperature the hydrogen disulfide turned yellow. A few semiquantitative measurements of the vapor

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[1] National Research Council Fellow in Chemistry.

[2] Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[3] Pauling and Brockway, *ibid.*, **2**, 867 (1934).

[4] Pauling and Brockway, THIS JOURNAL, **57**, 2684 (1935).

[5] Schomaker, to be published.

[6] Vanino, "Handbuch der präparative Chemie," Vol. I, 1925, p. 80.