electrolytes, is experimentally the concentration above which the simple laws of dilute solutions of electrolytes are no longer obeyed, so that a numerical significance is attached to the phrase "at low concentrations." At higher concentrations, higher types of association must be considered for the case of non-aqueous solutions.

PROVIDENCE, R. I. RECEIVED JUNE 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Potentiometric Determination of Quadrivalent Osmium with Chromous Sulfate

BY WILLIAM R. CROWELL AND HARLAN L. BAUMBACH

In previous papers we have presented a direct[1] and an indirect[2] method of determining quadrivalent osmium. The former method is highly inaccurate, and the latter has the disadvantages of having two volatile constituents involved and of being applicable only to dilute acid solutions. The work of Thornton and Sadusk[3] suggested to us the possibility of using chromous sulfate as the reducing agent and the present work deals with the use of solutions of this salt. As in the case of titration with titanous salts the osmium is reduced from the quadrivalent to the trivalent state.

Because of the rapid reaction between chromous sulfate and oxygen we found it most satisfactory to have the apparatus all of glass as far as possible, to have all rubber connections of best quality heavy rubber, and all joints sealed with a suitable material such as lacquer cement. Of lesser importance is the tendency for chromous sulfate to react with hydrogen ion. Asmanoff[4] states that solutions may be as high as 10 *N* in sulfuric acid or 3 *N* in hydrochloric acid before any appreciable evolution of hydrogen takes place. Thornton and Sadusk state that they prepared 0.07 *N* solutions 0.18 *N* in sulfuric acid which remained unchanged in titer for two months. The solutions used by us were not greater than 0.03 *N* in sulfuric acid.

Reagents

The chromous sulfate solution was prepared by a method developed by Messrs. Stone and Beeson of the Chemistry Department at the University of California at Los Angeles. A solution of 0.01 *M* chrome alum 0.01 *N* in sulfuric acid was reduced by passage over amalgamated zinc. The yield of chromous ion was nearly 100% and the acid concentration was practically unchanged by the process.

The potassium bromoosmate and the potassium chloroosmate were prepared from osmium tetroxide in much the same manner that Gilchrist[5] prepared the ammonium bromo and chloro compounds in his determination of the atomic weight of osmium. A potassium hydroxide solution of osmium tetroxide was prepared as previously described.[6] The solution was acidified with sulfuric acid, the osmium tetroxide distilled into hydrobromic or hydrochloric acid, and the procedure carried out according to the method of Gilchrist except that potassium instead of ammonium salts were used.

The hydrobromic acid was prepared from red phosphorus and bromine. The middle fraction of the distillation of the products of the reaction was redistilled several times until a water-white liquid was obtained.

The constant boiling hydrochloric acid was obtained by twice distilling a mixture of equal volumes of concentrated hydrochloric acid and distilled water and retaining the middle fraction of the second distillation.

The potassium ferricyanide and potassium iodate used in standardizing the chromous sulfate and the sodium thiosulfate were recrystallized from the chemically pure salts.

Apparatus, Experimental Procedure and Results

The titration beaker consisted of a heavy-walled Pyrex beaker of about 125-cc. capacity. The cover consisted of a large rubber stopper which was cemented in place. In this stopper were openings for a mercury-sealed stirrer calomel and platinum electrodes, carbon dioxide inlet and outlet, burets, apparatus for introducing solids, and apparatus for treating and transferring solutions. In the bottom of the beaker was sealed a heavy stopcock to allow solutions to be withdrawn and the beaker to be rinsed without admitting air.

Figure 1 shows a diagram of the apparatus used for storing and handling the chromous sulfate solution. The system was flushed with nitrogen and the standard solution forced into the 5-liter flask A and stored under a total pressure of about 1.5 atm. of nitrogen. The nitrogen was purified by passing it through a strong solution of chromous sulfate. The capacity of the flask was about two liters of solution. E, F and G are heavy stopcocks. The solution was allowed to flow into the buret C and fill the bulb B. I was sealed off and after standing long enough to remove all adsorbed oxygen from the walls of the buret and bulb, the solution was displaced by nitrogen at

---

[1] Crowell and Kirschman, THIS JOURNAL, **51**, 1695 (1929).

[2] Crowell, *ibid.*, **54**, 1324 (1932).

[3] Thornton and Sadusk, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 240 (1932).

[4] Asmanoff, *Z. anorg. allgem. Chem.*, **160**, 209 (1927).

[5] Gilchrist, *Bur. Standards J. Research*, **9**, 279 (1932).

[6] Crowell and Kirschman, THIS JOURNAL, **51**, 175 (1929).

one atmosphere pressure by passing the gas through D and allowing the solution to flow out through E and F. The solution in A was shaken over the walls of the flask occasionally over a period of a day or two and it was ready for use. Solutions stored in such a manner remained unchanged in titer for a month.

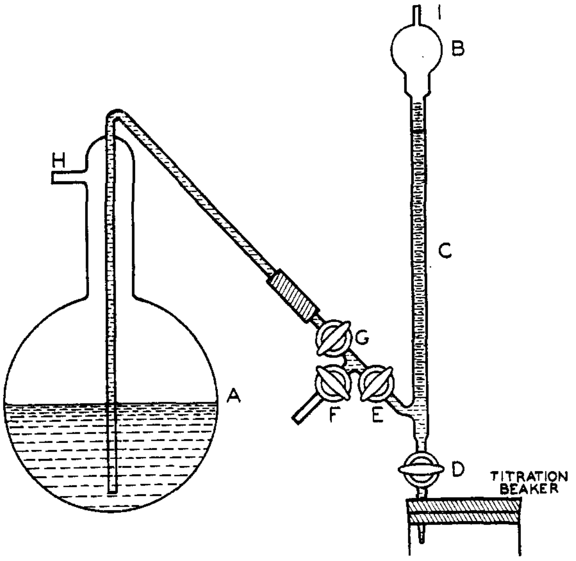

Fig. 1.—Apparatus for storing and titrating chromous sulfate solutions.

The oxygen-free water and acids were stored in bottles provided with heavy rubber stoppers and connected by siphon tubes to the side arms of burets. A slight pressure of carbon dioxide was maintained over the solutions in the bottles, burets and titration beaker at all times. The carbon dioxide was purified by passage through chromous sulfate solution.

The chromous sulfate solution, which was approximately 0.01 *N*, was standardized with solid potassium ferricyanide and with potassium dichromate solution. The high equivalent weight of potassium ferricyanide, the ease with which it can be prepared in the pure state, and the sharp end-point obtainable with it recommended its use as a standard. About 80 mg. of the crystals dried at 130° was introduced into an apparatus similar to that shown in Fig. 2 except that the tube connecting with the titration beaker was larger and attached in such a manner that the sample could be washed directly into the beaker with water. After carbon dioxide had been passed over the crystals for fifteen minutes, they were washed into the beaker with 20–40 cc. of oxygen-free water, 5 cc. of 2 *N* hydrobromic acid added, and the solution titrated potentiometrically with chromous sulfate. About 25 cc. of the reducing agent was required. It was not necessary to add zinc salt because the presence of the zinc ions in the reducing agent had sufficient influence on the potential of the solution to produce an end-point change of 600–800 millivolts per 0.1 cc. of reagent.

The normality of the dichromate solution was determined by means of thiosulfate standardized with potassium iodate. 0.9980 cc. of 0.2297 *N* dichromate was pipetted into the apparatus shown in Fig. 2 and 5 cc. of 6 *N* sulfuric acid added. Carbon dioxide was bubbled through the solution slowly from the titration beaker, escaping by way of the two-way stopcock while the solution was boiled gently for fifteen minutes to remove all oxygen. After cooling, the solution was forced into the beaker by connecting with a higher pressure of carbon dioxide than that in the beaker. Finally the flask was rinsed with 20–40 cc. of water and the contents of the beaker titrated. The end-point potential change was 400–600 millivolts per 0.1 cc.

In the titration of six chromous sulfate solutions with ferricyanide the average deviation of each normality from the mean was 0.05%. In the titration of three solutions with dichromate the average deviation was 0.02%. The difference between the averages of two ferricyanide and three dichromate titrations was 0.03%.

Table I shows the results of determinations of the equivalent weights of potassium bromoosmate and potassium chloroosmate. About 150 mg. of the salt was introduced into the beaker in the same manner as the ferricyanide and sufficient acid added to furnish the concentration stated in column 3. The titration was conducted with the chromous sulfate which had been standardized with ferricyanide. The volume of reagent required was about 19–24 cc. in the case of bromoosmate and 21–33 cc. in the case of chloroosmate. The potential change per 0.1 cc. at the end-point was about 75 millivolts for the bromoosmate in 1 *N* hydrobromic acid, 130 millivolts in 0.1 *N* hydrobromic acid, and for the chloroosmate 80–100 millivolts in the 0.8 *N* hydrochloric acid. In column 4 are shown the values of the equivalent weights calculated from the titration data, and in the last column the percentage differences between these values and those calculated by use of Gilchrist's atomic weight of osmium. The results

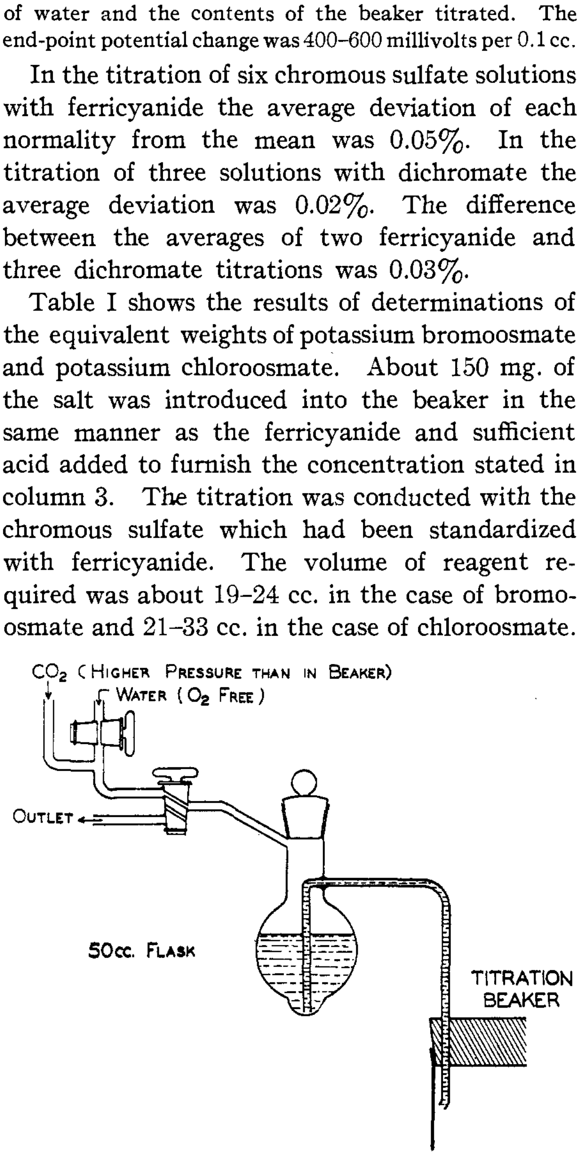

Fig. 2.—Apparatus for treating and transferring solutions.

indicate that the acid concentration should not be below 0.1 N in the case of bromoosmate and 0.5 N in the case of chloroosmate.

At the foot of the table are shown the average deviations of the values of the equivalent weights obtained with the two salts. In spite of the fact that the percentage deviation in the values of the corresponding atomic weights of osmium is multiplied by about four in the case of bromoosmate and 2.5 in the case of chloroosmate, it is interesting to note how closely the two averages agree with that reported by Gilchrist.

TABLE I

THE DETERMINATION OF THE EQUIVALENT WEIGHTS OF POTASSIUM BROMOOSMATE AND POTASSIUM CHLOROOSMATE

Salt used	Detns.	Acid used and its concn., N	Average equiv. wt. by titrn.	Av. diff. between equiv. wt. found and Gilchrist's value, %
K_2OsBr_6	3	0.02–0.05 HBr	752.7	+0.45
K_2OsBr_6	8	0.13–0.25 HBr	749.1	− .03
K_2OsBr_6	2	0.60–0.95 HBr	749.8	+ .07
K_2OsCl_6	4	0.10–0.40 HCl	484.4	+ .39
K_2OsCl_6	8	0.50–0.80 HCl	482.6	+ .02

Average deviation last 10 results with K_2OsBr_6 = 0.10%
Average deviation last 8 results with K_2OsCl_6 = 0.10%
Average atomic weight of osmium by K_2OsBr_6 = 191.5
Average atomic weight of osmium by K_2OsCl_6 = 191.7
Gilchrist's value of atomic weight of osmium = 191.55

Since considerable difficulty due to hydrolysis was experienced when solutions of the osmium salts were heated to remove the last traces of oxygen, several solutions of the bromoosmate were treated in the apparatus shown in Fig. 2, and titrated in the same manner as the dichromate solutions. It was found that the concentration of the hydrobromic acid in the flask during boiling could be as low as 2 N without decomposition of the osmium salt taking place. Six 20.00-cc. portions of bromoosmate ranging in normality from 0.01333 to 0.01335 were titrated with 0.01187 N chromous sulfate and the maximum difference between the titrated value of the normality and that based on the amount of salt in the solution was less than 0.2%.

Summary

Apparatus and procedure are described for storing and handling chromous sulfate solutions, for standardizing these solutions with potassium ferricyanide and potassium dichromate, and for determining the osmium in potassium bromoosmate and potassium chloroosmate by potentiometric titration.

Solutions stored as described remained constant in titer for a month. Standardizations of chromous sulfate by the two methods agreed within 0.1% and the error in the osmium determinations was less than 0.2%.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 27, 1935

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

The Preparation of Potassium Molybdo- and Molybdicyanides[1]

BY HOBART H. WILLARD AND R. C. THIELKE

In attempting to prepare potassium molybdocyanide, $K_4Mo(CN)_8 \cdot 2H_2O$, the methods previously used were found to give very poor yields. This investigation was undertaken to find a more satisfactory method for preparing this compound. The methods of Rosenheim and co-workers,[2] Chilesotti,[3] later used by Bucknall and Wardlaw,[4] were found to be unsatisfactory. The method of Jakob and Turbiewicz[5] was not tried because it seemed to offer difficulties. Sand and Burger[6] reported that ammonium thiocyanate and molybdate when dissolved in dilute hydrochloric acid and reduced electrolytically gave a product which could be extracted by ether and which was precipitated by pyridine from the dry ethereal solution. The oil after separation from ether solidified to a dark solid which melted at 189°. This reaction was modified to prepare potassium molybdocyanide.

---

(1) From a dissertation by R. C. Thielke presented to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

(2) Rosenheim and Koss, *Z. anorg. Chem.*, **49**, 148 (1906); Rosenheim, *ibid.*, **54**, 97 (1907).

(3) Chilesotti, *Gazz. chim. ital.*, **34**, ii, 493 (1904).

(4) Bucknall and Wardlaw, *J. Chem. Soc.*, 2981 (1927).

(5) Jakob and Turbiewicz, *Roczniki Chem.*, **11**, 569 (1931).

(6) Sand and Burger, *Ber.*, **38**, 3384 (1905).