$$E_t = \frac{2RT}{F}\left[(1-A)\ln\frac{m_2}{m_1} + A\ln\frac{1+B\sqrt{m_2}}{1+B\sqrt{m_1}} + \left[\frac{0.8152}{N} + \frac{1.153\,A}{B-N\sqrt{2}}\right]\times \left[\frac{1}{1+N\sqrt{2m_2}} - \frac{1}{1+N\sqrt{2m_1}}\right] + \frac{1.153\,AB}{(B-N\sqrt{2})^2}\left[\ln\frac{1+B\sqrt{m_2}}{1+B\sqrt{m_1}} + \ln\frac{1+N\sqrt{2m_2}}{1+N\sqrt{2m_1}}\right] + 4.6052\,P(m_2-m_1) - \frac{9.2103\,AP}{B^2}\left[B\sqrt{m_2} - B\sqrt{m_1} - \ln\frac{1+B\sqrt{m_2}}{1+B\sqrt{m_1}}\right]\right] \quad (4)$$

than in the case of the amalgam electrodes. Even though errors are rather large in higher dilutions, the constants are sufficiently well defined to render transference numbers accurate beyond the third decimal place as they were formerly expressed.

Summary

1. The electromotive forces of concentration cells of potassium iodide have been measured.
2. The Debye–Hückel constants have been determined for potassium iodide and the activity coefficients have been calculated.
3. Transference numbers have been accurately determined.

Pullman, Washington

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[Contribution from the Chemical Laboratory of Washington University]

Intermediate States of Reduction of Chromic Acid[1]

By T. R. Ball and Keith D. Crane

Weinland and his co-workers[2] have prepared several double salts of pentavalent chromium oxychloride, $CrOCl_3$, with the chlorides of the alkali metals and with the hydrochlorides of organic bases.[3] Olsson[4] has repeated this work and also prepared a double fluoride of CrO_2F with potassium fluoride. A search of the literature has failed to reveal the isolation of any other pentavalent chromium compounds. However, a number of authors have postulated the intermediate formation of penta- and tetravalent chromium in the reduction of chromic acid.[5] This has

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(1) This work was made possible by assistance to the senior author from a grant made by the Rockefeller Foundation to Washington University for research in science.

(2) Weinland, *Ber.*, **37**, 3784 (1905); Weinland and Fiederer, *ibid.*, **39**, 4042 (1906); **40**, 2090 (1907).

(3) Weinland and Beck, "Darstellung anorganischer Präparate," J. C. B. Mohr, Tübingen, 1913, p. 97.

(4) Olsson, *Arkiv. Kemi. Mineral Geol.*, **9**, No. 10, 10 (1924).

(5) Bray, *Z. physik. Chem.*, **54**, 463 (1906); Luther and Rutter, *Z. anorg. Chem.*, **54**, 1 (1907); Jablczyński, *ibid.*, **60**, 38 (1908); Mitchell, *J. Chem. Soc.*, **125**, 564 (1925); Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1931, 2d ed., p. 275.

been done to explain reaction velocities or induction factors. Bohle[6] found that the reduction of chromic acid by ferrous sulfate in the presence of hydriodic acid resulted in the induced liberation of iodine in quantities that could be accounted for by the formation of pentavalent chromium sulfate as an intermediate stage in the reduction. Assuming that the reaction between pentavalent chromium and hydriodic acid is fast, there should be two equivalents of iodine liberated for each mole of ferrous sulfate added, as the following equations show

$$2FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = Fe_2(SO_4)_3 + Cr_2(SO_4)_5 + K_2SO_4 + 7H_2O$$
$$Cr_2(SO_4)_5 + 4HI = Cr_2(SO_4)_3 + 2H_2SO_4 + 2I_2$$

Induction factors approaching 2 were found.

Manchot[7] offers an alternative theory involving the initial oxidation of the iron to the pentavalent state. This would also account for an induction factor of 2 through the following stages

$$2FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = Fe_2(SO_4)_5 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$
$$Fe_2(SO_4)_5 + 4HI = Fe_2(SO_4)_3 + 2H_2SO_4 + 2I_2$$

The data available prior to the present investigation do not prove either of the above mechanisms. It seemed advisable, therefore, to investigate the reduction of chromic acid by ferrous sulfate and other reducing agents by the Allison[8] magneto-optic method. The positions of the minima in this method are a function of the equivalent weights of the cations and are also dependent upon the anion. The method is, therefore, admirably suited to the detection of intermediate stages in chemical reactions. Working in the sulfate series, the minima for $Cr_2(SO_4)_5$ (equiv. wt., 58.42) and for $Fe_2(SO_4)_5$ (equiv. wt., 59.18) should fall between those of $Al_2(SO_4)_3$ and $MgSO_4$ whose minima occur at 9.66 and at 10.04, 10.40 and 10.62, respectively. The last three minima are characteristic of the three isotopes of magnesium as sulfates. At the present stage of development of the method, it is not possible to distinguish between two compounds whose equivalent weights are as close together as those of pentavalent chromium and iron sulfates by the position of the minima unless the compounds could be isolated in the pure state. However, it is possible to distinguish them by depending upon the fact that iron and chromium salts exhibit two and four minima, respectively. In the data which follow, it will be shown that four minima are observed in the range appropriate to pentavalent chromium sulfate and that it is an intermediate in the reduction of chromic acid with four different reducing agents.

Experimental

General Procedure.—All of the chemicals used were of the highest purity available from commercial sources. The water was redistilled from an all glass Pyrex still equipped with two Kjeldahl traps in series.

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(6) Bohle, Thesis for the M.S. degree at Washington University, 1931.

(7) Manchot, *Ann.*, **325**, 165 (1902).

(8) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

Standard ferrous and mercurous sulfates were prepared in 5% sulfuric acid and the stannous chloride in concentrated hydrochloric acid. Oxalic acid was prepared in aqueous solution.

Ten ml. of 0.10 *N* potassium dichromate was added to about 500 ml. of water acidified with sulfuric acid. The reducing agent was added dropwise with constant stirring in such quantities as to leave the dichromate in 10% excess and the solution was examined at once for intermediate oxidation–reduction products. Each reducing agent and the dichromate was tested separately for minima in the critical ranges to be studied and showed no minima in these regions of the scale.

Results.—Table I shows the data obtained using four different reducing agents. The first column shows the reducing agent used and the second the number of independent mixtures which were examined. The total number of minima observed are listed in the third column and their position in the fourth column. Each of the mixtures was observed at various intervals to get information as to the persistence of the intermediate compound. The approximate time of the disappearance of the minima is given in the last column.

TABLE I

POSITIONS OF THE MINIMA OF THE INTERMEDIATE REDUCTION COMPOUNDS OF CHROMIC ACID

Reducing agent	No. of mixtures examined	Total no. of rdgs.	Positions of minima				Persistence of minima
$FeSO_4$	6	121	9.73	9.80	9.86	9.92	46–60 hours
$H_2C_2O_4$	4	256	9.73	9.80	9.86	9.93	21–42 days
Hg_2SO_4	2	212	9.73	9.80	9.86	9.92	10–15 days
$SnCl_2$	3	26	9.73	9.80	9.86	9.91	1.5–4 hours
Total readings		615					

Figure 1 contains a compilation of all the minima observed with all the reducing agents listed in Table I. The scale readings are plotted against the number of times each minimum was observed. The curve is a summation of the individual curves for each reducing agent. The positions of the peaks on the composite curve fall, within the limits of experimental error, at the same points as on the individual curves from which the positions of the minima in Table I are deduced.

A total of 615 minima were observed, 93.4% of which fall within 0.02 scale division (3 mm.) of some peak and 31% fall on a peak. The uniform distribution of the readings on either side of the peaks places the minima at 9.73, 9.80, 9.86 and 9.92. These occur in the range between aluminum and magnesium sulfates and show the presence of some compound of intermediate equivalent weight. Since there are four distinct minima they are attributed to pentavalent chromium sulfate.

Ball and Bohle[9] in a study of the induced reaction between chromic and hydriodic acids, using ferrous sulfate as the inductor, at first postulated

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(9) Ball and Bohle, Washington University Studies, New Ser., *Science and Technology*, No. 6, 82 (1932).

the formation of pentavalent chromium. But in a brief preliminary study by the magneto-optic method only two minima were observed at 9.72 and 9.80. From these data the induced reaction was attributed to pentavalent iron, confirming the hypothesis of Manchot. In the above paper by Ball and Bohle this explanation was given. However, in view of the present more complete investigation, we believe that this conclusion was erroneous, since four minima were observed in the case of all reductants, three of which contained no iron.

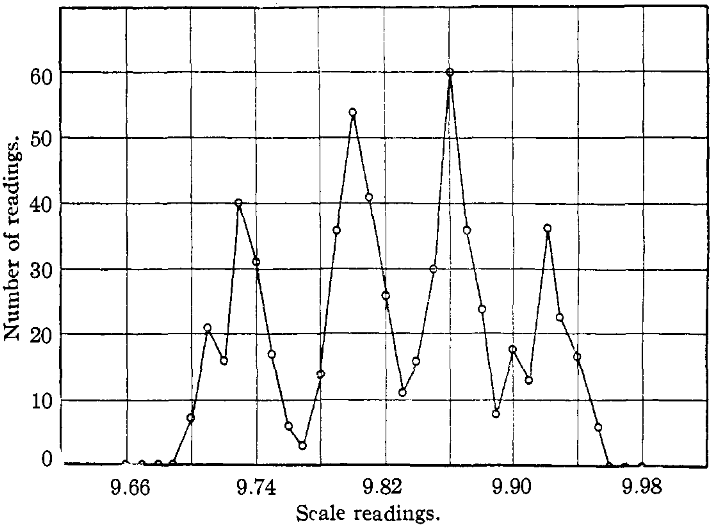

Fig. 1.—Distribution of scale readings.

Discussion

In the solutions, after mixing, there would be present potassium and chromic ions as well as the oxidized form of the metallic ion added as reductant. There would also be present, sulfate, chromate and dichromate ions, and chloride ions in the case of stannous chloride. It might be assumed that the four minima which appeared as a result of the reaction are due to salts formed between some of the above ions. This possibility is precluded by the fact that the minima disappear after some time, indicating an unstable compound. Moreover, we have found that chromic acid gives minima at 6.03 and 6.13, sodium chromate at 7.52, 7.65 and 7.77, and potassium chromate at 8.38 and 8.58. Since the equivalent weight of chromic chromate, $Cr_2(CrO_4)_3$, which is common to all the solutions, is between that of chromic acid and sodium chromate, its minima should fall between 6.13 and 7.52. Chromic sulfate minima occur at 11.15, 11.24, 11.35 and 11.45. These salts are therefore precluded as sources of the four minima observed. Calculations based upon the equivalent weights of the sulfates, chromates and dichromates of all the other positive ions, such as mercuric, stannic and ferric, preclude these from this range.

Mitchell[10] has assumed that an acid, $H_2Cr_2O_6$, containing pentavalent chromium is formed in the reduction of chromic acid by hypophosphorous acid and that it is rapidly reduced by excess of hypophosphorous acid, possibly passing through a tetravalent state. If such an acid is formed, it would have a higher equivalent weight than chromic acid, H_2CrO_4, and its minima would fall below those of the latter acid. Similarly, the minima of its chromic salt would fall below those of chromic chromate which has already been calculated to fall below 7.52 on the scale. Therefore it is concluded that the minima observed at 9.73, 9.80, 9.86 and 9.92 in all solutions, are those of pentavalent chromium sulfate.

It is highly probable that tetravalent chromium may be a step in the reduction, but a search of the scale in its possible range failed to yield any evidence of its presence in any of the solutions. A further study with other reducing agents might yield positive results.

In the case of stannous chloride, eleven minima were observed in the range about midway between those of stannous and stannic chlorides. These were observed when the stannous chloride was in excess of that required for the complete reduction of the chromic acid and were never observed when the chromic acid was in excess. This preliminary indication of trivalent tin will be further investigated.

Summary

1. When chromic acid is partially reduced by ferrous sulfate, mercurous sulfate, stannous chloride and oxalic acid, pentavalent chromium has been found as an intermediate product.

2. No evidence has been found for tetravalent chromium.

3. When stannous chloride is partially oxidized by chromic acid, evidence for the existence of trivalent tin has been obtained. This will be further investigated.

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[10] Mitchell, *J. Chem. Soc.*, **125**, 564 (1925).