2. The solubility product of barium manganate has been calculated on the assumptions that the solubility-product relationship is applicable to moderately dilute solutions of two salts in contact with the solid phases of both and that the two salts, potassium manganate and potassium carbonate, which are of the same ionic type, are ionized to the same extent in solutions containing both of them. The value of the solubility product calculated on these assumptions has been found to be 2.46×10^{-10} when the value 8.1×10^{-9} is used for the solubility product of barium carbonate. The fact that the values for the solubility product thus calculated are actually constant over fairly wide ranges of concentration of the two salts and of the potassium hydroxide present to prevent hydrolysis, and that they are unaffected by substituting sodium for potassium compounds has been taken to lend a considerable degree of plausibility to the assumptions made.

3. The conductivity method for determining the end-point of an acidimetric titration has been applied to extremely dilute solutions. Special precautions necessary under these conditions are pointed out and a convenient apparatus is described.

4. The equilibrium between manganate and permanganate ions has been studied at 25°. The preliminary value for the equilibrium constant,

$$K_{\text{eq.}} = \frac{[\text{MnO}_4^-]^2\,[\text{OH}^-]^4}{[\text{MnO}_4^{--}]^3}$$

has been found to be 16 ± 7.

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[Contribution from the Chemical Laboratory of Ohio State University]

THE THERMAL DECOMPOSITION OF SODIUM BARIUM AND CADMIUM DITHIONATES IN WATER SOLUTION[1]

By Jacob Cornog and W. E. Henderson

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In several places in the literature[2] may be found the statement that solutions of dithionate salts when heated decompose according to the general reaction

$$MS_2O_6 = MSO_4 + SO_2 \tag{1}$$

where *M* is any metal coming above hydrogen in the displacement series. Yet nowhere can be found record of quantitative investigation of the end products of decomposition nor is there any record indicating that solutions of alkali or alkali earth dithionates have thus been decomposed.

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[1] Abstract of a part of a thesis submitted in 1922 to the Graduate School of the Ohio State University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Welter and Gay Lussac, *Ann. chim. phys.*, **10**, 312 (1819). Heeren, *Pogg. Ann.*, **7**, 55, 171 (1826). Klüss, *Ann.*, **246**, 179 (1888).

We have had occasion to study quantitatively the decomposition of solutions of the three salts mentioned in the title, and have recorded observations as follows:

1. Neutral solutions of approximately 1 *N* concentration, even after being boiled several days in flasks provided with reflux condensers, suffered no appreciable decomposition.

2. Approximately complete decomposition follows heating of 1 *N* solutions in sealed tubes at 150–180° during six to eight hours.

3. When an excess of air (oxygen) is present within the sealed tube during the time of decomposition the general reaction is approximately represented by the equation,

$$MS_2O_6 + H_2O + (O) = MSO_4 + H_2SO_4 \qquad (2)$$

but when the substance is decomposed in the presence of an inert gas (nitrogen) the quantities of end products obtained remotely suggest the reaction

$$3MS_2O_6 + 2H_2O = 3MSO_4 + 2H_2SO_4 + S \qquad (3)$$

4. When the solutions in sealed tubes are incompletely decomposed either through working at lower temperatures or for a shorter time, the final products are metallic sulfate, sulfuric acid, sulfur dioxide and free sulfur in variable proportions. Small quantities of metallic sulfite and, in case of cadmium, sulfide were observed.

5. Qualitative observation was made of the fact that increasing concentration and low pressures favor decomposition. Hence, in preparing dithionate salts it is not desirable to concentrate mother solutions by boiling much beyond a concentration of approximately 1 *N* nor to use suction in filtration.

6. The initial presence of sulfur dioxide accelerates decomposition. The initial presence of other final products does not influence decomposition.

The foregoing observations seemingly conflict with results predictable from Equation 1. We believe the following theory of the mechanics of the decomposition of these salts in solution explains the apparent conflict and at the same time affords a fair explanation of observed results.

a. In all cases the primary decomposition results in the formation of metallic sulfate and sulfur dioxide.

b. All other end products result from secondary actions between these primary products, the solvent and the air enclosed within the tube.

c. The chief of these secondary actions is probably

$$3SO_2 + 2H_2O = S + 2H_2SO_4 \qquad (4)$$

This interesting reaction, mentioned by Priestley, has been more recently studied by Bichowsky,[3] who also records the reaction

$$4S + 4H_2O = 3H_2S + H_2SO_4 \qquad (5)$$

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[3] Bichowsky, This Journal, **44**, 116 (1922).

The reaction indicated in Equation 4 has also been studied by Foerster and others.[4] Interaction between the items recorded in Equations 1, 4 and 5 account for the end products observed in our work.

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[CONTRIBUTION FROM THE COLLOID LABORATORY OF THE UNIVERSITY OF WISCONSIN]

FORMATION OF COLLOID SOLUTIONS BY ELECTRICAL PULVERIZATION IN THE HIGH-FREQUENCY ALTERNATING CURRENT ARC

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One of the most general methods for preparing colloid solutions of the metals consists in pulverizing metallic electrodes in an electric arc immersed in a suitable liquid. The method was studied in some detail first for the direct current arc,[1] and subsequently decidedly improved by the substitution of the high-frequency arc for the direct current arc.[2] The use of high-frequency current of the order of magnitude of 10^6 in general not only increases the degree of dispersion in the resulting sol,[3] but also makes it possible to disperse metals into organic liquids with decreased decomposition of the medium.[2] Various sources of high-frequency current, however, have been found to be of unequal merit, and yet it has not been possible to establish the causes for these differences. In previous studies of electrical pulverization, the discharge of a condenser through an oscillatory circuit and across a spark gap immersed in a liquid has been used invariably as the source of the high-frequency current. Under such conditions, as will be shown in this paper, there is superimposed upon the oscillatory condenser discharge across the spark gap the direct or low-frequency current which charges the condenser. In view of the inferiority in many ways of direct and low-frequency current methods for preparing colloids, it seems justifiable to suppose that the elimination of the direct or low-frequency components from the circuit in which colloid formation takes place would be advantageous. Accordingly, a study has been made of the electrical pulverization of metals with the Tesla coil as the source of current. For comparison purposes, parallel studies have been made of circuits in which the direct or low-frequency components were present in the pulverizing circuit. In this paper are presented the results of these

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[4] Foerster, *Z. anorg. Chem.*, **128,** 245 (1923).

[1] Bredig, "Anorganische Fermente," Engelmann, Leipzig, **1901.**

[2] Svedberg, *Nova Acta Reg. Soc. Scient. Upsaliensis,* [4] **2,** No. 1 (1907).

[3] Börjeson, *Dissertation,* Upsala, **1921,** p. 117.