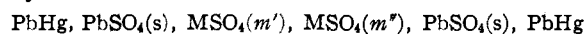


Fig. 2.—Cadmium sulfate: small circles, present data; large circles, data of Redlich and Goldlust, as reported by Jahn.<sup>16</sup>

We have no explanation to offer for the discrepancy. We can, however, point out that the presence of complex-formation, which our results indicate, is strongly supported by the low values of the

activity coefficients. According to Masaki and Ikkatai,<sup>16</sup> Bray,<sup>10</sup> and LaMer and Parks,<sup>12</sup> the activity coefficients of both zinc and cadmium sulfate are about 0.08 in a 0.3 molal solution. This is approximately the concentration above which our results indicate negative cationic transference numbers. It has also been shown by McBain and Van Rysselberghe<sup>17</sup> that the cations in solutions of magnesium, zinc and cadmium sulfates form negatively charged complexes in the presence of excess alkali sulfate. The cationic and the anionic transference numbers must necessarily add up to unity. We have determined the anionic transference number. The cationic transference number can be determined in a quite similar manner, by means of the cell



The use of lead amalgam requires the rigid exclusion of air,<sup>10</sup> and a cell must be used which makes this possible. Such a cell vessel differs from the one used in the present investigation. For this reason, measurements on the above cell have not been included in this work, but it is hoped to make such a report in a future communication from this department.

#### Summary

The transference numbers of zinc and cadmium sulfate have been investigated at 25° by the method of electromotive forces.

WASHINGTON SQUARE COLLEGE  
NEW YORK 3, N. Y.

RECEIVED<sup>18</sup> JULY 14, 1948

(16) Masaki and Ikkatai, *Bull. Chem. Soc. Japan*, **7**, 238-246 (1932).

(17) McBain and Van Rysselberghe, *This Journal*, **52**, 2326 (1930).

(18) Original manuscript received December 18, 1947.

[CONTRIBUTION NO. 57 FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF TENNESSEE]

## The Salts of Perrhenic Acid. II. The Iron Family and Manganese<sup>1</sup>

BY WILLIAM T. SMITH, JR., AND GROVER E. MAXWELL

The perrhenates of cobalt, nickel and manganese have been previously prepared and the colors and compositions of these salts reported.<sup>2,3,4</sup>

This paper deals with a more extensive examination of the composition and properties of the perrhenates of these metals in the divalent state as well as the perrhenates of iron in both di- and tri-valent states.

**Preparation of the Salts.**—The carbonate or hydroxide of the metal was treated with a solution of perrhenic acid<sup>5</sup> and the hydrated salt was

(1) This paper is based on a thesis presented by Grover E. Maxwell to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the M.S. degree, August 4, 1948.

(2) Briscoe, Robinson and Rudge, *J. Chem. Soc.*, 2211 (1931).

(3) Druce, *ibid.*, 966 (1933).

(4) Wilke-Dorfurt and Gunzert, *Z. anorg. allgem. Chem.*, **215**, 369 (1938).

(5) Smith and Long, *This Journal*, **70**, 354 (1948).

crystallized from the solution by evaporation at room temperature. All of these salts are deliquescent at the prevailing humidity in Knoxville during summer and were consequently crystallized by evaporation in a vacuum. In winter the crystallizations take place spontaneously in contact with the ambient air. The preparation of ferrous perrhenate was first attempted in an atmosphere of hydrogen. In spite of the precautions, approximately 10% of the iron present was oxidized to the ferric state, and the perrhenate so obtained suddenly became very viscous and black on evaporation at room temperature in a vacuum. This black semi-solid was very soluble in water giving a brown solution which on repeated evaporation gave the black semi-solid again. This solid was very soluble in ether although tests showed that neither the pure ferrous nor ferric perrhenate was

TABLE I  
 PROPERTIES OF THE PERRHENATES

| Compound   | Color        | Solv.,<br>g./100 g.<br>H <sub>2</sub> O at<br>approx. 27° | F. p.,<br>°C. | Density,<br>g./cc. at<br>approx. 25° | Composition, %          |        |
|--|--------------|---|---------------|--------------------------------------|-------------------------|--------|
|  |              |   |               |                                      | Found                   | Calcd. |
| Co(ReO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>                    | Deep purple  | 299   | 816           | 5.33                                 | Co, 10.54               | 10.53  |
| Co(ReO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O <sup>a</sup> | Pinkish-red  | 462   |               |                                      | H <sub>2</sub> O, 8.65  | 8.79   |
| Co(ReO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O              | Purple-red   | 548 <sup>d</sup>  |               | 3.90                                 | H <sub>2</sub> O, 11.54 | 11.40  |
|  |              |   |               |                                      | ReO <sub>4</sub> , 79.9 | 79.3   |
| Ni(ReO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>                    | Yellow       | 310   |               |                                      |                         |        |
| Ni(ReO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O              | Light green  | 408   |               |                                      | H <sub>2</sub> O, 6.04  | 6.04   |
| Ni(ReO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O <sup>a</sup> | Green        | 567 <sup>d</sup>  |               | 3.95                                 | H <sub>2</sub> O, 11.36 | 11.40  |
|  |              |   |               |                                      | Ni, 9.14                | 9.27   |
|  |              |   |               |                                      | ReO <sub>4</sub> , 80.0 | 79.3   |
| Mn(ReO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>                    | Pink         | 340   | 861           | 5.12                                 | Mn, 9.70                | 9.90   |
|  |              |   |               |                                      | ReO <sub>4</sub> , 90.1 | 90.1   |
| Mn(ReO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O              | Pink         | 464 <sup>d</sup>  |               | 4.32                                 | H <sub>2</sub> O, 6.30  | 6.10   |
| Fe(ReO <sub>4</sub> ) <sub>2</sub>                                 | Dark red     | 233   |               |                                      | Fe, 10.4                | 10.0   |
|  |              |   |               |                                      | ReO <sub>4</sub> , 89.0 | 90.0   |
| Fe(ReO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O              | Orange       | 355 <sup>d</sup>  |               | 3.64                                 | H <sub>2</sub> O, 11.6  | 11.5   |
| Fe(ReO <sub>4</sub> ) <sub>3</sub>                                 | Black        | 270   |               |                                      | Fe, 6.80                | 6.92   |
|  |              |   |               |                                      | ReO <sub>4</sub> , 91.9 | 93.1   |
| Fe(ReO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O              | Black        | 318   |               |                                      | H <sub>2</sub> O, 4.35  | 4.27   |
| Fe(ReO <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O <sup>c</sup> | Light purple | 376 <sup>d</sup>  |               | 4.13                                 | H <sub>2</sub> O, 8.44  | 8.21   |

<sup>a</sup> Briscoe and co-workers<sup>2</sup> reported these compounds and also the pentahydrates of cobalt and nickel perrhenates.

<sup>b</sup> This compound has been previously reported.<sup>3</sup> The trihydrate of manganese perrhenate was also reported by the same investigator but was not found in this investigation. <sup>c</sup> One sample of ferric perrhenate on rapid evaporation yielded a brown hydrate. On dehydration the product was also brown. <sup>d</sup> Solubilities of the lower hydrates and anhydrous salts were calculated from these measurements on the actual equilibrium system.

very soluble in this solvent. The possibility of this product being a covalent complex is being investigated. A more satisfactory method for producing ferrous perrhenate was the reduction of ferric perrhenate in solution with powdered electrolytic iron. The reduction, decantation and crystallization were carried out in a vacuum. On one such preparation of ferrous perrhenate the concentrated solution separated into two immiscible liquid phases. Both phases produced crystals of the same appearance and composition.

The anhydrous salts and lower hydrates were produced by dehydration of the salts which crystallized from water solution.

**Analysis of the Salts.**—The analyses were all duplicated and good checks were obtained. The method used for rhenium was a modification<sup>5</sup> of the method of Willard and Smith.<sup>6</sup> The iron was determined gravimetrically as ferric oxide.<sup>7</sup> The method used in determining cobalt as the pyrophosphate and oxide was one described by Schoeller.<sup>8</sup> The standard dimethylglyoxime method<sup>9</sup> was used for nickel. The pyrophosphate method<sup>10</sup> was used for manganese.

The determination of water in the different hydrates was made by dehydration. Ferrous per-

rhenate tetrahydrate was dehydrated over calcium chloride at room temperature. No inflection points in the dehydration curves were observed. No further significant loss in weight occurred in an oven at 105°. Ferric perrhenate tetrahydrate lost water over calcium chloride at room temperature. There is a decided break in the curve at a loss in weight corresponding to the conversion to the dihydrate. The rate at which water was lost from the dihydrate was approximately one-fiftieth of the rate observed for the tetrahydrate. The dihydrate becomes anhydrous on heating in an oven at 105°. Cobalt perrhenate tetrahydrate on drying over calcium chloride yields the trihydrate. The trihydrate loses water very slowly over fresh calcium chloride and was found to maintain a constant weight over somewhat spent calcium chloride. The anhydrous salt is obtained on heating in an oven at 105°. Although six samples were dehydrated under varying conditions the previously reported pentahydrate<sup>2</sup> was not observed. The tetrahydrate of nickel perrhenate is the most stable of the tetrahydrates of the perrhenates of the iron family. Some samples of this hydrate remained over calcium chloride for several months with only slight visible evidence of efflorescence on the corners of some crystals. This hydrate has been reported to be stable<sup>2</sup> at 100° but it was found in this study that heating to 100° yields the anhydrous salt and heating at 80° to constant weight yields the dihydrate. The pentahydrate which has been previously reported<sup>2</sup> was not found. Manganous perrhenate crystallizes

(6) Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

(7) Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 5th ed., 1939, Vol. I, p. 467.

(8) Schoeller, *Analyst*, **69**, 8 (1944).

(9) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y. 1929 p. 216.

(10) Kolthoff and Sandell, "Textbook of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1938, p. 350.

water solutions as the dihydrate. The dehydration curve for this salt over calcium chloride gave no indication of a lower hydrate. After dehydrating the salt to constant weight over calcium chloride no further loss in weight was observed at 105° in an oven. The results of the analyses are presented in Table I.

**Density Determination.**—The densities of the solid salts were determined by displacement of benzene at 25°. The pycnometer, containing the salt and benzene, was placed in a desiccator and the system evacuated until the benzene boiled for a few minutes. After the removal of dissolved and adherent bubbles of gas in this manner, the temperature of the system was allowed to rise to 25° before weighings were made. The method was checked using salts of known density. Results indicate that the method is good to about 0.5%. The densities for the hydrates which crystallized from water and anhydrous salts which had been fused were determined.

**Solubility Determinations.**—The solubility was determined by evaporation of water from weighed quantities of the saturated solutions. Since all of the salts are very soluble (see Table I) the solubility was determined at only one temperature, approximately 27°. The solubilities of the salts other than those which exist in equilibrium with the saturated solution were calculated from the data on those that do exist in the equilibrium mixture. While the solubilities are all of the same order there is a distinct increase in solubility of the salts in the following order: ferrous, ferric, cobalt, nickel and manganese.

**Freezing Points.**—None of the hydrates listed in Table I are stable at the melting point. In fact, all of them decompose to form anhydrous salts at or below 105°. Three of the anhydrous salts decomposed without melting. The decompositions resulted in the volatilization of the rhenium as heptoxide. Ferrous perrhenate, the least stable, decomposed rapidly in a low bunsen flame. A full bunsen flame was necessary to rapidly decompose ferric perrhenate while nickel perrhenate required an oxygen flame for rapid decomposition. The anhydrous cobalt and manganese perrhenates can be melted, although some decomposition occurs at the temperatures required. Despite the decomposition excellent checks on the freezing points were obtained (see Table I). The decomposition products apparently are insoluble in the molten perrhenates. The method used for determining the freezing points has been previously described.<sup>5</sup> The thermocouple gave standard Chromel-Alumel voltages at the freezing point of sodium chloride, 800.4 = 0.5°.<sup>11</sup>

**Microscopic Examination of Crystals.**—All of the salts which were obtained by primary crystallization either from water solution or from the

fused substance were examined in polarized light with a microscope. These crystals are all anisotropic.

**Magnetic Susceptibility Measurements.**—The unusual colors of the ferrous and ferric perrhenates indicate some different type of structure from that in most salts of iron. Magnetic susceptibility measurements were made in an attempt to throw some light on the structure. The molar magnetic susceptibility of ferric perrhenate in a saturated solution was found to be  $14,000 \times 10^{-6}$  and for the solid tetrahydrate  $15,200 \times 10^{-6}$ . This gives 5.83 and 6.08, respectively, as the magnetic moments. The molar susceptibility for the ferrous perrhenate tetrahydrate was measured as  $11,300 \times 10^{-6}$  which gives a magnetic moment of 5.21. According to Selwood<sup>12</sup> a moment of 4.90 corresponds to four unpaired electrons per molecule and 5.92 to five unpaired electrons. Thus, within the limits of experimental error, the iron appears to be in the states normally found in simple salts. The magnetic susceptibility measurements were made using a modification of the Curie-Cheneveau balance.<sup>13,14</sup> The modification consisted principally in having the magnet stationary and measuring the torsion on a wire necessary to pull a sample of given volume and shape from the field between the poles of the magnet. Solid ferrous ammonium sulfate which has about the same susceptibility as the perrhenates measured was used in standardizing the apparatus.

### Summary

The perrhenates of the iron family and manganese have been prepared and the formulas verified by analysis. The solids which crystallize from solution at room temperature are the tetrahydrates of ferrous, ferric, cobalt and nickel perrhenates and the dihydrate of manganese perrhenate. The dihydrates of nickel and ferric perrhenates and the trihydrate of cobalt perrhenate were also isolated. All of these salts are deliquescent at high summer humidities. All of the hydrates produced anhydrous salts at 105° or below. The densities of those substances obtained by primary crystallization were determined. The solubilities have been measured at room temperature. Freezing points have been obtained for the salts which could be melted under atmospheric pressure. Microscopic examinations of all primary crystals revealed they are optically anisotropic. The unusual colors of the perrhenates of iron are indicative of complex formation, although magnetic susceptibility measurements indicate that if complex linkages do exist in these compounds they have an ionic rather than a covalent nature.

KNOXVILLE, TENN.

RECEIVED AUGUST 20, 1948

(12) Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 144.

(13) Selwood, *ibid.*, p. 10.

(14) Cheneveau, *Phil. Mag.*, **20**, 357 (1910).

(11) Roberts, *Phys. Rev.*, **23**, 386 (1924).