[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

# X-Ray Studies of the System Nickel–Oxygen–Water. II. Compounds Containing Trivalent Nickel[1]

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## Introduction

The chemistry of the oxides of nickel and their hydrates has been a controversial subject for a great many years. A number of higher oxides of nickel have been reported, but there has followed positive proof that such oxides do not exist. Wöhler and Balz,[2] Baubigny,[3] Rose,[4] Glaser,[5] Moissan,[6] Vaubel,[7] Lunde,[8] and Clark, Asbury and Wick[9] have reported preparations of oxides such as $Ni_3O_4$, $Ni_2O_3$ and $NiO_2$. For the most part the compounds were analyzed for their nickel content alone and the oxygen content determined on this basis. The general methods of preparation in use involved the dry heating of nickel compounds such as the hydroxide, oxide, nitrate, chloride or basic carbonate in air or oxygen, at temperatures of 200 to 500°. Subsequent work by Leblanc and Sachse[10] has shown the above work to be erroneous. The latter made preparations of the black oxide of nickel according to the above methods, and analyzed the products completely, for nickel, active oxygen and water. In all cases, the active oxygen content was very low, corresponding to less than 10% of $Ni_2O_3$. The errors in the previous results were due to the fact that the water contents were not taken into account. Leblanc and Sachse therefore assumed that the black oxide of nickel, as prepared in the above ways, was not a homogeneous higher oxide of nickel, but was a system of nickelous oxide, active oxygen and water, containing less than ten per cent. of higher oxides. x-Ray diagrams of their products showed only the diffraction lines for NiO. Their work was substantiated by Hendricks, Jefferson and Schultz[11] who were unable to obtain anything but nickelous oxide with traces of active oxygen, by any of the above methods.

It appears quite clear that anhydrous higher oxides of nickel do not exist. However, there remains for consideration another class of nickel compounds containing active oxygen, prepared by quite different methods. These compounds have been previously referred to as higher oxides or oxide-hydrates. The general method of preparation has been oxidation

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[1] From a thesis submitted by Robert W. Cairns in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wöhler and Balz, *Z. Elektrochem.*, **27**, 406 (1921).

[3] Baubigny, *Compt. rend.*. **87**, 1082 (1878); **141**, 1232 (1905).

[4] Rose, *Pogg. Ann.*, **84**, 571 (1851).

[5] Glaser, *Z. anorg. Chem.*, **36**, 1 (1903).

[6] Moissan, *Ann. chim. phys.*, [5] **21**, 239 (1880).

[7] Vaubel, *Chem. Z.*, **46**, 978 (1922).

[8] Lunde, *Z. anorg. allgem. Chem.*. **163**, 352 (1927).

[9] Clark, Asbury and Wick, THIS JOURNAL, **47**, 2661 (1925).

[10] Leblanc and Sachse, *Z. Elektrochem.*, **32**, 59 and 204 (1926).

[11] Hendricks, Jefferson and Schultz, *Z. Kryst.*, **73**, 376 (1930).

of nickel salt solutions by basic solutions of oxidizing agents such as bromine, chlorine and persulfates. Belluci and Clavari[12] made a series of preparations, using different oxidizing agents and various temperatures of preparation. The products were analyzed for active oxygen and nickel. They computed the Ni:O ratios from the data and found the values to range from 1:1.3 to 1:1.9, the oxidation taking place to the greatest extent at a temperature of precipitation of 0°. They obtained no definite evidence of the existence of an intermediate oxidation product such as $Ni_2O_3$, and therefore assumed the products to be mixtures of NiO and $NiO_2$. No attempt was made to determine the water content of the products, or to find whether this was bound or simply adsorbed. Clark and co-workers[9] reported the preparation of $NiO_2 \cdot xH_2O$ by the same method, and found the product to be amorphous, giving no x-ray diffraction pattern. Howell[13] studied the decomposition of the precipitates formed when basic solutions of chlorine were added to nickel sulfate solutions. The products were instable in suspension at 100°, losing active oxygen fairly rapidly. Howell determined the Ni:O ratios in the manner described above. Initial values for this ratio reached 1:1.65, and approached 1:1 for precipitates decomposed at 100°. There was a rapid initial loss of about 25% of the active oxygen, followed by a more gradual loss of the remainder. He interpreted the results to indicate that two higher oxides were present, $NiO_2$, which was very instable and accounted for the rapid initial loss of active oxygen, and $Ni_2O_3$, which lost active oxygen much less rapidly. He made no mention of the possibility that the products might contain bound water.

Hüttig and Peter[14] studied the system nickelic oxide–water. Products prepared by the method of Belluci and by oxidation of suspended nickelous hydroxide had compositions expressible as $Ni_2O_3 \cdot 3\text{–}4H_2O$. The Ni:O ratios were exactly 1:1.5, but the water contents varied with conditions of drying. By the isobaric decomposition of the products at temperatures of 100 to 140° and a total pressure of about 10 mm. they believed to have found evidence for the existence of a monohydrate of $Ni_2O_3$. They also found that the composition of the product obtained by heating the above preparations in water at 200° was approximately $Ni_2O_3 \cdot H_2O$. x-Ray diagrams of the first two products and of the product of the water heating were obtained. No correspondence between any of the patterns was noticeable. They assumed the latter pattern to be characteristic of the monohydrate of $Ni_2O_3$, but did not succeed in placing any interpretation on the x-ray results on the original products, other than to suggest that a trihydrate might exist. No evidence of such a compound was indicated in the isobaric decomposition experiments. They found the water con-

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(12) Belluci and Clavari, *Gazz. chim. ital.*, **36**, 58 (1906); **37**, 409 (1907).

(13) Howell, *J. Chem. Soc.*, **123**, 669 and 1772 (1923).

(14) Hüttig and Peter, *Z. anorg. allgem. Chem.*, **189**, 190 (1930).

tents of the products to be completely reversible at temperatures below 138°, at which temperature the composition of the residue became $Ni_2O_3 \cdot H_2O$. At temperatures above this irreversible decomposition took place according to the equation

$$2(Ni_2O_3 \cdot H_2O) \longrightarrow 4NiO + 2H_2O + O_2$$

Leblanc and R. Müller[15] published a thesis which we received after completion of our work in which they study the system of higher nickel oxides and water. Their attempted x-ray study was unsuccessful, due to experimental reasons. They were able to obtain preparations giving a Ni:O ratio as high as 1.75. The isothermic decomposition gave no evidence of any definite oxides or hydrates in strong contrast to the findings of Hüttig and Peter.[15] It is also our conviction that the results of the latter authors were accidental.

## Experimental Part

**Chemical Analyses.**—Nickel was determined electrolytically. Samples were dissolved in very dilute sulfuric acid to avoid loss in spray caused by rapid evolution of oxygen. After electrolysis solutions were tested with hydrogen sulfide to assure that all nickel was recovered.

Active oxygen was determined by a modified Bunsen method, using an apparatus described by Gooch.[16] Samples were dissolved in dilute hydrochloric acid. The chlorine evolved was swept into potassium iodide solution with carbon dioxide, while the acid solution was gently boiled. The free iodine was titrated with thiosulfate.

Water and carbon dioxide were determined by heating the samples in a quartz tube in an electric furnace at about 1000°. The vapors were swept into absorption tubes by a stream of purified nitrogen. The carbon dioxide contents were approximately 0.5% for all materials analyzed in this work.

**x-Ray Analyses.**— The method was identical with the one in our previous article.[17] The powder pictures thus obtained were measured with a millimeter rule. Since diffraction lines in all cases were rather broad it was not feasible to use a micro-comparator. The x-ray data recorded in the report include the linear distances between corresponding lines on each side of the film, and the estimated relative intensities of the diffraction lines.

**Preparation of Samples.**—A. A solution of 55 g. of potassium hydroxide and 12 cc. of bromine in 500 cc. of water was added dropwise to a solution of 100 g. of $Ni(NO_3)_2 \cdot 6H_2O$ in 1500 cc. of water, with rapid stirring. Precipitation was carried out in absence of carbon dioxide as described in the preceding article.[17] The temperature of precipitation was 25°. The precipitate was washed five times by decantation, then filtered and washed thoroughly on the filter, as described in the preparation of nickelous hydroxide. The product was dried over concentrated sulfuric acid for a few days and then over 1:1 sulfuric acid for two weeks. The final analysis corresponded to the composition $Ni_2O_3 \cdot 3.19H_2O$ ($Ni_2O_3$ 73.5%, $H_2O$ 25.7%, $CO_2$ 0.5%). This preparation was designated as product A.

The product A was dried more thoroughly at various temperatures: (1) in a vacuum desiccator over calcium chloride, at about 1 mm. pressure, (2) in an electric oven in air,

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(15) R. Müller, Dissertation, Leipzig, 1931.

(16) Gooch. "Representative Procedures in Quantitative Analysis," John Wiley and Sons, Inc., New York, 1916, p. 187.

(17) Cairns and Ott, This Journal, **55**, 527 (1933).

and (3) in a metal tube under 10 atmospheres of oxygen, with phosphorus pentoxide present to absorb water. Analyses of products are given in the following table.

| Method of drying | Temp., °C. | Time of drying | % $Ni_2O_3$ | % $H_2O$ | % NiO by diff. | $NiO_2O_3:H_2O$ mol. ratio |
|---|---|---|---|---|---|---|
| (1) | 25 | 3 days | 80.8 | 17.3 | 1.9 | 1:1.97 |
| (2) | 130 | 24 hours | 41.3 | 9.7 | 49.0 | 1:2.16 |
| (3) | 320 | 20 hours | 30.7 | 8.8 | 60.5 | 1:2.65 |

The x-ray diagrams of product A and of the product dried by method (1) were identical. Data are given in Table I, 1, and Fig. 1A. The products dried by methods (2) and (3) gave only lines for NiO (see Table I, 4, and Fig. 1B) the decomposition probably destroying the crystallinity of the undecomposed portion. No other foreign diffraction lines were observed.

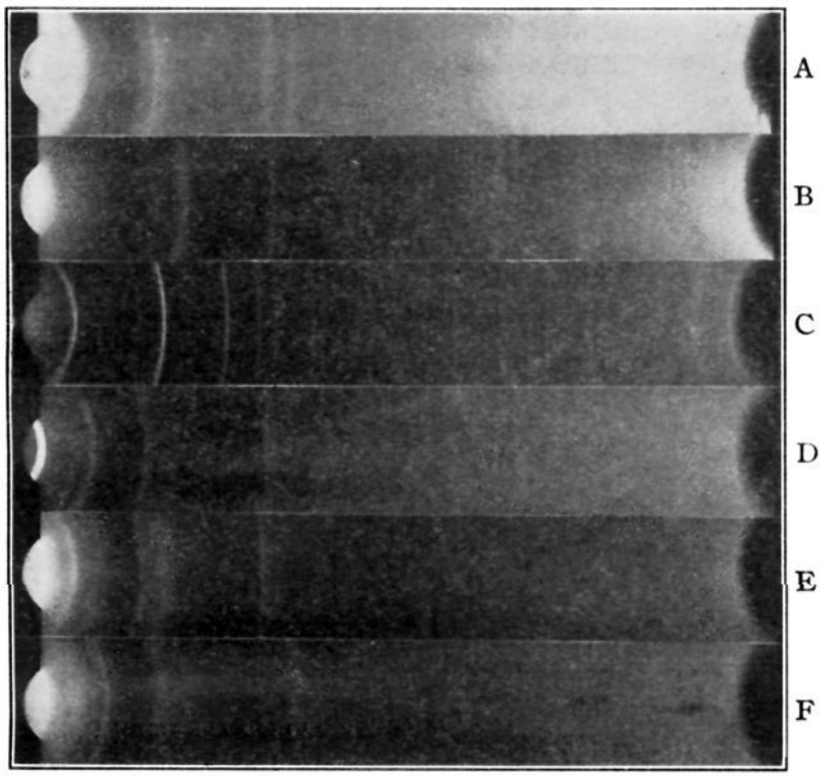

Fig. 1.—A, $Ni_2O_3 \cdot 2H_2O$ (A); B, NiO by decomp. of $Ni_2O_3 \cdot 2H_2O$ in air at 120°; C, $Ni(OH)_2$, obtained by decomposition of $Ni_2O_3 \cdot 2H_2O$ in water at 150°; D, preparation $E_1$ ($Ni_3O_4 \cdot xH_2O$); E, preparation $E_2$ ($Ni_6O_7 \cdot xH_2O$); F, preparation F ($Ni_2O_3 \cdot H_2O$).

It was quite evident that removal of water alone above a content of two mols per $Ni_2O_3$ would not affect the x-ray diffraction, and that beyond this point the decomposition took place with loss in active oxygen. This strongly indicated that the original product was $Ni_2O_3 \cdot 2H_2O$, with some adsorbed water.

B. A solution of 20 g. of potassium hydroxide in 250 cc. of water was added dropwise to 50 g. of $Ni(NO_3)_2 \cdot 6H_2O$ in 250 cc. of water at 25°. A solution of 6 g. of potassium hydroxide and 6 cc. of bromine in 500 cc. water was then added to the suspended nickelous hydroxide. The reaction mixture was allowed to stand for five hours with intermittent stirring, before decantation was started. Purification was carried out as in A. The product was dried in an oil-pump vacuum over calcium chloride for three days. The x-ray diagram of the product was identical with that of product A (see Table I, 2). The Ni/O ratio in this case was 1/1.38, compared with the theoretical value of 1/1.5 for a hydrate of $Ni_2O_3$.

TABLE I

X-RAY DIFFRACTION DATA

1. Preparations A, C and D Dried *in vacuo*

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 18 | m, br | $Ni_2O_3 \cdot 2H_2O$ |
| 24 | s, br | $Ni_2O_3 \cdot 2H_2O$ |
| 31 | s, br | $Ni_2O_3 \cdot 2H_2O$ |
| 39 | vs, br | $Ni_2O_3 \cdot 2H_2O$ |
| 68 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 74 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 121 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 132 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 143 | vw | $Ni_2O_3 \cdot 2H_2O$ |
| 155 | vw | $Ni_2O_3 \cdot 2H_2O$ |

2. Preparation B Dried *in vacuo*

| $l$ in mm. | Intensity | Compound |
|---|---|---|
| 25 | s, br | $Ni_2O_3 \cdot 2H_2O$ |
| 31 | s, br | $Ni_2O_3 \cdot 2H_2O$ |
| 39 | vs, br | $Ni_2O_3 \cdot 2H_2O$ |
| 68 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 74 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 122 | m | $Ni_2O_3 \cdot 2H_2O$ |
| 133 | m | $Ni_2O_3 \cdot 2H_2O$ |

3. Preparation A Heated in Water at 150°

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 39.0 | vs | $Ni(OH)_2$ |
| 66.6 | ms | $Ni(OH)_2$ |
| 72 | vvw | NiO |
| 77.4 | vs | $Ni(OH)_2$ |
| 87 | vw | NiO |
| 104.3 | ms | $Ni(OH)_2$ |
| 118.2 | ms | $Ni(OH)_2$ |
| 125.3 | mw | $Ni(OH)_2$ |
| 127 | vw | NiO |
| 138.8 | vw | $Ni(OH)_2$ |
| 140.7 | mw | $Ni(OH)_2$ |
| 145.4 | mw | $Ni(OH)_2$ |
| 165.1 | mw | $Ni(OH)_2$ |

4. Preparation A Dried in Air at 130°C.

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 73 | m | NiO |
| 86 | s | NiO |
| 125 | s | NiO |
| 149 | mw, br | NiO |
| 157 | mw, br | NiO |
| 219 | mw, br | NiO |

5. Preparation C Dried in Air at 110° C.

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 37 | s | $Ni_2O_3 \cdot 2H_2O$ |
| 68 | wm | $Ni_2O_3 \cdot 2H_2O$ |
| 74 | s | $Ni_2O_3 \cdot 2H_2O$, and NiO |
| 85 | s, br | NiO |
| 121 | mw | $Ni_2O_3 \cdot 2H_2O$ |
| 123 | m | NiO |
| 132 | mw | $Ni_2O_3 \cdot 2H_2O$ |

6. Preparation $E_1$ Dried *in vacuo*

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 21.2 | s | $Ni_3O_4 \cdot xH_2O$ |
| 23.0 | vs | $Ni_3O_4 \cdot xH_2O$ |
| 45.1 | s | $Ni_3O_4 \cdot xH_2O$ |
| 67.8 | m | $Ni_3O_4 \cdot xH_2O$ |
| 69.2 | m | $Ni_3O_4 \cdot xH_2O$ |
| 76.7 | mw | $Ni_3O_4 \cdot xH_2O$ |
| 90.5 | w | $Ni_3O_4 \cdot xH_2O$ |
| 120.2 | ms | $Ni_3O_4 \cdot xH_2O$ |
| 122.7 | ms | $Ni_3O_4 \cdot xH_2O$ |
| 129.8 | mw | $Ni_3O_4 \cdot xH_2O$ |
| 141.6 | w | $Ni_3O_4 \cdot xH_2O$ |
| 200 | vw | $Ni_3O_4 \cdot xH_2O$ |
| 242 | vw | $Ni_3O_4 \cdot xH_2O$ |

7. Preparation $E_2$ Prepared from $E_1$ at 110°C.

| $l$ in mm. | Intensity | Compd. |
|---|---|---|
| 25.0 | vs | $Ni_6O_7 \cdot xH_2O$ |
| 37.8 | ms | $Ni_6O_7 \cdot xH_2O$ |
| 48.7 | w | $Ni_6O_7 \cdot xH_2O$ |
| 66.9 | s | $Ni_6O_7 \cdot xH_2O$ |
| 76.0 | m | $Ni_6O_7 \cdot xH_2O$ |
| 118.5 | s | $Ni_6O_7 \cdot xH_2O$ |
| 121.8 | vw | $Ni_6O_7 \cdot xH_2O$ |
| 125.2 | vw | $Ni_6O_7 \cdot xH_2O$ |
| 139.3 | vw | $Ni_6O_7 \cdot xH_2O$ |
| 145 | vw | $Ni_6O_7 \cdot xH_2O$ |
| 196 | vw | $Ni_6O_7 \cdot xH_2O$ |
| 235 | vw | $Ni_6O_7 \cdot xH_2O$ |

$l$ = linear distance between corresponding lines on each side of film. The following abbreviations are used to indicate relative intensities: s, strong; m, medium; w, weak; v, very; br, broad. The substances to which the various reflections were assigned appear in the columns headed "compd."

It was evident that oxidation of the suspended $Ni(OH)_2$ took place quite slowly, as another preparation with only a half-hour oxidation period resulted in a product of incomplete oxidation and showed only the diffraction of $Ni(OH)_2$. Precipitation and oxidation of $Ni(OH)_2$ at 100° produced a partially oxidized mixture showing the strongest diffraction lines of product A and $Ni(OH)_2$. Longer oxidation periods would doubtless have resulted in complete oxidation. The ultimate oxidation product was the same as by the method A, which was quite clearly revealed by the x-ray diffraction data.

C and D. These preparations were identical with A, except that the nitrate solutions were kept at 50 and 75°, respectively, during precipitation. The products were dried *in vacuo* for three days. The x-ray diffraction patterns in both cases were identical with A. The only effect of higher temperatures of precipitation was to cause incomplete oxidation. If the unoxidized portion of product C was assumed to be $Ni(OH)_2$ the composition of the product was expressible as $0.25Ni(OH)_2 \cdot Ni_2O_3 \cdot 1.91H_2O$. With such a relatively small amount of $Ni(OH)_2$ present (*ca.* 10%) no diffraction effects of this compound were observed.

The product C was heated in air (water vapor pressure *ca.* 10 mm.) at 110° for periods of two, five and twenty hours. x-Ray diffraction patterns of the products (see Table I, 5) showed lines corresponding to the diffraction of NiO, increasing in intensity as the time of heating was increased. The original pattern became much weaker. Analysis of the residue after twenty hours showed the material to contain 45.5% NiO, 40.5% $Ni_2O_3$, 13% $H_2O$ and 0.5% $CO_2$. The $Ni_2O_3 : H_2O$ ratio was 1 : 2.9, somewhat higher than would be expected if the initial product was assumed to be $Ni_2O_3 \cdot 2H_2O$. However, about 10% of $Ni(OH)_2$ was evidently present in the initial product C. and as this would not lose water at the temperature of heating,[18] some of the water in the heated product must have been bound to divalent nickel (calculated as NiO).

The products A, B and C decomposed to $Ni(OH)_2$ when heated in Pyrex bomb tubes with water at temperatures of 130 to 150° for sufficiently long periods of time (several days). The end-products after three days heating at 150° showed very well defined diffraction patterns of $Ni(OH)_2$. (See Table I, 3, and Fig. 1C.) A few of the strongest diffraction lines of NiO appeared with very weak intensity. This might be expected since the material in the center of the particles would be in poor contact with water and tend to decompose as in the dry way. A portion of product A was partially decomposed in water at 128°, over a period of twelve hours. The analysis of the product was 34.0% NiO, 48% $Ni_2O_3$, 17.1% $H_2O$ and 0.8% $CO_2$ showing the $Ni_2O_3 : H_2O$ ratio to be 1 : 1.7 on the assumption that all the divalent nickel was present as $Ni(OH)_2$. Since a small percentage of NiO always formed in such decompositions, this assumption was not strictly correct. Hence the $Ni_2O_3 : H_2O$ ratio would fall closer to 1 : 2, if all the water bound to trivalent nickel was taken into account. Such a value would be in agreement with decomposition according to the equation

$$Ni_2O_3 \cdot 2H_2O \longrightarrow 2Ni(OH)_2 + O$$

$E_1$. This preparation was identical with A, except that the nitrate solution was kept at 100° during precipitation. The product was purified in the usual manner, and dried *in vacuo* over calcium chloride for three days. The product was quite incompletely oxidized, the composition being 62.3% $Ni_2O_3$, 17.8% NiO, 19.9% $H_2O$, 0.5% $CO_2$ or $Ni_3O_{4.14} \cdot 3.34\ H_2O$. The x-ray diagram of the product was completely different from that of product A (see Table I, 6, and Fig. 1D). No lines of $Ni(OH)_2$ were visible. The product $E_1$ decomposed almost completely to $Ni(OH)_2$ when heated in water for three days at 150°. The end-product showed a very clear diffraction pattern of $Ni(OH)_2$, and very weak NiO lines (see Table II, 1).

$E_2$. Product $E_1$ was heated for four hours at 110° in air. The x-ray diagram of

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[18] Hüttig and Peter, *Z. anorg. allgem. Chem.*, **189**, 183 (1930).

the product was completely different from that of A or $E_1$ (see Table I, 7, and Fig. 1E). No lines of NiO or $Ni(OH)_2$ were visible. The composition of the product was 31.4% $Ni_2O_3$, 51.7% NiO, 16.3% $H_2O$, 0.4% $CO_2$ or $Ni_6O_{7.06}\cdot 5.01H_2O$. Further heating at 110° for twenty hours caused no further change in the diffraction pattern. The product was heated for one day at 140° in air. The end-product gave a diffraction pattern showing the principal lines of NiO and a weakened pattern of the original product $E_2$. Product $E_2$ also decomposed to $Ni(OH)_2$ when heated in water at 150° for three days (see Table II, 2). The pattern of the end-product was identical with that of the end-product of the water-decomposition of $E_1$.

TABLE II

1. Preparation $E_1$ Heated in Water at 150°

| *l* in mm. | Intensity | Compd. |
|---|---|---|
| 38.6 | vs | $Ni(OH)_2$ |
| 66.9 | s | $Ni(OH)_2$ |
| 72 | w | NiO |
| 76.9 | vs | $Ni(OH)_2$ |
| 87 | mw | NiO |
| 103.8 | ms | $Ni(OH)_2$ |
| 117.5 | ms | $Ni(OH)_2$ |
| 124.8 | ms | $Ni(OH)_2$ |
| 138.2 | w | $Ni(OH)_2$ |
| 140.2 | m | $Ni(OH)_2$ |
| 144.9 | m | $Ni(OH)_2$ |
| 164.3 | m | $Ni(OH)_2$ |

2. Preparation $E_2$ Heated in Water at 150°

| *l* in mm. | Intensity | Compd. |
|---|---|---|
| 39.2 | vs | $Ni(OH)_2$ |
| 66.5 | ms | $Ni(OH)_2$ |
| 73 | mw | NiO |
| 77.6 | vs | $Ni(OH)_2$ |
| 88 | ms | NiO |
| 104.5 | ms | $Ni(OH)_2$ |
| 118.1 | m | $Ni(OH)_2$ |
| 125.2 | m | $Ni(OH)_2$ |
| 127.3 | mw | NiO |
| 138.3 | w | $Ni(OH)_2$ |
| 141.1 | m | $Ni(OH)_2$ |
| 145.4 | m | $Ni(OH)_2$ |
| 165.1 | mw | $Ni(OH)_2$ |

3. Preparation F Dried *in vacuo*

| *l* in mm. | Intensity | Compd. |
|---|---|---|
| 25.7 | vs | $Ni_2O_3\cdot H_2O$ |
| 51.5 | s | $Ni_2O_3\cdot H_2O$ |
| 68 | vw, br | $Ni_2O_3\cdot H_2O$ |
| 73.5 | m | $Ni_2O_3\cdot H_2O$ |
| 76 | mw, br | $Ni_2O_3\cdot H_2O$ |
| 85 | vw | $Ni_2O_3\cdot H_2O$ |
| 122 | vw, br | $Ni_2O_3\cdot H_2O$ |
| 131.5 | m | $Ni_2O_3\cdot H_2O$ |
| 134.7 | mw | $Ni_2O_3\cdot H_2O$ |
| 144 | vw | $Ni_2O_3\cdot H_2O$ |
| 156 | vw | $Ni_2O_3\cdot H_2O$ |
| 225 | vw | $Ni_2O_3\cdot H_2O$ |

4. Preparation F Heated in Air at 120°

| *l* in mm. | Intensity | Compd. |
|---|---|---|
| 25 | s, br | $Ni_2O_3\cdot H_2O$ |
| 51 | w, br | $Ni_2O_3\cdot H_2O$ |
| 69 | vw, br | $Ni_2O_3\cdot H_2O$ |
| 74 | ms, br | $Ni_2O_3\cdot H_2O$ and NiO |
| 87 | m, br | NiO |
| 124 | mw, br | NiO |
| 132 | m, br | $Ni_2O_3\cdot H_2O$ |

Preparation F Heated in Water (Steel Bomb) at 150°

| *l* in mm. | Intensity | Compd. |
|---|---|---|
| 39.2 | w | $Ni(OH)_2$ |
| 66.6 | vvw | $Ni(OH)_2$ |
| 73 | s | NiO |
| 77.5 | w | $Ni(OH)_2$ |
| 87 | vs | NiO |
| 104.5 | vw | $Ni(OH)_2$ |
| 118.4 | vvw | $Ni(OH)_2$ |
| 124 | s | NiO |
| 141 | vvw | $Ni(OH)_2$ |
| 145 | vvw | $Ni(OH)_2$ |
| 150 | m | NiO |

F. Since it appeared that $E_1$ was a compound containing both di- and trivalent nickel, and not a mixture of compounds, it was important to know the effects of further oxidation. $E_1$ was prepared as described above. After precipitation the suspended product was divided into two equal portions. One was purified and dried in air. The x-ray diffraction of this product was identical with that of $E_1$, and the composition of the product was 54.1% $Ni_2O_3$, 19.8% NiO, 23.8% $H_2O$, 1.9% $CO_2$ or $Ni_3O_{4.07}\cdot 4.31H_2O$. The other half of the precipitate was further oxidized at 25° by addition of a solution containing 20 g. of potassium hydroxide and 5 cc. of bromine in 250 cc. of water. The product was allowed to stand for an hour and then decanted ten times, filtered, washed and dried *in vacuo*. It was quite noticeable that this precipitate settled more rapidly than the previous preparations. In most cases peptization occurred on the third decantation, and a large percentage of the product was lost during decantation. In this preparation peptization did not occur to any great extent until the eighth decantation, indicating that the excess base was more strongly adsorbed by the product than in the previous cases. The x-ray diffraction pattern of this product, F, was entirely different from any of the foregoing (see Table II, 3, and Fig. 1F). The product had the composition $Ni_2O_{3.10}\cdot 1.57H_2O$. The product was heated for ten hours at 110°. The partially decomposed product contained 77.6% $Ni_2O_3$, 12.3% NiO, 8.5% $H_2O$ and the $Ni_2O_3 : H_2O$ ratio of the undecomposed material was 1 : 1.01. Faint indications of NiO lines appeared on the diffraction diagram of the heated product, along with the weakened lines of the original pattern. Further heating at 120° for five hours produced a mixture the diffraction pattern of which clearly showed the principal lines of NiO (see Table II, 4). These results indicated that the product F was essentially the monohydrate of $Ni_2O_3$, and decomposed according to the equation

$$2(Ni_2O_3\cdot H_2O) \longrightarrow 4NiO + 2H_2O + O_2$$

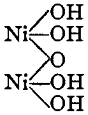
The product F was heated at 150° for three days in a Pyrex bomb tube. The x-ray diagram of the product showed NiO lines and also some new lines which must have been caused by the presence of a nickel silicate, since analysis showed that the end-product contained about 20% of silica. The decomposition in water was repeated in a steel bomb, and the product gave strong diffraction lines of NiO along with very weak $Ni(OH)_2$ lines. Comparison with the diffraction pattern of a known mixture of 20% $Ni(OH)_2$ and 80% NiO formed by decomposition of $Ni_2O_3\cdot 2H_2O$ at 160° in air showed that the amount of $Ni(OH)_2$ present in the end-product was less than 20%. Thus it appeared that the primary decomposition product of $Ni_2O_3\cdot H_2O$ in both air and water was NiO. The small amount of $Ni(OH)_2$ that formed during the decomposition in water was apparently due to impurities in the original product F.

## Discussion

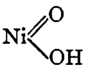
Due to their fine state of subdivision the compounds prepared in this work contained quite variable amounts of water. However, the analyses of the partially decomposed products, obtained by heating in air, coupled with the results of the x-ray diffraction experiments, were successful in establishing for the first time the existence of compounds having the compositions $Ni_2O_3\cdot 2H_2O$ and $Ni_2O_3\cdot H_2O$. Although such compounds have been previously termed "hydrates," there is considerable evidence to indicate that they do not possess the properties of true hydrates. Since the compound $Ni_2O_3\cdot H_2O$ was prepared in water at a temperature at which $Ni_2O_3\cdot 2H_2O$ was stable, and since there was no indication of formation of the latter compound after the monohydrate had stood in water for two weeks during the purification process, it was evident that the transition $Ni_2O_3 \cdot H_2O + H_2O \longrightarrow Ni_2O_3 \cdot 2H_2O$ did not take place. Furthermore, the reverse change did not take place when the dihydrate was decomposed by heat, but instead a complete decomposition took place

$$2(Ni_2O_3 \cdot 2H_2O) \longrightarrow 4NiO + 4H_2O + O_2$$

The fact that the dihydrate could be prepared by oxidation of $Ni(OH)_2$, and decomposed to that compound on heating in water, was not consistent with the assumption that the compound was a true hydrate. It has been impossible to prepare $Ni_2O_3$ by dehydration of such compounds, since the loss in water is always accompanied by a loss in active oxygen. There is no reason to believe that the removal of water of crystallization would affect the oxygen linkage. On the other hand, the assumption that the compounds $Ni_2O_3 \cdot 2H_2O$ and $Ni_2O_3 \cdot H_2O$ have the following structures was in complete accord with the experimental observation


I

or $Ni_2O_3 \cdot 2H_2O$


II

or $^1/_2\ Ni_2O_3 \cdot H_2O$

The decomposition of product F into NiO in water and air alike was strongly indicative of a structure of type II. It was previously shown[17] that the transition $NiO + H_2O \longrightarrow Ni(OH)_2$ would not take place under the conditions of the above experiments, and that $Ni(OH)_2$ was stable in water at the temperatures employed.[18] Hence any NiO or $Ni(OH)_2$ formed in the above decompositions must have been primary decomposition products. It would be expected that $Ni(OH)_2$ could be formed directly from a compound of type I, but not from one of type II, and this expectation was borne out by the results of the decomposition of the mono- and dihydrates in water. Hence the above structures were satisfactory from this standpoint.

Hofmann and Hiendlmaier[19] reported a compound which had the composition $KNiO_2$, by fusion of nickel powder with potassium peroxide. This was possibly a salt of the compound II. Hydrolysis took place in water, and the hydrolyzed product gave the analysis $Ni_2O_3 \cdot 2H_2O$, but part of this water might well have been adsorbed. The acidic nature of the product F was indicated by its relatively slow rate of peptization, indicating a strong retention of base, as would be the case if a weak salt were formed.

It was apparent that the method of isobaric decomposition employed by Hüttig and Peter[14] in establishing the existence of the monohydrate was not

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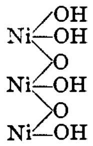
(19) Hofmann and Hiendlmaier, *Ber.*, **39**, 3184 (1906).

conclusive, for the decomposition of the dihydrate has been shown to be irreversible. Their initial preparation consisted of the dihydrate, and in view of the present work it is improbable that they obtained the monohydrate by decomposition of this product. Furthermore, they found no evidence for the existence of the dihydrate, which they should have obtained had the method been reliable. Also the later work of LeBlanc and Müller[15] supports this conclusion very strongly.

The present results are not in accord with those of Hüttig and Peter in two other important respects. They found that no active oxygen was lost when a compound corresponding to the dihydrate was heated for several hours in water at temperatures of 120 and 200°. The product formed in the latter case was assumed to be the monohydrate of $Ni_2O_3$. In the present work it was found that the decomposition in water at 130 to 150° took place directly to nickelous hydroxide. The heating times were much longer than in the case of the previous work, but there was no evidence of intermediate compounds formed in the decomposition. Also the x-ray diagram of the "monohydrate" obtained by them in this way did not correspond to the pattern of that compound obtained in this work.

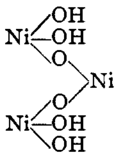
The identity of the diffraction patterns of products A and B left no doubt as to the fact that the oxidized product was the same in each case, *i. e.*, whether by simultaneous oxidation and precipitation, or by oxidation of previously precipitated nickelous hydroxide. Hüttig and Peter obtained differing diffraction patterns for preparations similar to the above, and this might have been due to incomplete oxidation of the nickelous hydroxide, since the oxidation of the suspended material was found to take place quite slowly.

Little could be said as to the exact nature of the preparations $E_1$ and $E_2$ other than that it was evident that they were compounds containing both di- and trivalent nickel and not mixtures of a trivalent oxide-hydrate and NiO or $Ni(OH)_2$. If $E_1$ had been such a mixture, further oxidation would only have oxidized the divalent compounds present and left the trivalent compound unchanged. Thus the properties of the product would have changed very little due to such an oxidation. However, the results were quite different from this. The oxidized product F not only gave a different diffraction pattern, but also behaved completely differently on decomposition in water and air. Hence the original product $E_1$ must have been completely changed by the oxidation, and this would only be the case if it were a *compound* of di- and trivalent nickel. The chemical analyses indicated that the compositions of $E_1$ and $E_2$ could be expressed as hydrates of the hypothetical oxides $Ni_3O_4$ and $Ni_6O_7$, but their properties indicated that the water was bound in the compounds as hydroxyl groups. The following were the simplest structures which could be devised



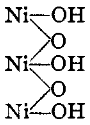
IIIa

or $Ni_3O_4{\cdot}2H_2O$
Mono nickelous (basic)
salt of I



IIIb

Mono nickelous salt of
ortho nickelic acid



IV

or $^1/_2Ni_6O_7{\cdot}3H_2O$
Di-nickelous (basic) salt of
ortho nickelic acid

It is obvious that such compounds might hydrolyze to nickelous hydroxide, as was observed when $E_1$ and $E_2$ were heated in water. The water contents of compounds of types III and IV are somewhat below the observed contents of $E_1$ and $E_2$, but this does not exclude the possibility that these are the correct structures, for considerable amounts of water are frequently adsorbed by such precipitates, as shown in the previous discussion. We favor formula IIIa over IIIb since IV may be obtained from it without rearrangement. (This transition takes place upon heating of compound III.)

## Summary

1. The existence of compounds having the compositions $Ni_2O_3{\cdot}H_2O$ and $Ni_2O_3{\cdot}2H_2O$ has been shown. Characteristic x-ray diffraction patterns of these compounds have been obtained.

2. The modes of decomposition of these "hydrates" in water and air at temperatures of 100 to 150° have been established with the aid of x-ray analysis. The results indicated that the compounds were not true hydrates, but contained the water bound as hydroxyl groups. Structural formulas have been assigned.

3. Two compounds of nickel, oxygen and water, at lower stages of oxidation than the above, have been isolated, and their diffraction patterns obtained. Chemical analyses indicated that they were hydrates of the hypothetical oxides $Ni_3O_4$ and $Ni_6O_7$, but their behavior on decomposition showed them to be of a type analogous to the above compounds. Reasonable structural formulas have been proposed.

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