[CONTRIBUTION FROM THE MAGNETIC PIGMENT CO., TRENTON, N. J., DIVISION OF COLUMBIAN CARBON CO.]

The Oxidation of Certain Metallic Hydroxides by a Current of Air

BY PETER FIREMAN

Having had considerable experience in the use of a current of air industrially, for the oxidation of precipitated ferrous hydroxide,[1] it has occurred to the writer as desirable to undertake a systematic exploration of the possibilities of this procedure in lines of purely scientific interest.

I. Oxidation of Cobaltous Hydroxide

The general procedure was the passage of a lively current of air through freshly precipitated cobaltous hydroxide. To produce the latter a 0.1 *M* solution of cobaltous chloride and a 1.2 *M* solution of sodium hydroxide were used. The reaction was carried out in a half-liter flask provided with a funnel tube and an outlet tube connected with a filter suction pump which drew the air through the apparatus.

Oxidation of Cobaltous Hydroxide at Room Temperature.—One experiment with an 18% excess of sodium hydroxide after a two and a half hour operation gave a dark brown product. Washed and air dried it contained 2.64% of active oxygen. On drying to a constant weight, in the end at 260–270°, it lost 19.93% of water. An analysis of the product now gave 6.55% of active oxygen, an amount approximating that contained by pure cobaltosic oxide, Co_3O_4, namely, 6.64%. The percentage of active oxygen based on the original weight of the undried product is then 0.8007×6.55. The original product, therefore, picked up during the drying 5.24 minus 2.64 or 2.60% of active oxygen. It follows that the actual loss of water was greater by this amount, or $19.93 + 2.60 = 22.53\%$ of the original product. Recalculating the percentage of active oxygen in the original product to a dry basis, such for instance as might have been obtained by drying the original product in the absence of oxygen, gives 3.41% of active oxygen, an amount close to that represented by Co_6O_7 (calcd. 3.44%).

In another experiment the excess of sodium hydroxide was about 1%. The product after a four-hour passage of a current of air was gray brown. Analysis of the air-dried hydrous oxide gave 2.85% of active oxygen. Dried at 260–270° it lost all its water, 18.62%. The anhydrous oxide contained 6.63% of active oxygen (calcd. 6.64% for Co_3O_4). By a like computation as in the preceding experiment the actual water lost in the drying amounted to 21.17% and the active oxygen contained in the original product was 3.62% (calcd. 3.44% for Co_6O_7).

The method of analysis for active oxygen used was boiling with an excess of sodium oxalate in dilute sulfuric acid and titrating the remaining excess with 0.1 *N* potassium permanganate solution.

Five more experiments were carried out with variations in the excess of sodium hydroxide between 2 and 35%, and in the duration of the experiments between two and four hours. The air-dried products were either gray brown or dark brown and contained 1.67, 1.86, 2.08, 1.21, 1.38% of active oxygen. The anhydrous oxides which were obtained after heating at 250 to 290° contained 6.50, 6.67, 6.70, 6.60 and 6.76% of active oxygen; they all showed a composition close to that of Co_3O_4 (calcd., 6.64%), that of cobaltosic oxide.

It appeared of interest to learn something about the course of the absorption of the oxygen during the drying. Samples from the air-dried products of earlier experiments were heated eight hours at 98–99° and thereupon found to contain 7.61 and 6.90% of active oxygen after having lost 9.97 and 13.45% of water. Corrected for the 10.29 and 11.06% of water still remaining in the samples the actual oxygen content was 8.48 and 7.76%. The examination of another air-dried sample heated for six hours at 106–107° showed that it contained 8.52% of active oxygen.

Up to 100° and a little higher the oxygen absorption increases gradually without there appearing any tendency to remain constant at any point.

The experiments described show that the oxidation in the mother liquor at room temperature does not proceed far, but that it continues to a considerable extent when the product, washed and air dried, is heated in the air to remove its copious water content. Indeed, the taking up of oxygen proceeds beyond the stage of Co_3O_4 which it already passes at 100°, proceeds until a reversal sets in with a loss of oxygen and ends with a return to Co_3O_4, now anhydrous.

Oxidation of Cobaltous Hydroxide at a Boiling Temperature.—With the application of heat the reaction proceeds to a considerably higher degree of oxidation in the mother liquor. The first two experiments of this group, no. 9 with an 18% excess and no. 10 with a 2% excess of sodium hydroxide, gave products which, air dried, upon filtering and washing, contained 7.78 and 6.32% of active oxygen, respectively. The two oxides lost 12.49 and 3.52% of water requiring 248–250° to come to a constant weight. Anhydrous, the dried products of the two experiments contained 6.81 and 6.55% of active oxygen (calcd. 6.64% for Co_3O_4). If we recalculate the oxygen content of the air-dried product of no. 9 on an anhydrous basis, it amounts to 8.89%. We see here again a tendency to form cobaltosic oxide at temperatures

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(1) P. Fireman, *Ind. Eng. Chem.*, **17**, 603 (1925).

required for the removal of the water content by a loss of oxygen if need be.

Three more experiments were made at a boiling heat: nos. 16 and 17 with a 20% excess and no. 18 with a 9% excess of sodium hydroxide. The air-dried products contained 8.02, 7.70 and 6.39% of active oxygen, respectively. Their drying was finished at 265–275° with the following water losses: 12.26, 11.04 and 3.85%. With the water removed, or allowed for in the last, their respective active oxygen contents were 6.78, 6.72 and 6.64% (calcd. for Co_3O_4 6.64%).

It may be pointed out that the air-dried products from nos. 10 and 18 were almost straight-out cobaltosic oxide with 6.55 and 6.64% of active oxygen and with only 3.52 and 3.85% of water. In these experiments the smallest excess of sodium hydroxide was used.

II. Oxidation of Manganous Hydroxide

The procedure in the oxidation of manganous hydroxide was the same as in that of cobaltous hydroxide. A 0.06 or 0.12 *M* solution of manganous chloride was precipitated with somewhat varying amounts of a solution of sodium hydroxide either in the cold or at a boiling temperature. The experiments carried out with the application of heat gave such definite clean-cut results that they will be described first.

Oxidation of Manganous Hydroxide at a Boiling Temperature.—An experiment with 3–4% of sodium hydroxide in excess, after a one and a half hour operation, gave 6.92% of active oxygen; another with a 1% in excess after a seventy minutes operation gave 6.93% of active oxygen. An experiment with 3–4% of manganous chloride in excess, after a two-hour run, gave 6.95% active oxygen; another with 18% in excess, after a one and a fourth hours run, gave 6.98%. Pure manganosic oxide contains 6.99% of active oxygen.

These products, air dried, contained the following amounts of moisture, respectively: 1.03, 0.82, 0.94, 1.12%.

The experiments just described establish definitely that the passing of a current of air through manganous hydroxide at a boiling temperature produces manganosic oxide, Mn_3O_4, which contains 6.99% of active oxygen: a moderate excess of either manganous chloride or sodium hydroxide is immaterial.

An indication that a well-defined manganosic oxide may be produced by the oxidation of manganous hydroxide with oxygen or air at a boiling temperature we find in a paper by A. R. Nichols and J. H. Walton,[2] who identified their product by an X-ray diffraction pattern. Their apparatus and procedure (*in vacuo*) are not suited for a practical process of preparation.

Oxidation of Manganous Hydroxide at Room Temperature.—About the experiments of this group we may be brief. In all of them there has been a tendency to end with a slight excess of oxygen[3] over the amount of 6.99% contained by pure manganosic oxide, Mn_3O_4. The largest amounts obtained were 7.38 and 7.40%, both in experiments with an excess of 18% of manganous chloride. In all the other cases the amounts of active oxygen were: 7.33, 7.06, 7.14, 7.23, 7.06, 7.10%. Within the limits indicated, variations of the proportions of the reacting substances are of no marked influence. Nor did the differences in the duration of the experiments seem to affect the results. In all cases the water contents of the air-dried products did not exceed 2% and was at times as low as 0.60 or 0.71%.

Discussion

It may be worth while to mention that solid manganosic oxide absorbs oxygen when heated in the air. The increases in active oxygen ranged between 3.65 and 7.51% when heated gradually up to about 200°.

Another interesting observation may be added. After a number of nine to ten hour heating periods, when the oxygen increments were about finished, fluctuations in weight set in. The decrements amounted in some instances to, say 1.9 mg. in a ten hour heating period in a sample weighing 0.3586 g. It suggested itself that the fluctuations may be due to variations in atmospheric pressure after a sort of state of saturation has been reached.

Summary

Cobaltous Hydroxide.—1. While the oxidation of cobaltous hydroxide at room temperature by a current of air does not proceed very far in the mother liquor, the air-dried product absorbs considerably more oxygen if heated in air. At a temperature between 250–290° the product becomes anhydrous cobaltosic oxide, Co_3O_4.

2. When heated the air-dried product absorbs more oxygen from the air. After having been kept several hours at 100° it takes up more oxygen than corresponds to Co_3O_4. At higher temperatures it absorbs still more oxygen until it becomes anhydrous when it loses all oxygen in excess of that required by the formula Co_3O_4.

3. At a boiling heat the oxidation in the mother liquor proceeds much further than at room temperature. The air-dried product contains more oxygen than corresponds to Co_3O_4 if made with an excess of sodium hydroxide of the order of 18 to 20%, and just to an amount of oxygen corresponding to Co_3O_4 when the excess is only a few per cent. The excess of oxygen over that contained by cobaltosic oxide is very nearly all driven off by the time all the water is expelled.

Manganous Hydroxide.—1. The oxidation of manganous hydroxide freshly precipitated by

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(2) Nichols and Walton, THIS JOURNAL, **64**, 1866 (1942).

(3) A. Gorgeu, *Compt. rend.*, **84**, 177 (1877).

sodium hydroxide by a current of air at a boiling temperature is a clean-cut method of preparing manganosic oxide.

2. Oxidation at room temperature invariably leaves in the product an excess of oxygen amounting to a fraction of 1%.

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Mechanism of the Precipitation of Alumina from Sodium Aluminate Solutions

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In several processes for the production of alumina, alumina trihydrate is precipitated by treating sodium aluminate solution with carbon dioxide. The present paper describes an investigation of the *p*H of sodium aluminate solutions during precipitation of alumina and the determination of the mechanism of precipitation at 60°.

Theory

Alumina in sodium aluminate solutions is believed to occur as $NaAlO_2$.[1] The form precipitated from these solutions in the present work was found by X-ray analysis to be gibbsite, $Al_2O_3 \cdot 3H_2O$; this finding is in agreement with the observations of Laubengayer and Weisz.[2] The precipitation reaction therefore may be postulated as

$$2AlO_2^- + 2H_3O^+ \longrightarrow Al_2O_3 \cdot 3H_2O \qquad (1)$$

This reaction is represented by the rate equation

$$-\mathrm{d}C_{AlO_2^-}/\mathrm{d}t = k'C^2_{AlO_2^-}C^2_{H_3O^+} \qquad (2)$$

where $C_{AlO_2^-}$ represents the concentration of aluminate ion in moles per liter, and t the time in hours. The velocity of the reverse reaction is negligible, since the solubility of gibbsite is small and is practically constant in the *p*H range of this investigation. At constant *p*H equation (2) would reduce to

$$-\mathrm{d}C_{AlO_2^-}/\mathrm{d}t = kC^2_{AlO_2^-} \qquad (3)$$

which is the simplest form of the differential equation for a bimolecular reaction. Integration yields

$$1/C_{AlO_2^-} = kt + \text{const.} \qquad (4)$$

from which it is apparent that a plot of $1/C_{AlO_2^-}$ *versus* t at constant *p*H should be a straight line.

The concentration of aluminate ion in moles per liter cannot be calculated exactly from the concentration of alumina found by analysis of the solution, because the analytically determined value represents the sum of the gibbsite, with which the solution may or may not be supersaturated, plus the aluminate ion. It is possible, however, to calculate the change in concentration of aluminate ion from the carbon dioxide consumption, because the carbon dioxide added is directly responsible for the conversion of aluminate ion to gibbsite. Let A represent the number of moles per liter of aluminate ion initially present in the solution, x the number of moles per liter of carbon dioxide reacting with the aluminate ion, and y the number of moles per liter of carbon dioxide reacting with the carbonate ion to form bicarbonate ion. If the equation for the formation of carbonic acid

$$CO_2 + 3H_2O = 2H_3O^+ + CO_3^{=} \qquad (5)$$

is added to equation (1), the equation

$$\begin{matrix} 2AlO_2^- & + & 3H_2O & + & CO_2 & = & Al_2O_3 \cdot 3H_2O & + & CO_3^{=} \\ (A - 2x) & & & & x & & x & & (x - y) \end{matrix} \qquad (6)$$

is obtained for the carbon dioxide used to precipitate the alumina. For the carbon dioxide used in converting carbonate to bicarbonate, the equilibrium equation may be written

$$\begin{matrix} CO_3^{=} & + & CO_2 & + & H_2O & = & 2HCO_3^- \\ (x - y) & & y & & & & 2y \end{matrix} \qquad (7)$$

If the carbon dioxide consumed in converting carbonate to bicarbonate is applied as a correction to the total carbon dioxide consumed, the remainder should represent the amount required for conversion of aluminate ion to gibbsite. The sum, $x + y$, represents the total number of moles per liter of carbon dioxide added to the solution.

For the second ionization of carbonic acid the equations are:

$$HCO_3^- + H_2O = CO_3^{=} + H_3O^+ \qquad (8)$$

$$K_2 = \frac{(CO_3^{=})(H_3O^+)}{(HCO_3^-)(H_2O)} = \frac{C_{CO_3^=}f_{CO_3^=}(H_3O^+)}{C_{HCO_3^-}f_{HCO_3^-}(H_2O)} \qquad (9)$$

where f is the stoichiometric ionic molar activity coefficient. Substitution of the equalities

$$C_{CO_3^=} = x - y \qquad (10)$$

$$C_{HCO_3^-} = 2y \qquad (11)$$

into equation (9) yields the equation

$$K_2 = \frac{(x - y)f_{CO_3^=}(H_3O^+)}{2yf_{HCO_3^-}(H_2O)} \qquad (12)$$

By extrapolation of the values of Harned and Scholes[3] for lower temperatures, K_2 at 60° was estimated to be 7.35×10^{-11}. Activity coefficients, f, for carbonate and bicarbonate ions were

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(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green & Co., London, 1929, p. 285.

(2) A. W. Laubengayer and R. S. Weisz, THIS JOURNAL, **65**, 247–249 (1943).

(3) H. S. Harned and S. R. Scholes, *ibid.*, **63**, 1706–1709 (1941).