

ART. LVIII.—*The Qualitative Separation of Chromium from Iron and Aluminium*; by R. B. RIGGS.†

THE separation of chromium from iron and aluminium depends on the conversion of chromium compounds, by oxidation, into soluble chromates. This oxidation is generally effected, either by fusing the hydroxide or basic acetate precipitates with sodium carbonate and potassium nitrate, or by dissolving them in concentrated nitric acid to which potassium chlorate has been added. In the hands of the general student the latter is probably the more satisfactory of the two methods. It is somewhat complicated however, involving, as it does, the separation of the aluminium by means of potassium hydroxide, solution of the residue in a potassium chlorate-nitric acid solution, and a reprecipitation of the iron.

In many cases the efficiency of hydrogen peroxide, in alkaline solutions, as an oxidizing agent, is well known. Its use in converting chromium hydroxide into the chromate was a natural suggestion. A few experiments showed that, under favoring conditions, this change is easily and completely brought about. Solutions, containing the equivalent of 0.05 grm. of chromium as hydroxide, 0.3 grm. of sodium hydroxide and quantities of hydrogen peroxide (15 per cent) varying from 5 to 20<sup>cc.</sup>, varying in volume from 50 to 500<sup>cc.</sup>, were digested

\* *Ib.*, pp. 397 and 368.

† Since writing this note my attention has been called to an article by Clark (*Jour. Chem. Soc.*, 1893, i, 1079), on "The use of Sodium peroxide as an Analytical agent." He makes very successful use of this reagent in decomposing ferro chromium ores, and says that it may be used for the qualitative separation of chromium from iron and manganese, in alkaline solutions, when it acts quickly even in the cold. As compared with hydrogen peroxide, sodium peroxide is the more powerful oxidant, and if the former has any advantage, it is to be found in convenience and, possibly, economy.

until oxidation seemed\* complete. This required from five to fifteen minutes: the more dilute the solution the longer the operation. 5<sup>cc.</sup> of the peroxide was sufficient for the oxidation.

The availability of hydrogen peroxide, as an oxidizing agent, having been determined, the influence of its presence on the iron and the effect of dilution, on the solubility of aluminium hydroxide in sodium hydroxide solutions, remained to be ascertained. Filtrates from ferric hydroxide, which had been digested in sodium hydroxide solutions containing hydrogen peroxide, gave no sign of the presence of iron except to the sulphocyanide test, showing the influence to be rather favorable than otherwise.

In determining the effect of dilution on the solubility of alumina, quantities of the hydroxide, equivalent to 0.05 grm. of the element, were severally treated with 0.5 grm. of sodium hydroxide in solutions varying in volume from 50 to 500<sup>cc.</sup> In every case solution was effected within five minutes. The influence of dilution was however appreciable.

Experiments, made, to test the practical workings of the method, on mixtures of the three substances, confirmed the observations made in connection with their separate treatments, except that the presence of large quantities of iron hinders somewhat both the oxidation of the chromium and the solution of the aluminium. As to the limits of the method the impurities, of even the best of available reagents, render the detection of very small amounts of either iron or alumina uncertain. In mixtures, containing the equivalents of 0.2 m.grm. each of iron and chromium, and 0.5 m.grm. of aluminium, separations were made and the several constituents

\* In a majority of the experiments, in the more concentrated solutions, the precipitates disappeared quickly and completely. Where it was necessary to continue the heating for more than ten minutes, there remained an unoxidizable residual which increased rather than diminished on further heating. In all cases prolonged digestion resulted in a precipitation of what proved to be silica. The amount of this precipitate was found to be proportionate to the quantity of peroxide added and the following experiments showed that it came from the corrosive action of an alkaline solution of the peroxide on the glass. 50<sup>cc.</sup> of water, containing 1 grm. of sodium hydroxide, digested for an hour in glass, remained clear to the end. 50<sup>cc.</sup> of hydrogen peroxide, similarly heated, remained clear, evaporating quietly. 50<sup>cc.</sup> of the peroxide, containing 0.5 grm. of sodium hydroxide, was also similarly digested (the alkaline solution effervesces energetically on being heated). In fifteen minutes the solution had become perceptibly clouded. At the end of an hour, the effervescence having ceased, a considerable precipitate had formed. From 200<sup>cc.</sup> of the peroxide, containing 2 grm. of sodium hydroxide, 4 m.grm. of silica (carrying a trace of iron) were obtained. 500<sup>cc.</sup> of the peroxide, containing 5 grm. of sodium hydroxide, heated in platinum for an hour, remained perfectly clear.

The reagents used were Rosengarten's 15 per cent hydrogen peroxide, 500<sup>cc.</sup> of which gave, on evaporation, a residue of 0.2908 grm. (silica 0.1067 grm., alumina 0.02 grm.,) and sodium hydroxide made from sodium.

were identified beyond a doubt. With half the above quantities the results were not so satisfactory. The color tests for both iron and chromium are sufficiently delicate to detect even smaller amounts. The sulphocyanide test will, under favorable conditions [a solution containing not over  $\frac{1}{10}$  per cent of hydrochloric acid and an excess of sulphocyanide ( $5^{\text{c.cs.}}$  1:15)], show the presence of 0.01 m.grm. of iron in  $100^{\text{c.cs.}}$  of water (depth of liquid in cylinder  $14^{\text{cm}}$ ). The yellow color of sodium chromate is unmistakable in  $100^{\text{c.cs.}}$  of solution containing the equivalent of 0.2 m.grm. of the element.

*Summary.*—The following is an outline of the method of treatment. Given a mixture of the hydroxide or basic acetate precipitates equivalent to 0.1 grm. of each of the three elements. Digest this precipitate in  $100^{\text{c.cs.*}}$  of water, to which  $10^{\text{c.cs.}}$  of hydrogen peroxide and 1 grm. of sodium (or potassium) hydroxide have been added, until effervescence ceases.† Separate the iron by filtration. Acidify the filtrate slightly with acetic acid and precipitate the alumina by means of ammonia. (Where small quantities are present long continued boiling and a concentration of the solution may be necessary.) Filter off the alumina and test the filtrate for chromium. The yellow color of either the iron or alumina filtrates is characteristic. A confirmatory and more delicate test may be made by acidifying the filtrate from alumina slightly and adding a few c.cs. of hydrogen peroxide, obtaining the blue color so characteristic of chromium compounds thus treated.

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