rate that about four minutes is required in running in the 22 cc. necessary; the rate is best regulated by attaching a suitable capillary tip to the buret containing the barium chloride solution. Evaporate the whole to dryness on the steam-bath (this may be done immediately after precipitation), take up with hot water, filter through paper, wash until the washings are free from chloride, ignite very carefully (so as to obviate reduction) and heat to constant weight over a Bunsen burner. The necessary correction is determined by a concurrent calibration of the method; that is, by dissolving an equivalent weighed amount of pure dry sodium (or potassium) sulfate in a medium such that the resulting solution is as nearly as may be of the same composition as the solution to be analyzed; the sulfate in this comparison solution is then determined precisely as above. The difference between the calculated amount of barium sulfate and that actually found is the correction to be applied to the weight of the precipitate obtained in the actual analysis.

This procedure, as compared with that advocated by Allen and Johnston, is easier and much more rapid; it is however not so generally applicable, but may be used whenever the composition of the solution containing the sulfate to be determined is known approximately; and, we believe, will yield results, accurate to ±0.05 per cent. of the total sulfate present, in most cases likely to occur in general analytical work.

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ARTIFICIAL CRYSTALLIZATION OF BARIUM SULFATE.[1]

BY H. C. COOPER AND T. S. FULLER; with Crystallographic Study by A. A. KLEIN.

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Barium sulfate has a conspicuous place in the literature of the artificial production of crystals, because it has been crystallized by several different methods. The largest crystals, some as long as 2 mm., were obtained by Manross[2] in Wöhler's laboratory, as a result of chemical change in the molten condition, *viz.*, by fusing potassium sulfate with an excess of barium chloride and lixiviating the cooled mass. De Schulten[3] obtained crystals by chemical change in aqueous solution, *viz.*, by very slow precipitation. Senarmont[4] got a similar result by heating barium sulfate with hydrochloric acid in a sealed tube at 250° for 60 hours. This has been considered (by Fock[5]) as a solution method, but it seems more likely that we have here to do with a reversible chemical reaction. Ad-

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[1] Presented at the December, 1910 (Minneapolis) meeting of the American Chemical Society, see *Science*, 33, 345.

[2] *Ann.*, 82, 349.

[3] *Bull. soc. franc. min.*, 26, 103; *Chem. Zentr.*, 1903, II, 845.

[4] *Ann. chim. phys.*, [3] 32, 155.

[5] Fock-Pope, "Introd. to Chem. Crystallography," Oxford, 1895, p. 77.

ditional work on the artificial crystallization of barium sulfate is referred to in Gmelin-Kraut's "Handbuch der Anorganischen Chemie."[1]

We have obtained barium sulfate crystals by crystallization from molten solvents, namely, from barium chloride and from sodium sulfate. This method is probably more nearly physical than any of those already described. Ten grams of barium chloride were fused in a platinum crucible and 8 grams of barium sulfate added. The last three grams were added in gram portions and the eighth gram was found to dissolve very slowly with stirring at 1150°, the maximum temperature of the nickel-alloy resistance furnace. When solution was complete the furnace was enclosed and allowed to cool undisturbed for three hours. After leaching the mass with water for twelve hours, by placing it in a beaker into which water was slowly and continuously run, characteristic barite crystals were obtained, some as long as 5 mm. and as wide as 1 mm. These crystals showed a faint trace of chloride when tested by fusion with sodium sulfate, solution in water and addition of nitric acid and silver nitrate. Probably the barium sulfate takes up a minute amount of barium chloride to form mixed crystals.

Again, 9 g. of barium sulfate were stirred into 10 g. of anhydrous sodium sulfate at 1130°, one-gram portions being added at a time. Eight grams dissolved clear, but the ninth caused some opacity. However, after cooling and leaching, crystals were obtained very similar to those from barium chloride and of the same average size. After several hours' washing with a continuous flow of distilled water the crystals gave a faint flame test for sodium, so that the sodium sulfate, like the barium chloride, probably dissolves slightly in the barium sulfate crystals.

The dimensions of the $BaSO_4$ crystals from Na_2SO_4 averaged about the same as those of the $BaSO_4$ crystals from barium chloride.

Microscopic optical-crystallographic determinations of these crystals, as well as of those out of barium chloride, were made by Mr. A. A. Klein, Assistant in the Mineralogical Laboratory of the University of Michigan. Mr. Klein's report is appended.

The length of the crystals appeared to be limited mainly by the size of the crucible, the longest crystals corresponding to the radius of the crucible. Accordingly, we attempted to produce larger crystals by fusing 428 grams of barium sulfate with 535 grams of sodium sulfate at 1070° in a 500 cc. nickel crucible in an injector gas furnace, but the results were unsatisfactory, probably on account of too rapid cooling. We are confident that in a well-shielded resistance furnace of sufficient size, barite crystals as large as those in nature could be prepared. A nickel crucible is unsatisfactory, however, being disintegrated, apparently by reaction with the melt.

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[1] II, 2, p. 41 (1909).

Le Chatelier[1] has stated that the curve representing the melting points of mixtures of sodium sulfate with increasing proportions of barium sulfate consists of three parts, the first corresponding with the formation of isomorphous crystals containing the two constituents in varying proportions, the second to the formation of a double sulfate and the third to the recrystallization of the added sulfate itself. An experiment in which we dissolved barium sulfate in sodium sulfate to about a 10 per cent. solution yielded crystals which, after washing, were examined spectroscopically and found to be practically free from sodium. This does not harmonize with the Le Chatelier observations and a new thermal analysis of the system $BaSO_4$-Na_2SO_4 appears to be desirable.

Crystallographic Study by A. A. Klein.

The material examined was received from Professor H. C. Cooper and labeled (*a*) barium sulfate, recrystallized from $BaCl_2$, and (*b*) barium sulfate, recrystallized from Na_2SO_4. It consisted of some isolated crystals mounted on two slides in Canada balsam, and of fragments and loose crystals.

Under the microscope the crystals are long, tabular and colorless, with frequent indications of parallel growth. They show parallel extinction, which, with the characteristic outline, establishes the crystallization as orthorhombic. Excellent cleavage was observed parallel to the long direction of the crystals. The indices of refraction were determined by the Schroeder van der Kolk method and were found to be very close to that of monobromonaphthalene ($n = 1.648$), inasmuch as a red tint is observed on the side toward the darkened portion of the field, whereas a blue color is noted on the opposit side. This is an exceedingly close approximation to the values of the indices of refraction given by Groth[2] for the D line of the spectrum, $\alpha = 1.6369$, $\beta = 1.6381$, $\gamma = 1.6491$. In convergent light a distinct positive, biaxial interference figure is frequently observed.

The above observations agree fully with those given by Groth for natural barium sulfate, namely, the mineral barite.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE TRANSITION TEMPERATURES OF SODIUM CHROMATE AS CONVENIENT FIXED POINTS IN THERMOMETRY.

BY THEODORE WILLIAM RICHARDS AND GEORGE LESLIE KELLEY.

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Introduction.

In previous papers[3] from this laboratory it has been shown that the

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[1] *Compt. rend.*, 123, 746 (1896).

[2] Groth's "Chemische Krystallographie," 1908, II, 388–389.

[3] T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898); Richards and Churchill, Proc.