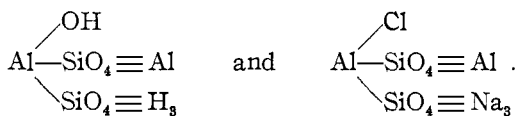


to synthesize by substitutions on kaolin, the sodium-chlorine derivative which is not known. Its relation to kaolin is shown by the formulas:



#### SUMMARY.

A method of fractional analysis has been devised and carried out on four minerals, both with and without previous ignition, in which the material abstracted and the residue left have been studied. This has given some data as to the structure. As a large number of minerals comes to be subjected to this treatment, and as the range of reagents possible to be used is widened, it promises to be a valuable aid in determining constitution.

The work on substitutions has shown that the metals are readily substituted, one for the other, even under the simplest conditions of heating in an open crucible. A type of formula accounting for the retention of chlorine, has been developed for chabazite, stilbite and thomsonite.

Incidentally, the surprising solubility of silica in fused barium chloride and of alumina under certain conditions has been noted and demonstrated.

I wish here to express my heartiest appreciation of the facilities provided, and to acknowledge my great obligation to Professor Clarke for his kindly interest and many invaluable suggestions during the progress of the work.

GEORGE WASHINGTON UNIVERSITY, 1905.

## FERRICYANIDES OF MERCURY.

BY GUSTAVE FERNEKES.

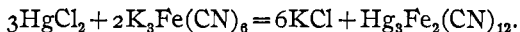
Received March 10, 1906.

IN A recent number of this Journal,<sup>1</sup> I described a compound,  $\text{K}_2\text{HgFe}(\text{CN})_6$ , which is obtained as a precipitate by the action of mercuric chloride on potassium ferrocyanide. When a solution of potassium ferrocyanide is added to a solution of mercurous nitrate, a precipitate is also obtained. Furthermore, potassium ferricyanide gives precipitates with solutions of both mercuric

<sup>1</sup> This Journal, 28, 87.

and mercurous salts. It is my intention in this paper to show the methods I employed to isolate these precipitates and to ascertain their composition.

*Mercuric Ferricyanide*,  $Hg_3Fe_2(CN)_{12}$ .—When an aqueous solution of potassium ferricyanide is added to an aqueous mercuric chloride solution, no precipitate is obtained. The reason for this is that the resulting compound is soluble in water. When, however, a concentrated aqueous solution of potassium ferricyanide is added to a solution of mercuric chloride in alcohol and ether, a heavy yellow precipitate is obtained. This precipitate consists of the compound  $Hg_3Fe_2(CN)_{12}$ , reprecipitated mercuric chloride and potassium ferricyanide. To remove the mercuric chloride and potassium ferricyanide, one of the two following methods may be employed: The whole precipitate can be transferred to a filter, washed several times with a mixture of alcohol and ether and finally with water. Or the entire precipitate is poured into a measuring cylinder, filled with water. The precipitate is allowed to settle and the supernatant solution removed by means of a siphon. The cylinder is again filled with water, shaken, and the precipitate allowed to settle and the supernatant solution removed as before. This method of washing is repeated four or five times. Finally the precipitate is treated with alcohol and ether, and then filtered and dried at  $100^\circ C$ . The latter method was the one employed for the preparation of the compound, as by this method less loss occurred by solution, and consequently a greater yield of the compound was obtained. The bright yellow compound is fairly stable when in a dry state. It is, however, quite soluble in water and its aqueous solutions decompose rapidly with the evolution of hydrocyanic acid. As a result of this decomposition the solution turns blue with the formation, probably, of Prussian blue. When the dried compound is treated with solutions of alkali hydroxides, the hydroxides of iron and mercury are formed, and the corresponding alkali ferricyanide is again produced. The compound, in its properties, is similar to Turnbull's blue obtained by the action of ferrous chloride upon potassium ferricyanide. It is probably also formed according to the same reaction:



Numerous analyses performed, as described in my previous paper, gave the following results:

## FERRICYANIDES OF MERCURY.

	Found.	Calculated.
Mercury .....	58.30	58.59
Iron .....	10.89	10.93
Cyanogen .....	29.82	30.48
	<hr/>	<hr/>
	99.01	100.00

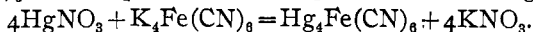
It may be seen that the percentage of cyanogen found is somewhat lower than the calculated percentage. This is due to the fact that a complete decomposition of the compound by boiling with yellow mercuric oxide is not effected. Cyanogen can always be detected in the mercuric oxide, even after boiling the latter with the compound for three hours, and after thorough washing. To attain perfectly accurate results an ultimate analysis by combustion would be necessary. The results are sufficiently accurate, however, to warrant the adoption of the formula  $\text{Hg}_3\text{Fe}_2(\text{CN})_{12}$ .

*Mercurous Ferricyanide,  $\text{Hg}_3\text{Fe}(\text{CN})_6$ .*—This compound is obtained as a cream-colored precipitate when a solution of mercurous nitrate is added to a potassium ferricyanide solution. The precipitate is flocculent and can be easily filtered through a Buchner's funnel. It is washed with water and dried at  $100^\circ \text{C}$ . The substance invariably turns blue when exposed to the air. From the analyses of this compound, the formula  $\text{Hg}_3\text{Fe}(\text{CN})_6$  is obtained, *i. e.*, three univalent mercury atoms have replaced the potassium in  $\text{K}_3\text{Fe}(\text{CN})_6$ .

The results of the analyses are as follows:

	Found.	Calculated.
Mercury .....	73.70	73.64
Iron .....	7.02	6.90
Cyanogen .....	18.91	19.46
	<hr/>	<hr/>
Total .....	99.63	100.00

Again, the percentage of cyanogen is found somewhat lower than the theoretical. In this case, however, a slight decomposition occurred on drying the compound. This decomposition fully accounts for the loss of some of the cyanogen, as correspondingly the percentage of mercury and iron are somewhat high. Finally, an attempt was made to isolate the yellow precipitate obtained by adding a solution of potassium ferrocyanide to mercurous nitrate in dilute nitric acid solution. The compound  $\text{Hg}_4\text{Fe}(\text{CN})_6$  was expected according to the following reaction:



It was found, however, that the dilute nitric acid oxidized the

ferrocyanide and consequently a homogeneous substance could not be obtained. I then tried to bring about the above reaction by shaking freshly precipitated mercurous chloride with a solution of potassium ferrocyanide, but no reaction took place. The following method, which was tried, might also be mentioned.

Mercurous carbonate was prepared by adding an excess of potassium bicarbonate solution to a mercurous nitrate solution. After a few days the mercurous carbonate is filtered and washed. The greater portion of the precipitate is transferred to an Erlenmeyer flask and acetic acid added in excess. To the turbid liquid obtained, a potassium ferrocyanide solution is added. A heavy precipitate is obtained on shaking, but analyses do not agree with the expected compound of the formula  $\text{Hg}_4\text{Fe}(\text{CN})_6$ . The analysis of the substances obtained by the first and last method of preparation approach more closely the formula  $\text{Hg}_3\text{Fe}(\text{CN})_6$ , which is the same compound obtained when potassium ferricyanide is added to mercurous nitrate. This seems to show that in the above-mentioned cases oxidation of the ferrocyanide occurred. The preparation of the compound  $\text{Hg}_4\text{Fe}(\text{CN})_6$  will therefore only become possible when a suitable solvent for mercurous chloride is found.

MICHIGAN COLLEGE OF MINES,  
HOUGHTON, MICH.,  
March 5, 1906.

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## THE PREPARATION OF BORON CARBIDE IN THE ELECTRIC FURNACE.

BY S. A. TUCKER AND H. J. W. BLISS.

Received March 8, 1906.

THE compound  $\text{B}_6\text{C}$  was first isolated by Joly<sup>1</sup> in some of the products prepared in connection with admantine boron, and Moissan<sup>2</sup> gives three methods for the preparation of the carbide.

(1) An arc is passed between carbon electrodes which are bound together with a mixture of boric oxide and aluminum silicate. Under these conditions the product is contaminated with silicon carbide.

(2) By heating amorphous boron with carbon to a temperature of about  $3000^\circ\text{C}$ ., either by placing directly in the arc, or by exposing it to the radiant heat from the arc.

<sup>1</sup> Compt. rend. 97, 456.

<sup>2</sup> "Le Four Électrique."