

the precipitate carries with it some ammonium oxalate. Upon washing the precipitate with water the complex, ammonium lanthanum oxalate, appears to undergo hydrolysis. When this takes place some lanthanum oxalate is produced in such a fine state of division that it passes through the filter paper. The first two results among the ammonium oxalate determinations illustrate this fact. It was observed that these filtrates were somewhat opalescent.

The amounts of oxide are high when sodium hydroxide is used. This is evidently not due to the formation of a basic salt since when a large amount of sodium hydroxide is used still higher results are obtained. The above facts indicate the carrying down of sodium. In order to prove the presence of sodium in the oxide it was dissolved in hydrochloric acid and the solution tested for sodium by means of the flame coloration and the spectroscopy. Both gave very decided tests for sodium.

Ammonium hydroxide was substituted for sodium hydroxide because of its volatile nature. But in this case also high results were obtained although not as high as when sodium hydroxide was used. A qualitative analysis of the lanthanum hydroxide revealed traces of chloride which would indicate the formation of a certain amount of basic chloride. It is highly probable that ammonium hydroxide would give quantitative results if the lanthanum were present as the nitrate because upon ignition the basic nitrate, if formed, would be readily broken down to oxide.

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THE PREPARATION AND PROPERTIES OF SODIUM ZINC CYANIDE.

BY NATHANIEL HERZ.

Received March 16, 1914.

Previous Work.—In THIS JOURNAL,¹ W. J. Sharwood gave a summary of previous work, and the results of his own experiments on the preparation of sodium zinc cyanide. Both his results, and those of Rammelsberg, quoted by him, indicate the existence of a compound, $\text{NaZnCy}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, which is very difficult to crystallize, while the mother liquor has the composition Na_2ZnCy_4 , agreeing with the compound existing in dilute solutions, and also with the corresponding potassium compound. None of these preparations analyzed, however, gave satisfactory molecular ratios either for the salt, or for the water of crystallization, the crystals being highly efflorescent.

One of the greatest difficulties in this preparation was due to impurities in the sodium cyanide then available. The material then on the market contained appreciable quantities of potassium cyanide and of carbonates,

¹ Vol. 25, 570-596 (1903), "A Study of the Double Cyanides of Zinc with Potassium and with Sodium."

causing the crystallization of the double potassium salt or of sodium carbonate. The compound crystallized in the most successful trials may have been influenced by the presence of free alkali in the solution. Recently it was suggested by Mr. Sharwood that it might be possible to prepare a purer solution with the high-grade commercial sodium cyanide now on the market, and thus find out whether the double cyanide splits up on crystallizing into $\text{NaZnCy}_3 + \text{NaCN}$, or whether at some point Na_2ZnCy_4 can be crystallized. The commercial sodium cyanide now sold as equivalent to "128-130% KCN" contains about 97% NaCN, with some carbonate and moisture, and only traces of potassium and sulfide.

Preliminary Experiments.—The principal points to consider in this preparation are as follows: The starting point is zinc cyanide, ZnCy_2 , which should be free from potassium (left in it by the precipitant used) and from carbonate; it should be as free from basic cyanide as possible. It hydrolyzes very easily on washing. The zinc cyanide is dissolved in sodium cyanide solution, which must also be free from potassium and carbonates. By using an excess of zinc cyanide, the solution can be saturated with zinc, without attacking much of the hydroxide of the basic cyanide, which would otherwise dissolve with the formation of sodium zincate. The excess of zinc cyanide also reacts with any free alkali present, forming double cyanide and zinc hydroxide.

The first attempt was made with quantities such as to give about 25 grams of anhydrous Na_2ZnCy_4 . The zinc cyanide was first prepared by dissolving zinc chloride in boiled water, acidified with a little hydrochloric acid. The free acid insured the presence of hydrocyanic acid in the solution after precipitation, lessening the tendency toward hydrolysis on washing. The precipitant was a solution of sodium cyanide, which had been treated with a slight excess of lime and filtered to remove carbonates. The solution was stirred vigorously while precipitating, and filtered with the aid of suction. The precipitate was then washed, starting with warm and finishing with cold, recently boiled distilled water. The zinc cyanide was then digested with a solution of sodium cyanide, also treated with lime to remove carbonates. Then the solution was filtered, evaporated to a sirupy condition, and placed in a vacuum desiccator over concentrated sulfuric acid. After a few days a white layer was seen on the surface of the solution, which may possibly have been the compound NaZnCy_3 as described by previous investigators. It was not further examined, however, as upon attempting to remove this film for investigation, it was found that below the surface there was a good crop of diamond-shaped crystals that were invisible when in the solution on account of having the same index of refraction as the strong solution. These crystals were removed, drained, dried on filter paper, and analyzed, with the following results:

	H ₂ O.	CN.	Zn.	Na (by diff).
Per cent.	20.20	39.44	24.60	15.76
Molecular ratio.	2.95	4.03	1.00	1.82

These results indicate a compound, $\text{Na}_2\text{ZnCy}_4 \cdot 3\text{H}_2\text{O}$, agreeing in composition with the solution. As the material was not sufficient for further investigation, a second preparation was made.

At this point an experiment was tried to determine whether any interference might be expected from the small amount of calcium left in the solution from the treatment with lime for removing carbonates. It was found that the double cyanide formed by digesting lime with a large excess of zinc cyanide was so soluble as to be almost impossible to crystallize, so this possible interference need not be considered.

Final Preparation.—The method used was similar to that outlined above, but the quantities used were three times as great. Two crops of crystals were obtained, but they were not recrystallized, as the quantity was too small for a salt of such high solubility, and the solution was sufficiently pure to insure very little contamination. Water of crystallization was determined by drying to constant weight at 105° . Cyanogen was determined by titration with $N/20$ silver nitrate solution, using potassium iodide as indicator, in the presence of sufficient ammonia to counteract the effect of the zinc. The solution was standardized under similar conditions by a solution of cyanide of known strength, to which an equivalent amount of zinc was added. Zinc was determined by titration with standard potassium ferrocyanide in acid solution, using uranium nitrate as an outside indicator. Sodium was determined in the last analysis by weighing the sulfates of sodium and zinc together, and subtracting the zinc sulfate as determined by the zinc titration. In other cases, sodium was taken by difference. All titrations were made on aliquot parts of the same solution, and water of crystallization was determined on a different sample, as it was not considered safe to dissolve the residue from the water determination and use it for analysis, although no appreciable decomposition was noted. The greatest difficulty was experienced because of the rapid efflorescence of the crystals, making it almost impossible to weigh out two portions with the same water content.

TABLE OF ANALYSES.

The figures in parentheses indicate the number of closely agreeing determinations averaged.

	Per cent.				Molecular ratios.			
	H ₂ O.	Zn.	CN.	Na.	Na.	Zn.	CN.	H ₂ O.
	(3)	(2)	(2)					
First crop of crystals.	19.95	23.81	37.24	19.00	2.20	1.00	3.85	2.96
First crop. Selected material.	(1)	(2)	(3)					
Partly effloresced.	19.80	24.05	38.15	18.00	2.06	1.00	3.88	2.91
	(1)	(2)	(3)	(1)				
Second crop (Total = 99.5%)	20.02	23.93	38.67	16.88	1.98	1.00	4.02	3.07

Solubility.—The specific gravity of a saturated solution at 15° was found to be 1.37. A portion of this solution was weighed and zinc determined. Calculated to Na₂ZnCy₄, the results are as follows: One part of the anhydrous salt is soluble in 0.83 part of water at 15°, and one part of the hydrated salt, Na₂ZnCy₄.3H₂O, is soluble in 0.47 part of water.

Crystalline Form.—A few of the best crystals were selected for measurement. The measurements were kindly made by Prof. W. E. Ford and Dr. W. M. Bradley, of the Sheffield Scientific School, Yale University. As the crystals effloresced to some extent in transit, some of the angles could not be measured with as great precision as desirable.

The system of crystallization is orthorhombic. The angles are:

Base (001) to pyramid (111).....	$c \wedge p$	62° 50.5'
Pyramid (111) to pyramid (111).....	$p \wedge p$	103° 49'
Pyramid (111) to brachypinacoid (011).....	$p \wedge b$	64° 16.5'

One other form, the brachydome (010) also occurs.
The axial ratio is $a : b : c = 0.56 : 1.00 : 0.95$

The simplest crystal consists of a prominent unit pyramid (111) and base (001) (Fig. 1). In the larger crystals modifications appear, consisting of the brachypinacoid (011) and the brachydome (010) shown in Fig. 2.

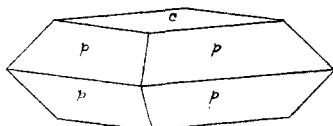
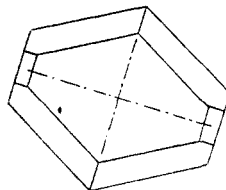
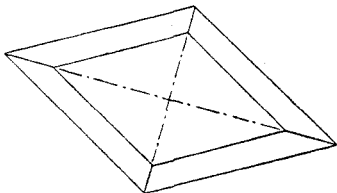


Fig. 1.

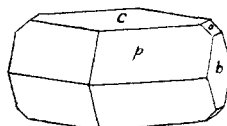


Fig. 2.

The pseudo-hexagonal plan is characteristic of the larger crystals, as is the diamond shape of the smaller ones. The largest crystals obtained were about 5 mm. long.

Conclusions.—From pure solutions of sodium zinc cyanide, free from less soluble salts and from excessive amounts of free alkali, the compound that crystallizes is Na₂ZnCy₄.3H₂O.

The hydrated salt is soluble in less than half its own weight of water. The crystals are orthorhombic, simple in form, either flat diamonds or pseudo-hexagonal plates. They are brilliant when removed from the solution, but effloresce rapidly, becoming dull and chalky. The dry salt is quite stable in air, being completely soluble in water after several days'

exposure. Even after complete dehydration at 105° , there was very little evidence of decomposition. When working with pure solutions, no evidence was found to indicate the separation of the compound $\text{NaZnCy}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ as obtained by previous investigators.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS (PUBLICATION NO. 17) AND FROM THE NATIONAL BUREAU OF STANDARDS.¹]

COMPARISON OF THE SILVER AND THE IODINE COULOMETERS² AND THE DETERMINATION OF THE VALUE OF THE FARADAY.

BY STUART J. BATES AND GEORGE W. VINAL.

Received March 16, 1914.

Introduction.

Of the many electrochemical reactions which may theoretically be employed to determine the Faraday, *i. e.*, the quantity of electricity associated with a chemical equivalent in any electrochemical change, that of the deposition of silver from a solution of silver nitrate is the only one that has been extensively investigated. The values which have been accepted for the Faraday from time to time, have almost entirely been based upon results with the silver coulometer. This naturally resulted from the fact that the international ampere is defined in terms of the silver deposited under more or less rigorously fixed conditions and, hence, this instrument has been the subject of many thorough investigations, both by the National Standardizing Laboratories and by private individuals. As a result of these investigations it has been possible, for the past few years so to define the conditions to be used in connection with the silver coulometer that a reproducibility of 1 or 2 parts in 100,000 may be obtained. Until recently no other coulometer had attained anything approaching such a degree of precision.

A little over a year ago, however, Washburn and Bates³ published the results of a study of an iodine coulometer which they had devised and which was found to have a reproducibility of the same order as that of the silver coulometer. The apparently complete reversibility and purity of the electrochemical reaction in the iodine coulometer, coupled with the fact that no solid deposit is obtained, made it a particularly valuable

¹ Published by permission of the Director of the Bureau of Standards.

² Although the word voltameter is still in quite extensive use, and on account of the decision of the London Conference is employed in the Bulletins of the Bureau of Standards, the name coulometer is employed throughout this paper. This word appears more appropriate because it is coulombs which the instrument directly measures, and because of the possibility of confusion between the words voltameter and voltmeter.

³ THIS JOURNAL, 34, 1341, 1515 (1912).