

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

**A STUDY OF THE PRODUCTS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA SOLUTION. I. INTRODUCTION. II. THE ACTION OF SODIUM UPON ZINC CYANIDE**

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RECEIVED APRIL 15, 1929

PUBLISHED JULY 5, 1929

### I. Introduction

When an alkali metal is dissolved in liquid ammonia, it ionizes, forming cations identical with the positive ion of a salt of this metal, and anions consisting of solvated electrons.<sup>2</sup> This solution containing free electrons is a most powerful reducing agent. Many reactions between solutions of this kind and both organic and inorganic compounds have been carried out.<sup>3</sup> A quantitative method for analysis of chlorine in organic compounds has been developed in this way.<sup>4</sup> Many of the reactions, however, have been studied chiefly from a qualitative point of view. A quantitative investigation of reactions of this type and of the products formed is being carried out in this Laboratory. The present series of papers deals with the results obtained with inorganic salts.

The type reactions that may take place between ammonia solutions of the metals and salts have been presented by Kraus and Kurtz.<sup>3j</sup> With the alkali or alkaline earth metals and salts of less positive metals, reaction may occur in which the cation is reduced and precipitated as free metal, or is reduced further and forms a compound, usually insoluble, with the reducing metal. These possibilities were illustrated by Kraus and Kurtz<sup>3j</sup> with numerous reactions. In some cases compounds of unusual composition were postulated as, for example,  $\text{NaZn}_4$ ,  $\text{Ca}_7\text{Zn}$ . These formulas were established only from the ratio of reacting materials, and not by analysis. It is the purpose of this investigation to isolate the products formed in reaction between salts and metal solutions, determine their composition by analysis and make a study of their properties.

### II. The Action of Sodium upon Zinc Cyanide

**Introduction.**—Kraus and Kurtz<sup>3j</sup> found that sodium reacts very readily with zinc cyanide in liquid ammonia solution, forming a finely-

<sup>1</sup> This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Arthur Rose in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Kraus, *THIS JOURNAL*, **30**, 1323 (1908).

<sup>3</sup> (a) Joannis, *Compt. rend.*, **113**, 795 (1891); (b) Moissan, *ibid.*, **136**, 1217 (1903); (c) Lebeau, *ibid.*, **140**, 1042, 1264 (1905); (d) Chablay, *ibid.*, **140**, 1262 (1905); (e) **154**, 364 (1912); (f) Peck, *THIS JOURNAL*, **40**, 335 (1918); (g) Kraus and White, *ibid.*, **45**, 768 (1923); (h) White, *ibid.*, **45**, 779, 1780 (1923); (i) Bergstrom, *ibid.*, **45**, 2788 (1923); (j) Kraus and Kurtz, *ibid.*, **47**, 43 (1925); and others.

<sup>4</sup> Chablay, *Ann. chim.*, [9] **1**, 469 (1914); Clifford, *THIS JOURNAL*, **41**, 1051 (1919).

divided metallic precipitate, extremely reactive with respect to water and air. From the reaction ratio they proposed the formula  $\text{NaZn}_4$ . Mathewson<sup>5</sup> obtained only the compound  $\text{NaZn}_{12}$  by the method of thermal analysis. In the present paper the precipitate formed as mentioned above is analyzed and shown to have the composition  $\text{NaZn}_4$ . The results of a study of the reactions between this compound and oxygen, air and water are also presented.

**Preparation of the Sodium Zinc Compound.**—The apparatus used for the reaction of sodium upon zinc cyanide is shown in Fig. 1. Anhydrous ammonia gas, obtained from

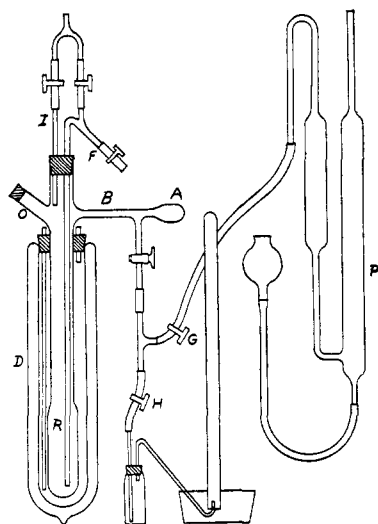


Fig. 1.—Apparatus used for the preparation of  $\text{NaZn}_4$ .

the liquid above the precipitate forced out through tube F. By careful manipulation 90% or more of the liquid could be drawn off without loss of the solid. Fresh ammonia was now condensed and the process repeated. In this way the precipitate was washed seven or eight times. The last trace of ammonia in the reaction tube was allowed to evaporate against a slight pressure.

The product of the reaction was left in the form of a black powdered material. Samples for analysis were obtained by tipping the reaction tube until a suitable quantity had entered the collection tube A. The collection tube was then sealed off at B, evacuated to about 0.01 mm. of mercury and weighed. The sample was then dissolved in 6 N hydrochloric acid, using a technique similar to that described by Franklin.<sup>6</sup> The solution was analyzed for zinc and ammonia.

**Composition of the Sodium-Zinc Compound.**—An aliquot part of the acid solution was analyzed for zinc by precipitating and weighing as  $\text{ZnNH}_4\text{PO}_4$ . Another portion was analyzed for ammonia by distillation, after the addition of concentrated sodium

<sup>5</sup> Mathewson, *Z. anorg. Chem.*, **48**, 196 (1906).

<sup>6</sup> Franklin, *J. Phys. Chem.*, **15**, 509 (1911).

a small supply tank of liquid ammonia, to which pieces of sodium had been added, entered the reaction tube, R, through a tube, I, and condensed under a pressure of 10 cm. of mercury as shown by the gage P. Cooling was provided by a bath of liquid ammonia in the Dewar flask D, through which a current of air was bubbled to secure a still lower temperature. After 100 cc. of ammonia had condensed, about 0.5 g. of sodium, freshly cut under petroleum ether, immediately transferred to a weighing bottle filled with dry nitrogen and weighed, was added through the side tube O. Then the calculated amount of Kahlbaum's zinc cyanide was added slowly. Reaction occurred very rapidly and a dense black precipitate quickly settled out. That a gaseous product insoluble in water was not formed was shown in several cases by closing the clamp, G, and opening the clamp, H, for the duration of the reaction.

When the reaction was completed, the clear solution was removed and the precipitate washed as follows. With a small pressure on the system, a clamp on tube F was opened and

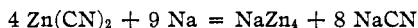
hydroxide and collection of the distillate in 0.1 *N* HCl. No more than a trace of ammonia was found in any sample. The results of the zinc analyses are given in Table I.

TABLE I  
COMPOSITION OF THE SODIUM-ZINC COMPOUND  
Calculated for  $\text{NaZn}_4$ : Zn = 91.9%

No.	Sample, g.	$\text{ZnNH}_4\text{PO}_4$ , g.	Zinc, g.	Zinc, %
30	0.2074	0.5155	0.1889	91.1
31	.1295	.3243	.1188	91.8
32a	.0778	.1960	.0718	92.3
32b	.0851	.2144	.0786	92.3
32c	.1479	.3700	.1356	91.7
20	.1058	.2636	.0966	91.3
23	.1046	.2635	.0965	92.3

The first three samples were prepared solely for the zinc analysis, the others were first treated in various ways. All samples, except 32, were prepared by adding zinc cyanide to a sodium solution in the ratio of 1  $\text{Zn}(\text{CN})_2$  to 2.25 Na. This ratio, first determined by Kraus and Kurtz,<sup>3j</sup> was checked and found to be correct. In preparing Sample 32 the addition of zinc cyanide was stopped while the solution was still blue, so that a slight excess of sodium was present.

The results establish the formula  $\text{NaZn}_4$  for the sodium zinc compound. The equation for the reaction is



A slight excess of sodium does not affect the composition of the precipitate. An excess of zinc cyanide, however, does change its composition. Thus by having a 20% excess of zinc cyanide present, the product analyzed once 98.1% of zinc and again, 99.3% of zinc.

**Oxidation of the Sodium-Zinc Compound.**—Kraus and Kurtz<sup>3j</sup> reported that this compound was very active toward air and water. Attempts were made to establish quantitatively the reactions taking place between  $\text{NaZn}_4$  and dry oxygen, dry air, moist oxygen and moist air.

In most of the experiments the  $\text{NaZn}_4$  was first prepared in a small reaction tube, the top of which was sealed before the final evaporation of the ammonia. The side arm of the reaction tube was then sealed to another tube which we shall call the oxidizing system. This system was also joined through stopcocks and glass tubing with an evacuating pump, a closed mercury gage and a buret. The top of the buret was also connected with a source of dry oxygen or air and the bottom was joined by rubber tubing to a leveling pear containing mercury. After the entire system had been evacuated to approximately 0.01 mm. of mercury, a measured volume of gas was allowed to enter from the buret. The process of the oxidation was followed by the decrease in pressure as shown on the mercury gage. The entire system was later calibrated so that the volume of gas in the system corresponding to any gage reading could be calculated. By subtracting the amount of gas in the system from the total amount let in, the volume used up at any stage of the reaction could be obtained. In a few cases the sample was weighed before and after oxidation, to get the weight of oxygen involved.

The oxidation reaction is divided into two distinct stages. At first oxygen is taken up rapidly, with considerable evolution of heat, but no noticeable change in the appearance of the sodium zinc takes place. This primary oxidation is followed by a secondary reaction which proceeds at a very slow rate for a long period of time, accompanied by a change in the color of the substance from black through gray to white.

Dry air acts in the same way as dry oxygen. Moist air or moist oxygen accelerates the oxidation so much that the two stages are not apparent. A higher temperature also speeds up the secondary reaction. The data for these statements are given in Table II.

TABLE II  
OXIDATION OF  $\text{NaZn}_4$  BY DRY OXYGEN AT ROOM TEMPERATURE FOR ONE-HALF HOUR

No.	$\text{NaZn}_4$ , g.	Oxygen, cc., (S. T. P.)	Oxygen, g.	Oxygen, mg. atoms	$\text{NaZn}_4$ , mill. moles	Ratio, mg. atoms of O to mill. moles of $\text{NaZn}_4$
3	0.4452	10.60	0.0152	0.950	1.565	0.61
5	.6460	12.76	.0182	1.138	2.270	.50
6	.3506	7.02	.0100	0.625	1.232	.51
7	.4101	8.37	.0120	.750	1.441	.52
8	.6084	10.66	.0152	.950	2.138	.45
10	.4701	14.12	.0202	1.263	1.652	.76
12	.4155	9.72	.0139	0.869	1.460	.59
Dry Air at Room Temperature						
30	0.1244	...	0.0031	0.194	0.437	.45
31	.1295	...	.0036	.225	.455	.49
Dry Oxygen at Room Temperature for 4 Weeks						
7	0.4101	12.18	0.0174	1.088	1.441	0.76
8	.6084	18.38	.0263	1.644	2.138	.77
Dry Oxygen at 150-200° for 25 Hours						
5	0.6460	93.95	0.1342	0.839	2.270	3.70
Moist Oxygen at Room Temperature						
4	0.4418	21.51	0.0307	1.919	1.553	1.2
14	.1185	7.13	.0102	0.638	0.417	1.5
Moist Air at Room Temperature						
16	0.5274	...	0.0912	5.700	1.854	3.1

The most remarkable feature of the oxidation experiments is that the  $\text{NaZn}_4$  rapidly takes up enough oxygen to form sodium monoxide. Then apparently the zinc is slowly oxidized. With moisture both the sodium and part of the zinc react rapidly with oxygen, the heat liberated increasing the speed of the reaction. Tests for peroxides were made on several samples, oxidized in different ways, without obtaining any evidence of their formation. That the amount of oxygen taken up by the sample varied considerably was due to variation in conditions. For

instance, if the oxygen were let in rapidly, considerably more heat was developed and more oxygen absorbed in a given time than when the gas was let in slowly. A further study and standardization of the conditions of oxidation are necessary for more definite conclusions.

**The Action of Water and Dilute Acid upon  $\text{NaZn}_4$ .**—The reaction between  $\text{NaZn}_4$  and water, and also dilute acid, was investigated by allowing a small amount of water, or acid, to enter the evacuated collection tube containing a known weight of sample. The hydrogen liberated by the reaction was removed by means of a Toepler pump and analyzed by explosion with air. With water the reaction, even at first, was a slow one, continuing with decreasing rate for some time. Thus during the first week approximately 20 cc. of hydrogen per gram of sample was liberated each day. At the end of a month about 1 cc. of hydrogen per day was formed. With dilute acid the reaction was over in a short time. The total amount of hydrogen liberated is given in Table III.

TABLE III  
HYDROGEN LIBERATED BY THE REACTION DURING A PERIOD OF TWO MONTHS

Expt. no.	With water		With 6 N HCl	
	18	19	32a	32b
$\text{NaZn}_4$ , g.	1.1316	1.9280	0.0778	0.1479
Hydrogen, cc. (S. T. P.)	189.0	334.6	27.4	53.1
Hydrogen, g.	0.0170	0.0301	0.0025	0.0048
Equiv. $\text{H}_2$ per mole $\text{NaZn}_4$	4.2	4.4	9.0	9.1

The reaction of the sodium in  $\text{NaZn}_4$  upon water and of the sodium hydroxide formed in this way upon zinc would account for less than half of the hydrogen obtained. Evidently the zinc reacted directly with water to furnish this extra hydrogen.

The hydrogen liberated when the sample was treated with acid is equivalent to the total sodium and zinc present. This result may be taken as additional evidence of the composition of the compound.

### Summary

The product formed when zinc cyanide is added to a solution of sodium in liquid ammonia has been shown by analysis to have the composition  $\text{NaZn}_4$ . This compound reacts with oxygen or air in two stages, the speed of the secondary reaction being increased by the presence of moisture or by heating. Reaction of the compound with dilute acid liberates nine equivalents of hydrogen per mole of  $\text{NaZn}_4$ ; with water, approximately 4.5 equivalents of hydrogen are liberated in two months.